POLITECHNIKA
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RADA NAUKOWA DYSCYPLINY NAUKI CHEMICZNE

ROZPRAWA DOKTORSKA

w formie zbioru opublikowanych i powiązanych tematycznie artykułów naukowych w dyscyplinie Nauki chemiczne

mgr inż. Piotr Ścigalski

NOWE MATERIAŁY SORPCYJNE DO IZOLOWANIA KSENOBIOTYKÓW ORGANICZNYCH I NIEORGANICZNYCH Z MATRYC ŚRODOWISKOWYCH

New sorptive materials for organic and inorganic xenobiotics isolation from environmental matrixes

DZIEDZINA: Nauki ścisłe i przyrodnicze
DYSCYPLINA: Nauki chemiczne

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POLITECHNIKA
BYDGOSKA
Wydział Technologii
i Inżynierii Chemicznej

Bydgoszcz, 2024

Podziękowania

Niniejszą pracę pragnę zadedykować moim kochanym Rodzicom,
bez wsparcia których odbycie tej niezwykłej podróży nie byłoby możliwe.

Gorące podziękowania składam mojemu Promotorowi,
dr hab. Przemysławowi Kosobuckiemu, prof. PBŚ,
za poświęcony czas i nerwy,
a przede wszystkim za nieocenione lekcje w laboratorium i poza nim.

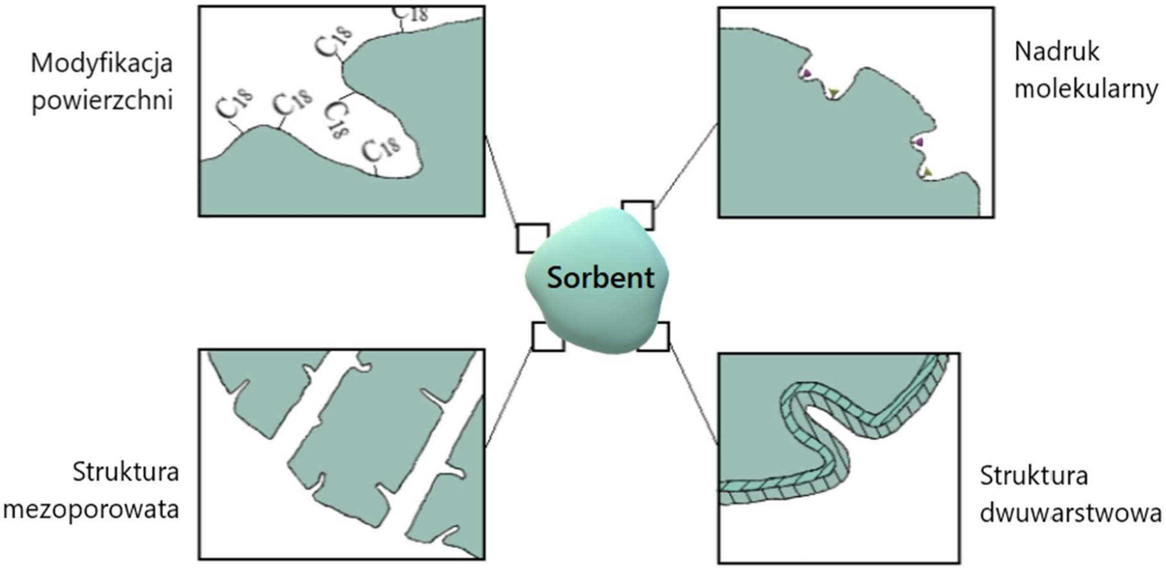
Chciałbym również podziękować wszystkim pracownikom
Zakładu Analityki Żywności i Ochrony Środowiska
Na Wydziale Technologii i Inżynierii Chemicznej
Politechniki Bydgoskiej,
którzy zawsze kiedy tego potrzebowałem
byli gotowi służyć radą i pomocą.

SPIS TREŚCI

1. WPROWADZENIE

Ciągły wzrost jakości życia widoczny w ostatnich latach jest skutkiem rozwoju gospodarczego. Prowadzi to do zwiększenia ilości uwalnianych do środowiska naturalnego potencjalnie szkodliwych substancji obcych (ksenobiotyków), zarówno organicznych, takich jak pestycydy czy farmaceutyki, jak i nieorganicznych, np. metali ciężkich. Pogłębianie naszej wiedzy o tych związkach i ich wpływie na środowisko skutkuje ustanawianiem ograniczeń, mających na celu utrzymanie ich emisji pod kontrolą. Konieczne staje się więc opracowanie i doskonalenie odpowiednich metod pomiaru, pozwalających na monitorowanie środowiska pod kątem obecności ksenobiotyków oraz mających wspomagać przemysł w redukowaniu ich emisji.

W celu przygotowania próbek o skomplikowanym składzie do oznaczenia zawartości zanieczyszczeń zostały opracowane liczne metody analityczne wykorzystujące szereg materiałów sorpcyjnych o różnej budowie wewnętrznej i funkcjonalnej powierzchni. Przykładowe struktury oraz własności powierzchniowe przedstawione zostały na rysunku 1.



Rys. 1. Przykłady podstawowych struktur funkcjonalnych sorbentów SPE.

Najczęściej spotykana struktura porowata oznacza powierzchnię pokrytą gęstą siatką nieregularnych porów i wnęk umożliwiających wnikanie substancji i unieruchamianie ich na powierzchni sorbentu. Istnieją jednak materiały, takie jak niektóre typy krzemionki, charakteryzujące się mezoporowatą strukturą wewnętrzną. Są to materiały, których wnętrze przecina sieć regularnych, równolegle ułożonych porów o znacznych średnicach. Ściany wewnętrzne tych mezoporów mają również charakter porowaty, co dodatkowo zwiększa aktywną powierzchnię sorpcyjną [1-5].

W celu zwiększenia zdolności materiału do adsorpcji wybranych analitów stosuje się szereg procesów fizycznych i chemicznych skutkujących modyfikacją jego powierzchni. Najczęściej spotykanym rozwiązaniem jest funkcjonalizacja sorbentu. Unieruchomienie na powierzchni długich łańcuchów organicznych, takich jak szeroko stosowane grupy oktylowe $–C_8$ i oktadecylowe $–C_{18}$ znacząco zmniejszają polarność sorbentu, natomiast zastosowanie podstawników takich jak grupa hydroksylowa –OH, karboksylowa –COOH czy aminowa $–NH_2$ wywołują skutek odwrotny. Regulacja polarności i siły jonowej sorbentu pozwala więc na dostosowanie materiału do warunków, w jakich będzie on stosowany oraz zwiększenie jego powinowactwa do analitu [2,3,6].

Szczególnym przypadkiem modyfikacji powierzchni jest tzw. nadruk molekularny. Po syntezie na powierzchni materiału tego typu pozostają „odciski" cząsteczki analitu bądź jego bliskiej pochodnej, odpowiadające mu rozmiarem, kształtem i funkcjonalnością. Oznacza to, że do wnęki tej przeniknąć może jedynie wybrany analit bądź związek bardzo mu bliski fizycznie i chemicznie, gwarantując niezwykle wysoką selektywność takiego sorbentu [3-7].

Jednym z najciekawszych mechanizmów adsorpcji charakteryzują się tzw. wodorotlenki dwuwarstwowe (z ang. *layered double hydroxide*). Materiały te są rodzajem syntetycznych anionowych materiałów ilastych, zbudowanych z warstw dwu- i trójwartościowych kationów oraz uwodnionych anionów znajdujących się w przestrzeniach międzywarstwowych. Stosowane są one przede wszystkim do izolacji jonów metali ciężkich, które uwięzione zostają w strukturze sorbentu. Ponieważ materiały te są łatwo rozpuszczalne w kwasach, uwolnienie analitu przed oznaczeniem jest niezwykle proste i przebiega praktycznie ilościowo [2-4,8,9].

2. METODY IZOLOWANIA KSENOBIOTYKÓW Z PRÓBEK ŚRODOWISKOWYCH

2.1. Ekstrakcja

Ekstrakcja jest procesem rozdzielenia składników. Opiera się na migracji analitów z badanej próbki, zwanej matrycą pierwotną do matrycy wtórnej (nazywanej też matrycą odbierającą), o nieskomplikowanym i jednoznacznie określonym składzie. Ekstrakcję kilku substancji można przeprowadzić jednocześnie lub prowadząc proces w kilku etapach.

Istotą ekstrakcji jest wyodrębnienie grupy poszukiwanych związków lub pojedynczych substancji poprzez rozpuszczenie ich w rozpuszczalniku i oddzielenie od pozostałych składników próbki. W wyniku przeprowadzonej ekstrakcji otrzymujemy ekstrakt, czyli mieszaninę analitu i substancji ekstrahujących, tzw. ekstrahentów. Najczęściej stosowane w tym celu rozpuszczalniki organiczne dają się odparować, pozwalając wzbogacić ekstrakt, tj. zwiększyć stężenie analitów w roztworze, ułatwiając ich końcowe oznaczenie. Jest to szczególnie pożądane w przypadku próbek o śladowej zawartości poszukiwanych substancji.

Techniki ekstrakcyjne dzielone są ze względu na stany skupienia próbki i ekstrahenta. W najstarszej i najczęściej stosowanej technice ekstrakcyjnej matrycą odbierającą jest ciecz. Nowoczesne metody ekstrakcji są często bezrozpuszczalnikowe, w których matrycą odbierającą może być gaz lub ciało stałe [10,11].

Zastosowanie konkretnej techniki ekstrakcyjnej uzależnione jest od właściwości analitu takich jak jego postać fizyczna, rozpuszczalność, lotność, odporność termiczna, odporność na promieniowanie nadfioletowe (UV), itp.

2.2. Ekstrakcja ciecz-ciecz

Ekstrakcja ciecz-ciecz (z ang. *liquid-liquid extraction*, LLE) jest najstarszym sposobem przygotowywania próbek, w którym zarówno matryca pierwotna jak i matryca wtórna są niemieszającymi się cieczami. Próbki ciekłe można podzielić na dwie grupy: wodne, w których matrycą jest woda oraz organiczne, w których matrycami są rozpuszczalniki organiczne. W LLE do izolacji substancji hydrofilowych, zawierających w swej strukturze ugrupowania polarne np. grupy hydroksylowe, aminowe czy karboksylowe, stosuje się ekstrahenty wodne, natomiast do ekstrakcji związków hydrofobowych (których cząsteczki zbudowane są głównie z łańcuchów i pierścieni węglowodorowych) – rozpuszczalniki organiczne. W przypadku zanieczyszczenia próbki makroskładnikami ekstrakcję wykonuję się dwustopniowo, wykorzystując dwa różne ekstrahenty, pierwszy do usunięcia makroelementów, drugi do wyizolowania badanego związku. Technikę tą stosuje się najczęściej do ekstrakcji substancji nielotnych [2,10,12-14].

W metodzie tej niezwykle istotne jest zastosowanie odpowiedniego rozpuszczalnika. Musi on charakteryzować się przede wszystkim wysoką czystością i dobrą zdolnością rozpuszczania analitu, a także mieć odpowiednią gęstość, lepkość i napięcie powierzchniowe. Powinien wykazywać jak najniższą rozpuszczalność w matrycy pierwotnej, gdyż obniża to wydajność ekstrakcji. Doboru odpowiedniego rozpuszczalnika dokonuje się przeprowadzając kilka ekstrakcji analitu na niewielką skalę różnymi rozpuszczalnikami i wybierając najskuteczniejszy. Niekiedy najwyższą wydajność ekstrakcji uzyskuje się poprzez zastosowanie mieszaniny rozpuszczalników. Przy zastosowaniu wody jako rozpuszczalnika, można wzbogacić próbki dodatkiem soli (np. chlorku sodu, chlorku wapnia(II)), zwiększając siłę jonową roztworu i ułatwiając ekstrakcję.

W celu zatężania ekstraktu, stosuje się usuwanie rozpuszczalnika przez odparowanie, dlatego też LLE stosuje się przede wszystkim do izolacji substancji średnio- i trudno lotnych. Przy ekstrakcjach wielostopniowych wskazane jest stosowanie rozpuszczalnika o większej gęstości niż próbka, ponieważ ekstrakt będzie wtedy tworzył dolną warstwę, ułatwiając rozdzielenie. Głównymi zaletami ekstrakcji metodą ciecz-ciecz jest prostota procedury oraz stosunkowo szybki przebieg, możliwa jest również automatyzacja procesu. Największą wadą jest duże zużycie rozpuszczalników oraz niewielki poziom wzbogacenia. Konieczność odparowania rozpuszczalnika może też skutkować utratą części analizowanej substancji [12,14-16].

2.3. Ekstrakcja do fazy stałej

Ekstrakcja do ciała stałego (z ang. *solid phase extraction*, SPE) polega na przetłoczeniu próbki lub roztworu zawierającego oznaczaną substancję (matrycy pierwotnej) przez złoże sorbentu, tj. materiału posiadającego właściwości sorpcyjne. Analit zostaje zaadsorbowany na powierzchni stałego złoża. W końcowym etapie zaadsorbowane związki wymywa się niewielką ilością rozpuszczalnika, tzw. eluentu, możliwa jest również desorpcja termiczna. Ekstrakcja do fazy stałej jest tania, łatwa w wykonaniu, i nie wymaga skomplikowanej aparatury [2,10-14,17].

Przygotowanie próbki do właściwej analizy ma na celu wyizolowanie poszukiwanych substancji w maksymalnie czystej i skoncentrowanej postaci. Stosując metodę SPE można to uzyskać poprzez:

- elucję analitu i zatrzymanie zanieczyszczeń na powierzchni sorbentu,
- zatrzymanie analitu na powierzchni sorbentu i usunięcie zanieczyszczeń.

Analit zatrzymany na powierzchni sorbentu odzyskuje się stosując elucję rozpuszczalnikiem lub desorpcję termiczną. Zastosowany eluent musi charakteryzować się większym powinowactwem do analitu niż sorbent. Rozpuszczalnikami najczęściej stosowanymi do tego celu są: aceton, acetonitryl, dichlorometan, metanol, izopropanol lub ich mieszaniny [15,18].

Na rynku ciągle pojawiają się nowe materiały sorpcyjne: laboratoria na całym świecie poszukują nowych sorbentów wykazujących różnorodne, często dedykowane własności fizykochemiczne. Wśród najczęściej stosowanych znajdują się modyfikacje powierzchniowe materiałów krzemionkowych czy polimerowych.

Do najważniejszych zalet metody zalicza się możliwość znacznego wzbogacenia analitu przed oznaczeniem, szybki przebieg procesu, znacznie niższe zapotrzebowanie na rozpuszczalniki niż w LLE, łatwość automatyzacji procedury a także potencjalna możliwość łatwego przechowania zaadsorbowanego analitu w fazie sorbentu, pozwalająca na oddzielenie w czasie ekstrakcji i oznaczenia.

Metoda ta jest szeroko stosowana w oznaczaniu zawartości pestycydów w produktach rolnych, żywności i tkankach zwierzęcych [10,15,18].

2.4. Dyspersyjna ekstrakcja do fazy stałej

Dyspersyjna ekstrakcja do fazy stałej (z ang. *dispersive solid phase extraction*, dSPE) jest odmianą techniki SPE, w której sorbent w postaci sypkiej dodawany jest bezpośrednio do całej objętości ciekłej lub stałej próbki, bez konieczności wcześniejszego przygotowania. Popularność zyskała jako skuteczna metoda oczyszczania matrycy w procedurze ekstrakcji pestycydów z produktów rolnych. dSPE jest metodą charakteryzującą się prostotą, krótkim czasem ekstrakcji, szerokim zakresem zastosowań, wysoką skutecznością oraz niskim zapotrzebowaniem na rozpuszczalniki. Cechy te sprawiają, że jest to metoda przyjazna dla środowiska. Sorbentami najczęściej stosowanymi w dyspersyjnej ekstrakcji do ciała stałego są: sadza grafityzowana (z ang. *graphitized carbon black*, GCB), nanorurki węglowe (z ang. *carbon nanotubes*, CNTs), pierwszorzędowa i drugorzędowa amina (z ang. *primary secondary amine*, PSA) oraz krzemionka zmodyfikowana grupą oktadodecylową (C_{18}) [10,19].

Rozwijającą się grupą metod umożliwiających połączenie różnych technik ekstrakcji są tak zwane łączone techniki ekstrakcyjne. Połączenie różnych technik ekstrakcyjnych w jeden proces pozwala na równoczesną izolację grupy związków o różnych właściwościach chemicznych. Techniki łączone pozwalają na połączenie różnych procesów przygotowania próbek takich jak ekstrakcja analitów z próbki, wzbogacanie czy oczyszczanie ekstraktów, jednocześnie eliminując szereg etapów pośrednich. Jednym z przykładów ekstrakcji łączonych jest metoda QuEChERS. Opisana w 2003 roku przez Anastiassiadesa i in., jest ona połączeniem metody ekstrakcji analitu za pomocą rozpuszczalnika z dSPE [20].

3. TYPY MATERIAŁÓW WYKORZYSTYWANYCH W EKSTRAKCJI

Sorbentami określa się substancje stałe lub ciekłe posiadające właściwości sorpcyjne, czyli posiadające zdolność pochłaniania powierzchniowego. Są to więc wszystkie materiały zatrzymujące inne substancje wewnątrz swojej objętości (absorpcja) lub też na swojej powierzchni zewnętrznej (adsorpcja). W ekstrakcji do ciała stałego proces adsorpcji polega na transporcie masy substancji rozpuszczonej (adsorbatu) w fazie ciekłej do porowatej powierzchni fazy stałej (adsorbentu) na granicy styku tych faz [10,14].

O możliwości zastosowania danego materiału w charakterze sorbentu decyduje szereg jego właściwości fizykochemicznych:

- powierzchnia sorpcyjna,
- porowatość,
- stabilność chemiczna, termiczna, mechaniczna,
- zdolność wchodzenia w interakcje (jonowe, π-π, van der Waalsa) ze związkami organicznymi i nieorganicznymi,
- rozpuszczalność w wodzie i rozpuszczalnikach organicznych,
- podatność na modyfikacje,
- możliwość wielokrotnego zastosowania.

Na podstawie tych cech uzależniony jest dobór odpowiedniego adsorbentu do zastosowania w izolacji konkretnego analitu z matrycy w procesie ekstrakcji do fazy stałej [10,12,16-22].

3.1. Sorbenty na bazie żelu krzemionkowego

Jednym z pierwszych materiałów stosowanych jako sorbenty w ekstrakcji do fazy stałej był żel krzemionkowy. Jego cechą charakterystyczną jest zdolność do tworzenia struktur porowatych i duża chłonność cieczy, co w połączeniu z łatwością modyfikacji jego powierzchni czyni go cennym surowcem stosowanym w produkcji nowych materiałów adsorpcyjnych w charakterze nośnika [6,9]. Żel krzemionkowy jest stabilny w zakresie pH od 2 do 7,5; alkaliczny odczyn powoduje rozpuszczanie się tego materiału, zaś w środowisku silnie kwasowym następuje hydroliza wiązań między grupami silanolowymi a podstawnikami modyfikującymi żel krzemionkowy [21-23].

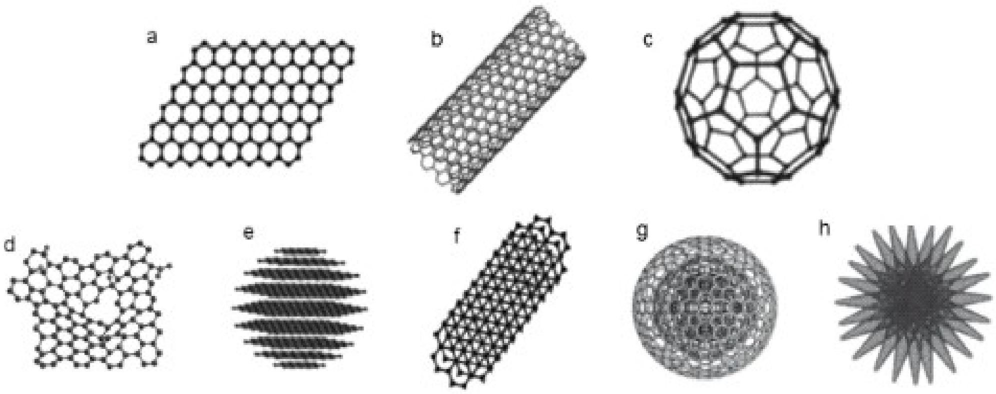
Żel krzemionkowy to materiał o dobrych właściwościach sorpcyjnych: dużej powierzchni właściwej, szczególnie w przypadku krzemionki mezoporowatej, wysokiej wytrzymałości mechanicznej oraz odporności na pęcznienie i kurczenie. Jest on prosty i tani w produkcji. Do podstawowych wad krzemionki należy zaliczyć stosunkowo niską tolerancję pH, szczególnie środowiska zasadowego oraz brak grup funkcyjnych na powierzchni, co jednak niwelowane jest łatwością jej modyfikacji. Żel krzemionkowy funkcjonalizuje się poprzez immobilizację przy pomocy grup silanolowych różnorodnych ugrupowań organicznych, takich jak łańcuchy oktylowe $–C_8$ czy oktadecylowe $–C_{18}$, grupy aminowe $–NH_2$, cyjanowe –CN i inne, na powierzchni materiału [2,6,23,24].

3.2. Nanomateriały węglowe

Węgiel jest tanim materiałem o dużej dostępności odznaczającym się wysoką wartością powierzchni właściwej i znakomitymi własnościami sorpcyjnymi. Dzięki posiadanym cechom jest ceniony i wykorzystywany jako sorbent w technikach ekstrakcyjnych, od wielu lat stosowany do usuwania ksenobiotyków ze środowiska wodnego, lądowego i atmosferycznego.

W analizie chemicznej najczęściej wykorzystywanymi odmianami alotropowymi węgla są: węgiel aktywny, grafit, grafen oraz nanorurki węglowe. Struktury różnych alotropów węgla (takich jak grafen, CNTs, fulereny, kropki kwantowe, czy nanowłókna, nanocebulki i nanorożki węglowe) przedstawiono na rysunku 2. Odznaczają się one wysoką stabilnością chemiczną i termiczną i niewielką gęstością, są to więc bardzo lekkie materiały o dużej powierzchni właściwej, wynoszącej od kilkuset do kilku tysięcy $m^2 \cdot g^{-1}$. Nanomateriały węglowe charakteryzują się również niską reaktywnością i tendencją do aglomeracji, czyli tworzenia zawiesin w wodzie. Grafen i nanorurki węglowe wykazują charakter hydrofobowy, dodatkowo utrudniając wykorzystanie ich jako adsorbenty w ekstrakcji z wodnych roztworów i próbek [2,23,25-28].

W celu zredukowania niekorzystnych właściwości związanych z hydrofobowością, słabą reaktywnością czy skłonnością do aglomeracji materiały węglowe poddaje się modyfikacjom powierzchni poprzez przyłączenie podstawników organicznych, polimerów czy też cząstek innych nanomateriałów. Dzięki modyfikacji powierzchni możliwe jest uzyskanie nowych sorbentów na bazie substancji węglowych o właściwościach i funkcjonalności znacznie odbiegających od materiału wyjściowego, dostosowanych do charakterystyki poszukiwanego analitu [26,29].



Rys. 2. Przykłady różnych nanomateriałów węglowych: grafen (a), nanorurki węglowe (b), fulereny (c), redukowany tlenek grafenu (d), węglowe kropki kwantowe (e), nanowłókna węglowe (f), nanocebulki (g) i nanorożki (h) [28].

3.3. Nanomateriały o własnościach magnetycznych

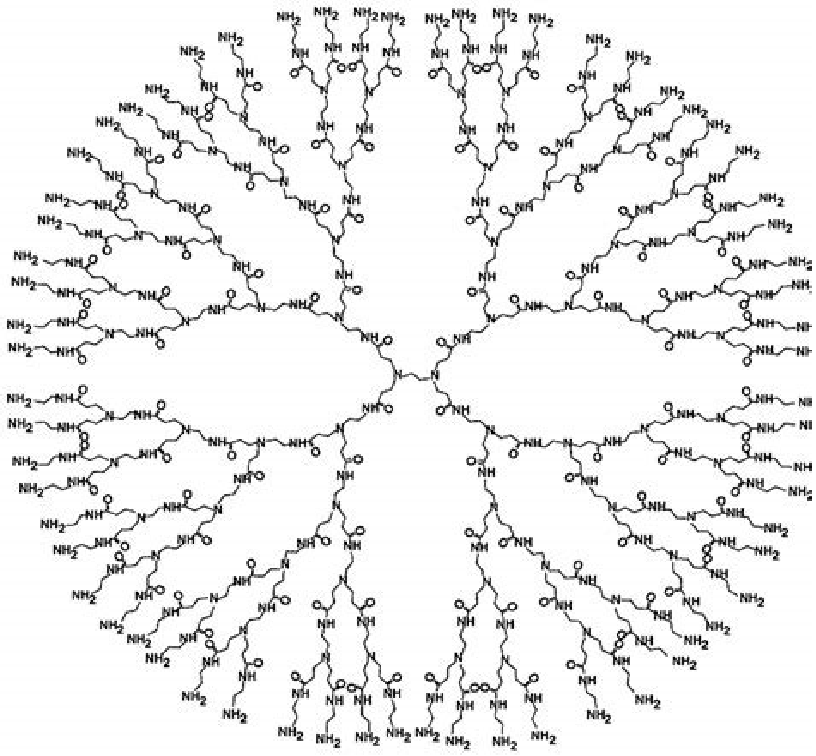
W ostatnich latach widać rosnące zainteresowanie wykorzystaniem nanocząstek magnetycznych (z ang. *Magnetic Nanoparticles*, MNPs) w procedurach ekstrakcyjnych w charakterze sorbentów. Materiały te wykazują wysoki stosunek powierzchni właściwej do objętości, a ich superparamagnetyczny charakter ułatwia separację przez zewnętrzne pole magnetyczne. Dzięki swoim właściwościom fizykochemicznym najczęściej stosowanym w SPE materiałem magnetycznym jest magnetyt (tlenek żelaza, Fe_3O_4), badana jest również możliwość użycia pochodnych materiałów spinelowych (tlenek glinu i magnezu, $MgAl_2O_4$). W celu zapobiegania utlenianiu oraz aglomeracji MNP stosuje się powłoki, zarówno organiczne jak i nieorganiczne, co z kolei umożliwia dalszą modyfikacją i funkcjonalizację materiału [30-33].

3.4. Sorbenty polimerowe

Polimery porowate otrzymywane z usieciowanych żywic organicznych syntezowane są w postaci jednorodnych ziaren o niezwykle regularnych kształtach, średnicach i rozmiarach porów. Ich właściwości fizykochemiczne zależą od zastosowanych monomerów oraz warunków prowadzenia reakcji polimeryzacji, co gwarantuje wysoki stopień kontroli nad końcowym produktem. jedną z najważniejszych zalet tych materiałów jest wysokie zróżnicowanie funkcjonalności, które w połączeniu z dużą powierzchnią właściwą i dobrą odpornością chemiczną, szczególnie wobec wody, przyczyniło się do ich praktycznych zastosowań w katalizie, fotoluminescencji, czy do magazynowania gazów. Strukturalna i funkcjonalna jednorodność będąca wynikiem wysokiego stopnia kontroli nad produktem polimeryzacji pozwala z powodzeniem stosować polimery porowate w charakterze wypełnień kolumn stosowanych w technikach separacyjnych. [2,23,34,35].

Jednym z najnowszych zastosowań polimerów w analityce chemicznej są tzw. polimery z nadrukiem molekularnym (z ang. *molecularly imprinted polymers*, MIPs), syntezowane zarówno w postaci ziaren jak i powłok. Materiały te należą do najbardziej selektywnych faz stosowanych w SPE i cieszą się rosnącą popularnością w oznaczaniu analitów w ilościach śladowych. Ich przygotowanie opiera się o kopolimeryzację monomeru sieciującego z monomerem funkcjonalnym, tj. zdolnym do interakcji z poszukiwanym związkiem, budując strukturę wewnętrzną ziarna. Reakcję tą prowadzi się w obecności szablonu, którym może być zarówno sam analit bądź jego bliska pochodna. Po zakończeniu polimeryzacji cząsteczki szablonu zostają usunięte z powierzchni pozostawiając po sobie puste przestrzenie odpowiadające analitowi kształtem, rozmiarem i funkcjonalnością chemiczną. Gwarantuje to bardzo wysoką specyficzność i selektywność MIPs i przyczyniło się do określenia ich mianem syntetycznych przeciwciał [4,34,36,37]

Kolejną grupą polimerów, zainteresowanie którą w ostatnich latach wyraźnie rośnie, są dendrymery. Są to materiały o złożonej, wysoce zdefiniowanej, symetrycznie rozgałęziającej się strukturze wewnętrznej i powierzchni zewnętrznej charakteryzującej się wysoką funkcjonalnością. Centrum dendrymeru tworzy rdzeń otoczony rozgałęziającymi się łańcuchami polimerowymi, zwanymi dendronami, na końcach których znajdują się grupy funkcyjne charakterystyczne dla monomerów zastosowanych do syntezy. Od długości łańcuchów węglowodorowych związków użytych w polimeryzacji zależą z kolei rozmiary przestrzeni pomiędzy ramionami dendrymeru, które mogą również odgrywać rolę w procesie adsorpcji. Na rysunku 3 przedstawiono strukturę polimeru dendrymerycznego na przykładzie poli(amidoaminy) (PAMAM) [34,38-41].



Rys. 3. Struktura dendrymeru na przykładzie polimeru PAMAM [39].

4. HIPOTEZA I CELE NAUKOWE

Hipoteza badawcza:

Możliwe jest zastosowanie kopolimeru dendrymerycznego oraz spinelowych związków koordynacyjnych jako wydajnych sorbentów do izolacji ksenobiotyków z naturalnych wód powierzchniowych w procesie ekstrakcji do fazy stałej.

Cele naukowe:

1. Przygotowanie i charakterystyka fizykochemiczna materiału o strukturze kopolimeru dendrymerycznego metyloaminy i eteru 1,4-dibutanodiolodiglycydylowego osadzonego na powierzchni nośnika krzemionkowego.

2. Przygotowanie i charakterystyka fizykochemiczna spinelowych związków koordynacyjnych o własnościach magnetycznych.

3. Opracowanie prostej i wydajnej procedury analitycznej do izolacji i oznaczania zawartości wybranych ksenobiotyków w wodzie.

4. Ocena zdolności otrzymanych materiałów do izolowania wybranych ksenobiotyków z próbek naturalnych wód powierzchniowych.

5. WYKAZ ARTYKUŁÓW NAUKOWYCH STANOWIĄCYCH CYKL PUBLIKACJI ROZPRAWY DOKTORSKIEJ

1. [**P1**] **Piotr Ścigalski**, Przemysław Kosobucki, *Recent Materials Developed for Dispersive Solid-Phase Extraction*, Molecules (MDPI), 2020, 25, 4869;
   https://doi.org/10.3390/molecules25214869,
   ilość punktów MNiSW: 140, *Impact Factor* 4.2.

2. [**P2**] Tetiana Tatarchuk, Mu. Naushad, Jolanta Tomaszewska, Przemysław Kosobucki, Mariana Myslin, Hanna Vasylyeva, **Piotr Ścigalski**, *Adsorption of Sr(II) ions and salicylic acid onto magnetic magnesium-zinc ferrites: isotherms and kinetic studies*, Environmental Science and Pollution Research (Springer), 2020, 27, 26681-26693;
   https://doi.org/10.1007/s11356-020-09043-1,
   ilość punktów MNiSW: 100, *Impact Factor* 5.8.

3. [**P3**] Tetiana Tatarchuk, Mariana Myslin, Ivan Mironyuk, Przemysław Kosobucki, **Piotr Ścigalski**, Volodymyr Kotsyubynsky, *Removal of Congo Red dye, polar and non-polar compounds from aqueous solution using magnesium aluminate nanoparticles*, Materials Today: Proceedings (Elsevier), 2021, 35, 4, 518-522,
   https://doi.org/10.1016/j.matpr.2019.10.012,
   ilość punktów MNiSW: 5, *Impact Factor* 0.

4. [**P4**] **Piotr Ścigalski**, Przemysław Kosobucki, *Dendrimer Coated Silica as a Sorbent for Dispersive Solid-Phase Extraction of Select Non-Steroidal Anti-Inflammatory Drugs from Water,* Molecules (MDPI), 2024, 29, 380,
   https://doi.org/10.3390/molecules29020380,
   ilość punktów MNiSW: 140, *Impact Factor* 4.2.

6. UZASADNIENIE SPÓJNOŚCI TEMATYCZNEJ CYKLU PUBLIKACJI ROZPRAWY

Na rozprawę doktorską pt. „*Nowe materiały sorpcyjne do izolowania ksenobiotyków organicznych i nieorganicznych z matryc środowiskowych*" złożył się cykl czterech artykułów naukowych opublikowanych w recenzowanych czasopismach naukowych znajdujących się w wykazie czasopism naukowych i recenzowanych materiałów konferencyjnych Ministerstwa Nauki i Szkolnictwa Wyższego i przypisanych do dyscypliny Nauki chemiczne, a mianowicie: „*Recent Materials Developed for Dispersive Solid-Phase Extraction*" [P1] (Molecules), „*Adsorption of Sr(II) ions and salicylic acid onto magnetic magnesium-zinc ferrites: isotherms and kinetic studies*" [P2] (Environmental Science and Pollution Research), „*Removal of Congo Red dye, polar and non-polar compounds from aqueous solution using magnesium aluminate nanoparticles*" [P3] (Materials Today: Proceedings), oraz „*Dendrimer Coated Silica as a Sorbent for Dispersive Solid-Phase Extraction of Select Non-Steroidal Anti-Inflammatory Drugs from Water*" [P4] (Molecules). Publikacje te przybliżają tematykę dyspersyjnej ekstrakcji do fazy stałej pokazując potencjał i elastyczność tej techniki przygotowania próbek wykorzystywanej do rozdzielania szerokiej gamy matryc i analitów przy użyciu różnorodnych sorbentów. Przedstawione badania opisują zastosowanie tej techniki w procedurach analitycznych opracowanych w celu oceny zdolności otrzymanych materiałów do izolacji wybranych analitów organicznych i nieorganicznych.

W celu zaplanowania badań przedstawionych w publikacjach P2 – P4 wykonano przegląd literatury, który zaowocował bardzo szerokim zbiorem artykułów opisujących różne techniki i materiały stosowane w dyspersyjnej ekstrakcji do fazy stałej (dSPE). Podczas opracowywania metodyki do przeprowadzenia zaplanowanych badań postanowiono wykorzystać tą właśnie technikę ze względu na jej przystępność oraz niewielkie wymagania odnośnie ilości próbki i sorbentu.

Po starannej selekcji wybrane artykuły przedstawiono w pracy przeglądowej P1. Przedstawia ona najciekawsze pod względem stosowanego sorbentu, wykazujące niezwykle niskie wartości czułości lub wysokie wartości dokładności nowe metodyki analityczne wykorzystujące dSPE. Analizując ten przegląd można wywnioskować, że najwyższą popularnością jako sorbenty cieszą się na chwilę obecną materiały pochodzenia węglowego, takie jak grafen i jego pochodne, węgiel aktywny czy nanorurki węglowe. Artykuł przedstawia również w unikatowy sposób problem doboru odpowiedniego materiału i techniki pomiarowej – nie ma idealnego sorbentu czy metody możliwej do zastosowania w każdej analizie. Spośród dostępnych opcji konieczny jest wybór tych, które najlepiej nadają się do analizy poszukiwanego analitu biorąc pod uwagę charakter matrycy próbki, dostęp do aparatury pomiarowej, pożądaną dokładność pomiaru itp.

Artykuł P2 przedstawia badania prowadzone we współpracy z zespołem Profesor Tetiany Tatarchuk z Wydziału Chemii Uniwersytetu Przykarpackiego im. Wasyla Stefanyka w Iwano-Frankiwsku w Ukrainie. Opisana została seria ekstrakcji kwasu salicylowego z roztworów wodnych przy użyciu grupy żelazianów cynku i magnezu o różnych stosunkach zawartości cynku i magnezu w strukturze krystalicznej, opisanych sumarycznym wzorem $Mg_{1-x}Zn_xFe_2O_4$. Materiały te, wykazujące własności magnetyczne, zostały otrzymane w procesie samozapłonu układu zol-żel z wykorzystaniem mieszaniny alaniny i mocznika w charakterze paliwa. Przeprowadzone próby ekstrakcji kwasu salicylowego miały na celu ocenę ich zdolności do adsorpcji jonowych związków organicznych z próbek wodnych. Wyniki zawartości przed i po ekstrakcji uzyskane za pomocą wysokosprawnej chromatografii cieczowej (HPLC) z detekcją spektrofotometryczną w świetle widzialnym i nadfiolecie (UV/Vis) wykazały, że zdolność do adsorpcji kwasu salicylowego rosła wraz ze wzrostem zawartości cynku w strukturze krystalicznej. Warto zauważyć, że w początkowych etapach ekstrakcja przebiegała szybciej w przypadku materiału o zawartości magnezu i cynku o stosunku 3:2 (opisanego funkcją x(Zn) = 0,4) pozwalając na szybkie uzyskanie stanu równowagi. Końcowa pojemność sorpcyjna tego preparatu była jednak wśród badanych substancji najniższa.

W publikacji P3, opisującej kontynuację współpracy z zespołem Profesor Tatarchuk przedstawiona została ekstrakcja kwasu salicylowego oraz mieszaniny wybranych wielopierścieniowych węglowodorów aromatycznych (WWA). Jako sorbent zastosowano glinian magnezu $MgAl_2O_4$, porowaty nanomateriał spinelowy zsyntezowany metodą analogiczną do syntezy opisanej w publikacji P2. Otrzymane wyniki, również uzyskane przy pomocy pomiaru HPLC-UV/Vis pokazały wysokie powinowactwo sorbentu do kwasu salicylowego, za co odpowiedzialne są oddziaływania jonowe pomiędzy kwasem a sorbentem o właściwościach magnetycznych. Zaobserwowane z kolei niskie powinowactwo w stosunku do WWA, mających charakter niepolarny wynika z braku silnych interakcji międzycząsteczkowych (jonowych, π-π, van der Waalsa). Dodatkowo znaczne rozmiary cząsteczek WWA utrudniają fizyczne przenikanie do porów sorbentu.

Publikacja P4 opisuje syntezę i zastosowanie hybrydowego materiału porowatego MA-BDDE do jednoczesnej izolacji wybranych niesteroidowych leków przeciwzapalnych (NLPZ): aspiryny, diklofenaku, ibuprofenu, ketoprofenu i naproksenu z próbek wodnych. W celu przeprowadzenia zaplanowanych badań wykorzystano metodyki opracowane do oznaczania kwasu salicylowego zmodyfikowane na potrzeby analizy NLPZ-ów. Materiał MA-BDDE zbudowany jest z dendrymerycznie rozgałęziającego się kopolimeru metyloaminy (MA) i eteru 1,4-butanodiolodiglicydylowego (BDDE) osadzonego na nośniku krzemionkowym. Charakterystyka fizykochemiczna materiału potwierdziła obudowanie rdzenia krzemionkowego warstwami polimeru, na powierzchni którego znajdują się czwartorzędowe grupy aminowe, nadając sorbentowi charakter jonowy. Miało to ułatwić sorpcję analitów o własnościach jonowych, takich jak NLPZ-y, z których wybrano do analizy pięć popularnych związków o charakterze kwasowym: aspirynę, diklofenak, ketoprofen, ibuprofen i naproksen. Na podstawie wcześniej opracowanej metody oznaczania kwasu salicylowego zaproponowano metodę HPLC-UV/Vis do jednoczesnego oznaczania wybranych związków, natomiast ich izolację prowadzono jak we wcześniejszych badaniach techniką dSPE. Przeprowadzono walidację opracowanej metody. Pozwoliło to na wyznaczenie limitów wykrywalności (LOD) badanych związków w granicach 57 – 241 ng·ml^{-1}. Wartości te porównywalne są z danymi znajdowanymi w literaturze opisującymi stosowanie procedur HPLC-UV/Vis. W próbkach rzeczywistych (wody z Brdy i Wisły) z poszukiwanych analitów udało się wykryć jedynie diklofenak i ibuprofen. Sorbent wykazał dobre powinowactwo do badanych analitów, natomiast ich odzyski określono w granicach 72 – 98 %.

O spójności cyklu prezentowanych publikacji świadczy konsekwencja w stosowaniu metodyki badawczej użytej do osiągnięcia postawionego celu. Metody analityczne opisane w literaturze i sprawdzone w toku badań posłużyły jako podstawa do przygotowania procedur analitycznych wykorzystanych i opisanych w kolejnych opracowaniach.

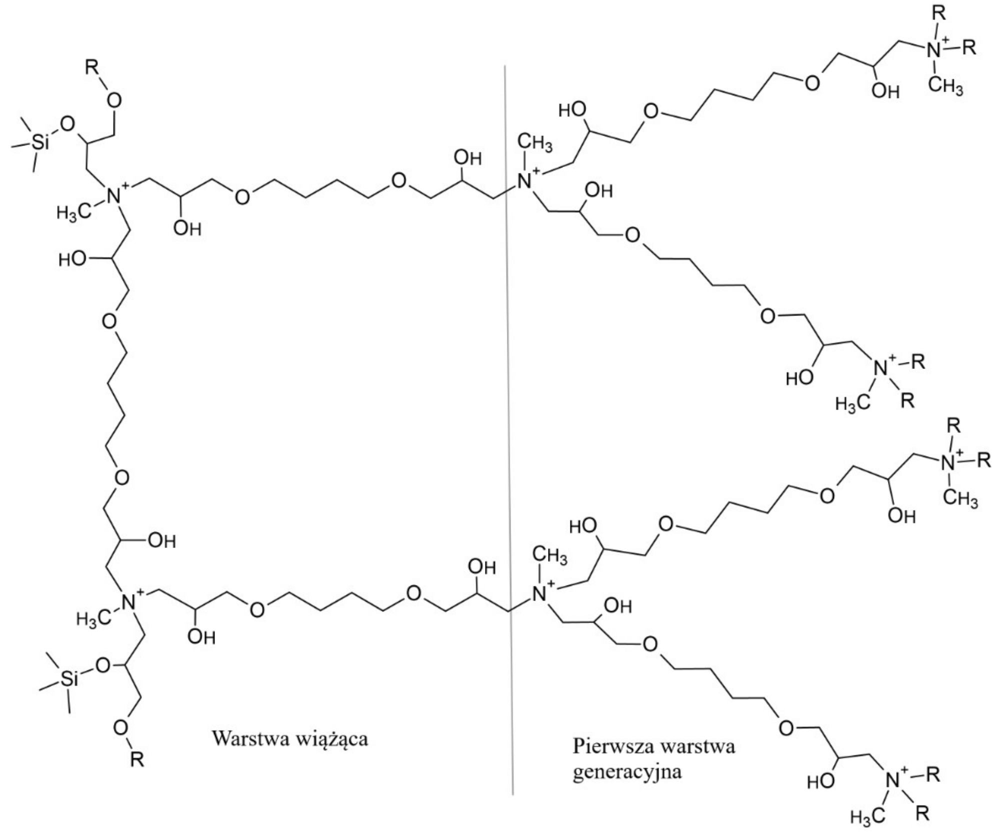
Autor niniejszej rozprawy opracował metodykę izolacji (wykorzystując dyspersyjną ekstrakcję do ciała stałego) i oznaczenia kwasu salicylowego oraz wielopierścieniowych węglowodorów aromatycznych, a także przeprowadził te analizy wraz ze wstępną analizą wyników i opisał je na potrzeby artykułów P2 i P3. W publikacjach P1 i P4 autor ma udział pierwszoplanowy, odpowiadając w zdecydowanym stopniu za plan badań, przeprowadzenie analiz i opracowanie wyników, jak również za ostateczny kształt i strukturę artykułów.

6.1.Metodyka badań

SYNTEZA I CHARAKTERYSTYKA MA-BDDE

Do syntezy hybrydowego nanomateriału porowatego MA-BDDE wykorzystano metyloaminę (MA 40%, Merck KGaA, Darmstadt, Niemcy) oraz eter

1,4-butanodiolodiglicydylowy (BDDE, 95%, Merck KGaA, Darmstadt, Niemcy). Sporządzono wodne roztwory metyloaminy (4%) i eteru 1,4-butanodiolodiglicydylowego (o stężeniu 10%) oraz mieszaninę MA+BDDE (o stężeniach 2,8% MA oraz 7,2% BDDE). W pierwszym etapie syntezy naważkę krzemionki mającej stanowić porowaty nośnik polimeru (Silica Gel 60, Merck KGaA, Darmstadt, Niemcy) umieszczono w zlewce i mieszanow obecności mieszaniny MA+BDDE w temperaturze 65 °C w celu wytworzenia warstwy wiążącej krzemionkę z polimerem jak przedstawiono na rysunku poniżej. Po upływie 30 minut materiał odsączono, przemyto wodą dejonizowaną i wysuszono.



Rys. 4. Hipotetyczna struktura wewnętrzna warstwy wiążącej oraz pierwszej warstwy dendrymerycznej polimeru MA-BDDE.

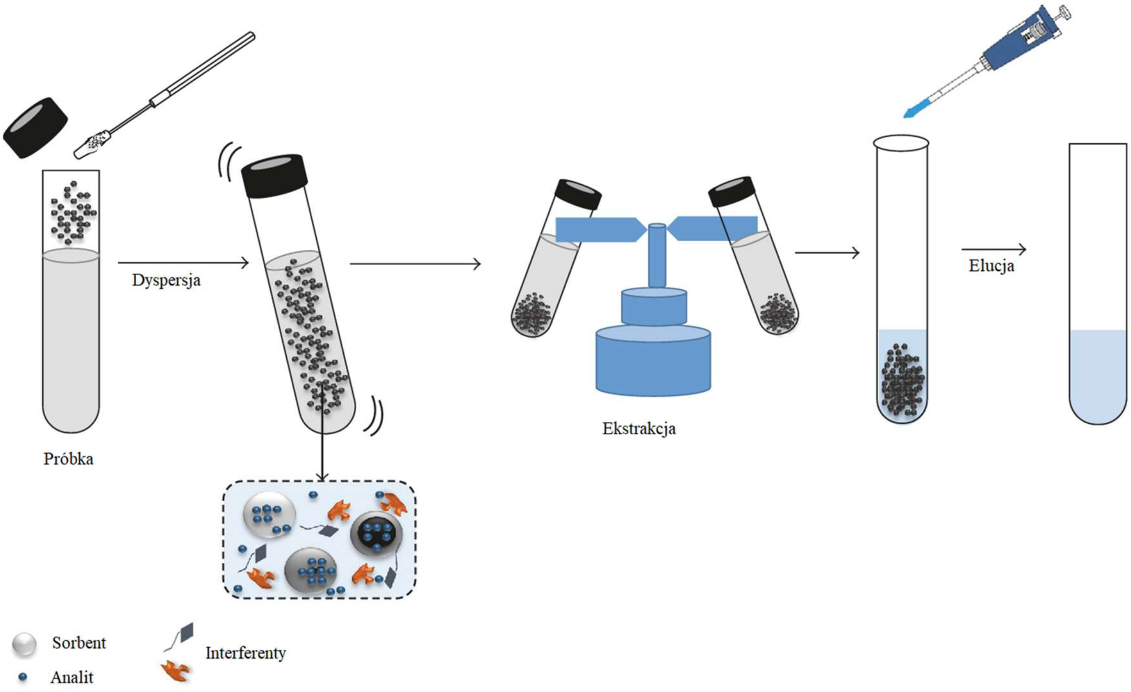
Następne dwa kroki opierały się na powtórzeniu powyższej procedury, tj. mieszaniu materiału przez 30 minut w 65 °C kolejno w roztworze metyloaminy a następnie w roztworze BDDE w celu wytworzenia pierwszej warstwy dendrymerycznej polimeru. Powyższe kroki z wykorzystaniem roztworu MA i roztworu BDDE powtórzono sześciokrotnie do uzyskania optymalnej ilości warstw kopolimeru na powierzchni krzemionki, po każdym etapie oraz po zakończeniu syntezy sorbent odsączając, przemywając i susząc. Badania właściwości serii materiałów MA-BDDE udowodniły, że najlepsze własności sorpcyjne wykazuje materiał po syntezie siedmiu warstw kopolimeru [42].

Analiza fizykochemiczna otrzymanego materiału przeprowadzona została z zastosowaniem spektroskopii w podczerwieni z wykorzystaniem transformaty Fouriera (FT-IR) w technice tłumionego całkowitego współczynnika odbicia (ATR) przy użyciu aparatu Alpha-P Attenuated Total Reflectance Fourier Transform (Bruker, Billerica, Stany Zjednoczone). Badanie techniką magnetycznego rezonansu jądrowego w ciele stałym wobec izotopu węgla ^{13}C (^{13}C CP/MAS NMR) wykonano za pomocą spektroskopu Bruker Ascend III 400 MHz (9,4T) z przystawką Avance III HD (Bruker, Billerica, Stany Zjednoczone). Uzyskane widma pozwoliły na potwierdzenie obecności kopolimeru MA-BDDE na powierzchni nośnika.

Wykonano mikroskopowe zdjęcia powierzchni sorbentu stosując aparaty LEO-1430 VP (LEO Electron Microscopy, Thronwood, Stany Zjednoczone) wykorzystujący technikę mikroskopii skaningowej (SEM) oraz Tecnai F20 X-Twin (FEI, Hillsboro, Stany Zjednoczone) wykonujący obrazowanie w technice transmisyjnej (TEM).

IZOLACJA ANALITÓW

Ekstrakcja opisana w publikacjach P2, P3 i P4 prowadzona była techniką dyspersyjnej ekstrakcji do fazy stałej (dSPE). Jest to technika, w której sypki sorbent wprowadza się bezpośrednio do całej objętości ciekłej próbki a następnie miesza, jak przedstawiono na schemacie poniżej:



Rys. 5. Schemat przebiegu ekstrakcji oraz desorpcji prowadzonej techniką dSPE [43].

Rozproszenie sorbentu w całej objętości próbki gwarantuje dużą powierzchnię kontaktu, przyspieszając wymianę masy i pozwalając na szybkie osiągnięcie stanu równowagi. Izolację z wykorzystaniem tej techniki charakteryzuje więc krótki przebieg, a także niskie wymagania odnośnie nakładu pracy oraz ilości analizowanej próbki czy sorbentu.

OZNACZENIE ZAWARTOŚCI ANALITÓW

Do badań starano się wykorzystać jak najprostsze metody separacji i detekcji. Oznaczenie zawartości analitów w publikacjach P1, P2 i P4 przeprowadzono metodą chromatografii cieczowej, stosując modularny układ do wysokosprawnej chromatografii cieczowej (HPLC) Prominence System (Shimadzu Corporation, Kyoto, Japonia) wykorzystując detekcję UV/Vis lub fluorescencyjną (FLD). Do rozdzielania i oznaczenia związków polarnych, takich jak kwas salicylowy (POCh, Gliwice, Polska) oraz niesteroidowe leki przeciwzapalne (Merck KGaA, Darmstadt, Niemcy) zastosowano kolumnę pracującą w odwróconym układzie faz Supelco Discovery HS C18 (Merck KGaA, Darmstadt, Niemcy) o długości 150 mm, średnicy wewnętrznej 4,6 mm i uziarnieniu o wielkości 5 µm. Do analizy wielopierścieniowych węglowodorów aromatycznych (Agilent, Santa Clara, Stany Zjednoczone) użyto kolumny Supelcosil LC-PAH (Merck KGaA, Darmstadt, Niemcy) o długości 250 mm, średnicy 4,6 mm i średnicy ziaren wypełnienia 5 µm. Widma absorpcyjne badanych NLPZ-ów wykonano spektrofotometrem JENWAY 7315 (Jenway, Staffordshire, Zjednoczone Królestwo).

6.2.Opis badań składających się na rozprawę doktorską

ADSORPCJA WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH

W ramach badań prowadzonych we współpracy z zespołem Profesor Tetiany Tatarchuk z Wydziału Chemii Uniwersytetu Przykarpackiego im. Wasyla Stefanyka w Iwano-Frankiwsku nad przygotowanym nanomateriałem spinelowym $MgAl_2O_4$ określono zdolność tego materiału do adsorpcji analitów o zróżnicowanej polarności. Jako związki niepolarne wykorzystano wybrane wielopierścieniowe węglowodory aromatyczne: fluoranten, benzo[b]fluoranten, benzo[k]fluoranten, benzo[a]piren, benzo[ghi]perylen oraz indeno[1,2,3-cd]perylen, które ekstrahowano jednocześnie z mieszaniny o stężeniach od 77 do 125 ng/ml. Ekstrakcję prowadzono stosując technikę dSPE, wytrząsając w fiolce polipropylenowej około 80 mg sorbentu w próbce o objętości 10 ml mieszaniny WWA przez 30 minut. Po zakończeniu ekstrakcji zawartość fiolki odwirowywano przez 20 minut z prędkością 4000 obrotów na minutę. Niewielką ilość roztworu pobierano po czym 20 µl dozowano do oznaczenia chromatograficznego. Analizę HPLC prowadzono w 30 °C w warunkach izokratycznego przepływu o prędkości 1 ml/min fazy ruchomej o składzie metanol:aceton w stosunku 95:5 v/v. Metoda została poddana uwiarygodnieniu. Detekcję WWA wykonano z wykorzystaniem detektora fluorescencyjnego (FLD) przy długości fali 365 i 470 nm. Wyznaczono wybrane parametry walidacyjne, które zostały zestawione w tabeli 1.

Tab. 1. Parametry walidacyjne wyznaczone dla stosowanej metody jednoczesnego oznaczania zawartości WWA w roztworze.

Analit	**LOD [ng·ml^{-1}]**	**LOQ [ng·ml^{-1}]**	**Zakres liniowości [ng·ml^{-1}]**	**R^2**
fluoranten	0,603	2,013	0,5 - 100	0,9996
benzo[b]fluoranten	0,113	0,376	0,5 - 100	0,9997
benzo[k]fluoranten	0,764	2,561	0,5 - 100	0,9998
benzo[a]piren	0,695	2,316	0,5 - 100	0,9998
benzo[ghi]perylen	0,149	0,496	0,5 - 100	0,9922
indeno[1,2,3-cd]perylen	0,494	1,648	0,5 - 100	0,9999

Wyniki porównania stężeń w roztworze przed i po ekstrakcji pokazały bardzo niewielkie ubytki WWA, co sugeruje słabe powinowactwo analitów z sorbentem. Brak silnych oddziaływań (jonowych, π-π, van der Waalsa) oraz znaczące rozmiary cząsteczek wielopierścieniowych węglowodorów aromatycznych utrudniające fizyczną adsorpcję na powierzchni $MgAl_2O_4$ uznano za główne przyczyny niskiej zdolności sorbentu do izolacji wybranych analitów. Ostatecznie uznano próby ekstrakcji WWA przy pomocy sorbentów o właściwościach jonowych za bezcelowe i zrezygnowano z ich prowadzenia w kolejnych badaniach.

ADSORPCJA KWASU SALICYLOWEGO

Glinian magnezu wykazał znacznie lepszą zdolność do izolacji związku polarnego jakim jest kwas salicylowy (SA). Ekstrakcję prowadzono w analogiczny sposób jak w przypadku WWA, tj. wytrząsając ok. 80 mg sorbentu w 10 ml roztworu SA o stężeniu 144 ng·ml^{-1} przez 30 minut, po czym zawartość fiolki wirowano, a następnie pobierano roztwór do oznaczenia HPLC. Analizę chromatograficzną prowadzono w temperaturze 30 ^{o}C utrzymując izokratyczny przepływ o prędkości 1 ml·min^{-1} fazy ruchomej o składzie: roztwór kwasu mrówkowego w wodzie o stężeniu 0,1%:metanol:acetonitryl (50:30:20 v/v). Detektor fluorescencyjny wykonywał pomiary przy długości fali 332 i 450 nm. Zawartość kwasu salicylowego po pomiarze chromatograficznym odczytywano z krzywej wzorcowej o zakresie liniowym od 20 do 200 ng·ml^{-1} i współczynniku determinacji R^2 równym 0,9948. Wartości granic wykrywalności LOD i oznaczalności LOQ wyniosły odpowiednio 1,60 i 5,34 µg·ml^{-1}. Po 30 minutach ekstrakcji zawartość SA w roztworze zmniejszyła się o ok. 70%, co dowodzi wysokiego powinowactwa $MgAl_2O_4$ do badanego związku o charakterze jonowym.

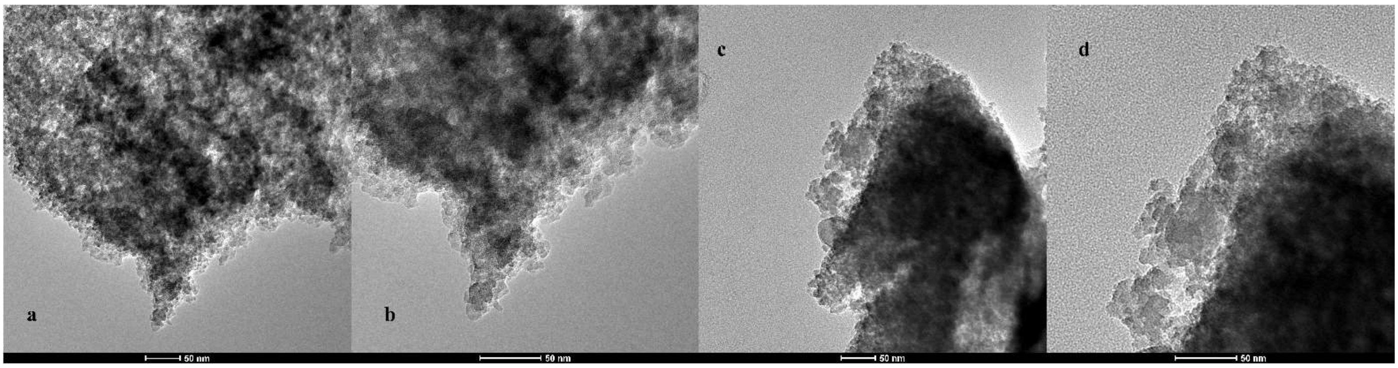
Publikacja P2 zawiera opis badań kinetycznych mających na celu określenie czasu, po jakim osiągnięta zostaje równowaga w procesie ekstrakcji kwasu salicylowego. Jako sorbentów użyto żelazianów cynku i magnezu o rosnącej zawartości cynku w strukturze krystalicznej w stosunku do ilości magnezu. Ekstrakcję prowadzono w objętości 5 ml roztworu SA o stężeniu 160,5 ng·ml^{-1} z naważką ok. 10 mg sorbentu. Proces prowadzono przez 24 godziny pobierając próbki do analizy po 1, 2, 5 i 10 godzinach oraz po zakończeniu ekstrakcji. Oznaczenie chromatograficzne wykonano korzystając z metody opracowanej na potrzeby badań przedstawionych w artykule P3 i przedstawionej powyżej. Uzyskane wyniki pokazują wyraźny wzrost pojemności sorpcyjnej SA wraz ze wzrostem zawartości cynku w żelazianach. Maksymalną pojemność sorpcyjną zaobserwowano dla materiału $Mg_{0,2}Zn_{0,8}Fe_2O_4$, gdzie zawartość kwasu salicylowego w roztworze ustabilizowała się na poziomie niższym o 90% od stężenia wyjściowego. Co istotne, równowagę tą udało się osiągnąć dopiero w ostatnim etapie ekstrakcji, między 10 a 24 godziną procesu.

W przypadku sorbentu o stosunku zawartości cynku x(Zn) = 0,4 układ osiągnął równowagę już po 5 godzinach ekstrakcji, jednak jego pojemność sorpcyjna była znacznie niższa – ten żelazian usunął z roztworu zaledwie 30% początkowej zawartości SA.

Badania adsorpcji kwasu salicylowego pozwoliły na próbę określenia kinetyki procesu, jednak żaden z proponowanych modeli nie opisywał go wystarczająco dokładnie dla każdego z analizowanych sorbentów. Najlepsze dopasowanie wyników teoretycznych do eksperymentalnych uzyskano w przypadku równania pseudo-drugorzędowego, dla którego współczynnik determinacji R^2 wyniósł 0,999 i 0,987 dla materiałów o zawartości cynku x(Zn) wynoszącej odpowiednio 0,4 i 0,8.

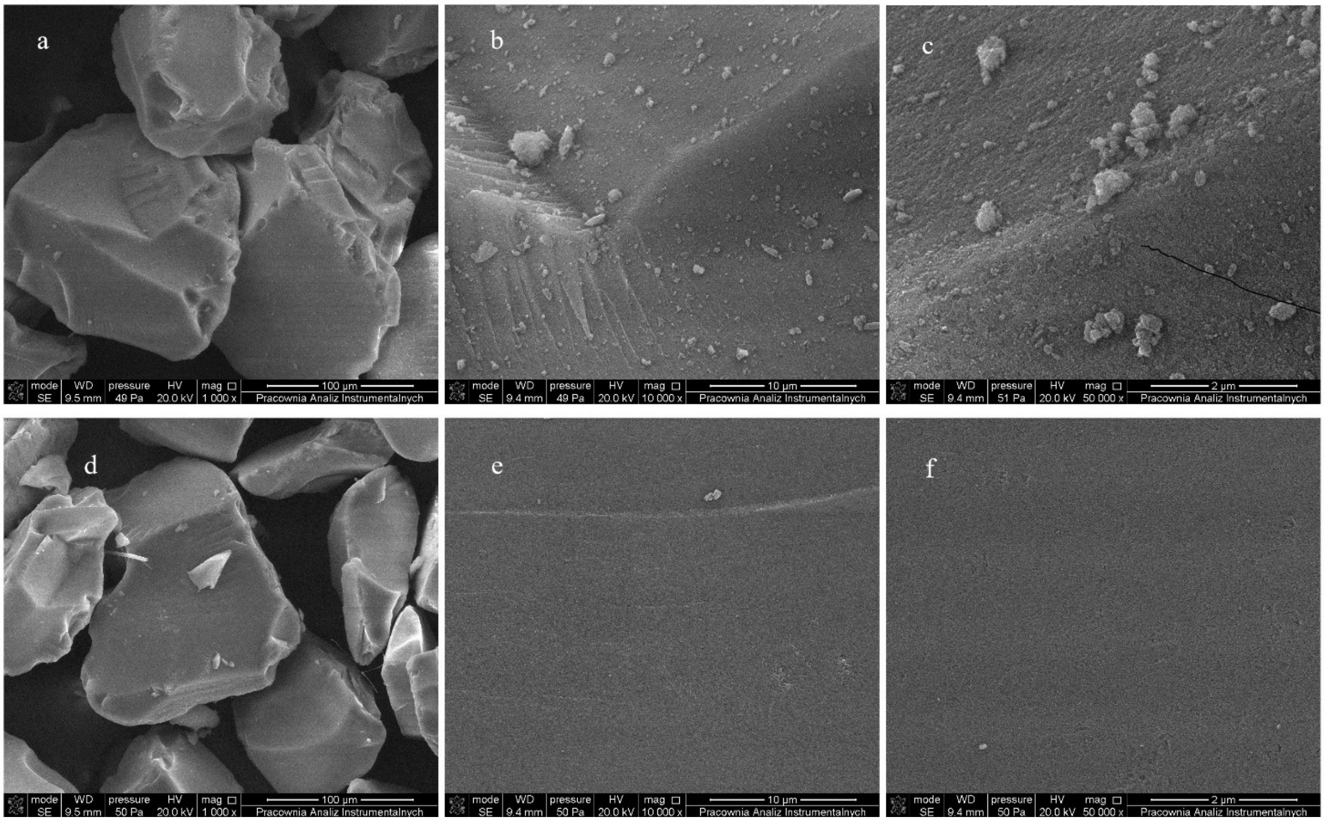
CHARAKTERYSTYKA SORBENTU MA-BDDE

Ostatnia z przedstawianych publikacji opisuje syntezę kopolimeru dendrymerycznego metyloaminy i eteru 1,4-dibutanodiolodiglicydylowego osadzonego na powierzchni porowatej krzemionki. W celu udokumentowania przeprowadzenia syntezy wykonano szereg analiz fizykochemicznych mających potwierdzić zmiany w strukturze wewnętrznej bądź morfologii zewnętrznej materiału. Rysunki 6 i 7 przedstawiają porównanie zdjęć niemodyfikowanej krzemionki oraz materiału MA-BDDE wykonanych odpowiednio technikami TEM i SEM.



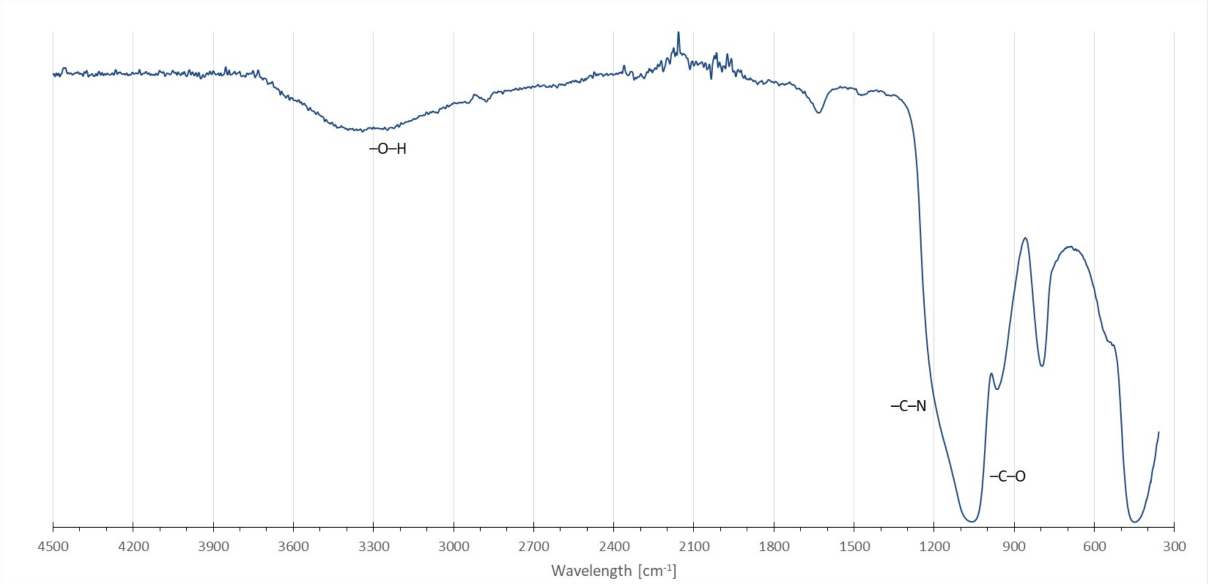
Rys. 6. Zdjęcia powierzchni sorbentu MA-BDDE (a,b) oraz niemodyfikowanego żelu krzemionkowego (c,d) wykonane techniką TEM.

Zdjęcia wykonane w technice TEM nie ujawniają wyraźnych zmian w morfologii zsyntezowanego materiału. Jednak porównanie obrazów otrzymanych z wykorzystaniem mikroskopu SEM pokazują zauważalne ujednorodnienie powierzchni spowodowane przyrostem warstw kopolimeru, skutecznie ukrywających heterogeniczności widoczne na powierzchni żelu krzemionkowego tworząc powierzchnię bardziej homogeniczną.



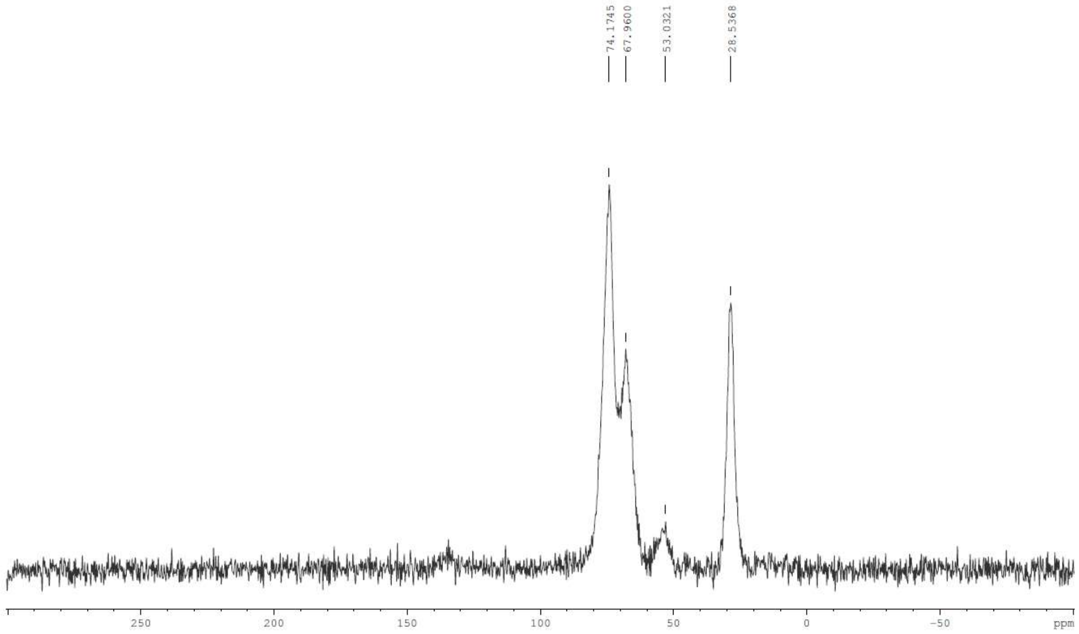
Rys. 7. Zdjęcia powierzchni niemodyfikowanego żelu krzemionkowego (a - c) oraz sorbentu MA-BDDE (d - f) wykonane techniką SEM.

Zsyntezowany materiał poddany został również analizom spektroskopowym: w podczerwieni (FT-IR) oraz magnetycznego rezonansu jądrowego (NMR) w celu potwierdzenia obecności kopolimeru MA-BDDE na powierzchni nośnika krzemionkowego. Widma uzyskane z wykorzystaniem tych metod przedstawiono na rysunkach 8 i 9.



Rys. 8. Widmo spektroskopowe w podczerwieni wykonane techniką ATR FT-IR.

Najsilniejszym sygnałem widocznym na widmie uzyskanym w podczerwieni jest szerokie pasmo przy długości fali 1050 cm^{-1}. Jest to pasmo charakterystyczne dla drgań rozciągających pojedynczego silnego wiązania alkoksylowego C–O, które w przypadku badanego materiału może być jedynie pochodną eteru 1,4-butanodiolodiglicydylowego wbudowanego w strukturę polimerową. Szerokość tego pasma oraz przegięcie wykresu widma przy długości fali około 1200 cm^{-1} wskazuje na obecność drugiego sygnału częściowo ukrytego zbyt niską rozdzielczością pomiaru, obniżoną prawdopodobnie przez polimerowy charakter sorbentu. Ostre pasmo o średniej sile przy tej długości fali przypisuje się drganiom rozciągającym wiązaniu aminowemu C–N, co świadczyłoby o wbudowaniu z powodzeniem metyloaminy w strukturę na powierzchni krzemionki. Ostatnim istotnym sygnałem widma FT-IR jest bardzo szeroki sygnał w granicach 2700 – 3800 cm^{-1}, charakterystyczny dla grup hydroksylowych –OH. Rysunek 4 potwierdza więc hipotetyczną dendrymerycznie rozgałęzioną strukturę otrzymanego materiału. Analizując otrzymane widmo w podczerwieni można również zwrócić uwagę na brak ostrych pasm o średniej intensywności w przedziale 2800 – 3000 cm^{-1}. Sygnały te odpowiadają ruchom rozciągającym azot – wodór (N–H) w grupach aminowych. Ich nieobecność może sugerować, że atomy azotu tworzące grupy aminowe w strukturze polimeru mają w przeważającej większości charakter trzecio- bądź czwartorzędowy.



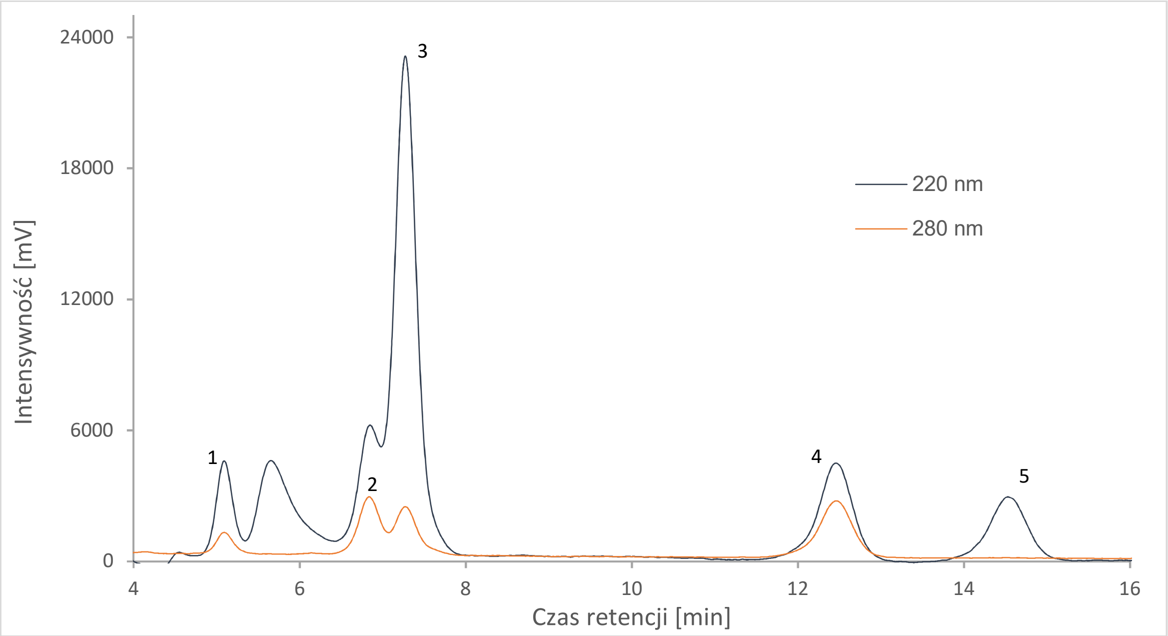
Rys. 9. Widmo ^{13}C CP/MAS NMR uzyskane dla materiału MA-BDDE.

Analiza izotopu węgla ^{13}C wykonana techniką magnetycznego rezonansu jądrowego (^{13}C CP/MAS NMR) pozwoliła na uzyskanie widma przedstawionego na rysunku 9, na którym widoczne są dwa główne sygnały. Pojedyncze pasmo widoczne przy przesunięciu o wartości 28,5 ppm znajduje się w zakresie, w którym obserwowane są sygnały pochodzące od ugrupowań zawierających grupy aminowe. Dublet pasm o przesunięciach 74,2 i 68 ppm jest natomiast obrazem charakterystycznym dla oddziaływań węgiel – wodór oraz interakcji węgla z grupami hydroksylowymi –OH. Można zatem stwierdzić, że badanie widma w podczerwieni jak i analiza jądrowego rezonansu magnetycznego przynosi dowody obecności na powierzchni materiału ugrupowań organicznych pochodnych zarówno metyloaminy jak i eteru 1,4-dibutanodiolodiglicydylowego.

OZNACZANIE ZAWARTOŚCI WYBRANYCH NIESTEROIDOWYCH LEKÓW PRZECIWZAPALNYCH

Na podstawie wykorzystywanej w badaniach opisanych w publikacjach P2 i P3 metodzie oznaczania kwasu salicylowego opracowano metodykę rozdziału chromatograficznego pięciu wybranych związków należących do grupy niesteroidowych leków przeciwzapalnych. NLPZ-y znajdują się wśród najpopularniejszych leków ze względu na łatwą dostępność i niską cenę, jak również dzięki szybkiemu i skutecznemu działaniu przeciwgorączkowemu i przeciwbólowemu. Powszechnie stosowane są więc zarówno w szpitalach jak i gospodarstwach domowych skąd trafiają do ścieków, a następnie oczyszczalni ścieków, nie zawsze wyposażonych w technologie zdolne radzić sobie z tego typu zanieczyszczeniami. W rezultacie uwalniane są one bezpośrednio do środowiska naturalnego wraz z odpływem. Innymi źródłami NLPZ w wodach są niezabezpieczone składowiska odpadów, w tym również nielegalne, mogące zawierać znaczące ilości przeterminowanych produktów farmaceutycznych. Rolnictwo, a konkretnie hodowla zwierząt, jest także istotnym źródłem ich emisji do środowiska, ponieważ niesteroidowe leki przeciwzapalne stosowane są również w weterynarii.

W celu oznaczenia zawartości pięciu wybranych do analizy NLPZ-ów, tj. aspiryny, diklofenaku, ibuprofenu, ketoprofenu i naproksenu zmodyfikowano metodę HPLC stosowaną wcześniej przy pomiarze stężenia kwasu salicylowego. Analiza widm absorpcyjnych UV-Vis badanych analitów pozwoliła na wybór odpowiedniej długości fali (220 nm) wykorzystywanej w końcowym etapie detekcji. Jak widać na chromatogramie przedstawionym na rysunku 10 sygnał ten pozwolił na pomiar zawartości czterech z pięciu badanych NLPZ-ów. Do dokładnego oznaczenia ilościowego piątego związku, ketoprofenu, konieczne okazało się wprowadzenie drugiego kanału pomiarowego, do tego celu wybrano falę o długości 280 nm.



Rys. 10. Chromatogram uzyskany dla mieszaniny NLPZ o stężeniu 1 μg·ml^{-1}. 1 – aspiryna, 2 – ketoprofen, 3 – naproksen, 4 – diklofenak, 5 – ibuprofen.

Pomiar chromatograficzny prowadzono w temperaturze 30 ^{o}C utrzymując przepływ fazy ruchomej o składzie: roztwór kwasu mrówkowego w wodzie o stężeniu 0,5%:metanol:acetonitryl (30:30:40 v/v) na poziomie 0,5 ml·min^{-1}.

Tab. 2. Parametry walidacyjne uzyskane dla jednoczesnego oznaczenia mieszaniny NLPZ-ów przy pomocy opracowanej metody HPLC-UV/Vis.

Analit	**LOD [ng·ml^{-1}]**	**LOQ [ng·ml^{-1}]**	**Zakres liniowości [ng·ml^{-1}]**	**R^2**
Aspiryna	118	396	100 – 2000	0,9936
Ketoprofen	241	802	100 – 2000	0,9744
Naproksen	103	346	100 – 2000	0,9952
Diklofenak	57	191	100 – 2000	0,9985
Ibuprofen	81	270	100 – 2000	0,9970

IZOLACJA NLPZ

Wstępną ekstrakcję analitów przy użyciu polimeru MA-BDDE prowadzono z wykorzystaniem techniki dSPE wytrząsając przez 30 minut w fiolce z polipropylenu naważkę 5 mg sorbentu w objętości 15 ml roztworu mieszaniny leków. Po zakończeniu ekstrakcji zawartość fiolki odwirowywano i pobierano próbkę do oznaczenia chromatograficznego. Sorbent odsączano i przemywano niewielką ilością metanolu. Analogicznie postąpiono z niemodyfikowaną krzemionką Silica Gel 60 w celach porównawczych. Wyniki otrzymane w toku tej analizy zestawiono w tabeli 3. Jednoznacznie potwierdzają one znaczny wzrost zdolności sorbentu MA-BDDE do adsorpcji NLPZ-ów w porównaniu do niemodyfikowanej krzemionki: pojemność sorpcyjna wszystkich badanych leków poza ketoprofenem wzrosła ponad dwudziestokrotnie po modyfikacji. Szczególnie wysokie wartości pojemności sorpcyjnej przekraczające 2 mg·g^{-1} zanotowano dla diklofenaku, naproksenu i aspiryny.

Tab. 3. Zestawienie pojemności sorpcyjnej NLPZ wyznaczone dla materiału MA-BDDE i krzemionki.

Analit	**Pojemność sorpcyjna [mg·g^{-1}]**		**Wzbogacenie**
	MA-BDDE	**Silica Gel 60**	
Aspiryna	2,01	0,08	~25x
Ketoprofen	1,07	0,11	~10x
Naproksen	2,13	0,11	~20x
Diklofenak	2,25	0,10	~22x
Ibuprofen	1,25	0,06	~21x

Przepłukany i wysuszony sorbent umieszczano w kolejnej fiolce wirówkowej, do której następnie wprowadzano 10 ml eluentu i całość ponownie wytrząsano przez 30 minut w celu przeprowadzenia desorpcji. 1% roztwór kwasu octowego w metanolu okazał się znacznie skuteczniejszy od czystego metanolu i acetonitrylu, zgodnie z doniesieniami literaturowymi [44-46]. Odzyski analitów przy użyciu różnych eluentów zestawiono w tabeli 4 i na podstawie tych danych eluentem wybranym do następujących prób desorpcji był roztwór kwasu octowego.

Tab. 4. Zestawienie odzysków analitów przy zastosowaniu różnych eluentów w procesie desorpcji.

Analit	**Odzyski [%] (RSD [%]; n = 3)**		
	Metanol	**Acetonitryl**	**1% HAc***
Aspiryna	22 (8,5)	16 (4,0)	86 (9,3)
Ketoprofen	4 (5,8)	11 (6,3)	96 (4,3)
Naproksen	9 (6,8)	12 (6,9)	103 (14,3)
Diklofenak	12 (6,1)	7 (8,2)	88 (9,7)
Ibuprofen	26 (11,0)	11 (10,3)	77 (10,1)

*Roztwór kwasu octowego w metanolu o stężeniu 1%

BADANIA PRÓBEK ŚRODOWISKOWYCH

Sorbent MA-BDDE zastosowano do izolacji wybranych NLPZ-ów z próbek wód rzek Wisły i Brdy. W tym celu w kolbce stożkowej umieszczano 100 ml wody przesączonej w celu usunięcia zawiesin oraz 50 mg sorbentu i mieszano na mieszadle magnetycznym przez 30 minut. Po zakończeniu ekstrakcji sorbent odfiltrowywano i przemyto metanolem, a po wysuszeniu przeprowadzono desorpcję roztworem kwasu octowego. Jak pokazuje tabela 5 jedynie w wodzie z Wisły udało się tą metodą wykryć niewielkie ilości diklofenaku i ibuprofenu.

Tab. 5. Wyniki oznaczenia zawartości NLPZ-ów w rzekach przy pomocy opracowanej metody dSPE-HPLC-UV/Vis.

Analit	**Stężenie [ng·ml^{-1}]**	
	Wisła	**Brda**
Aspiryna	n.d.	n.d.
Ketoprofen	n.d.	n.d.
Naproksen	n.d.	n.d.
Diklofenak	32,7	n.d.
Ibuprofen	31,6	n.d.

Prawdopodobnym wytłumaczeniem braku oznaczanych analitów w Brdzie jest niewielki rozmiar samej rzeki, a co za tym idzie dorzecza, na którym nie znajdują się liczne, duże centra populacji. Wisła natomiast będąc największą rzeką w Polsce i jedną z największych w Europie obejmuje swoim dorzeczem większość kraju, w tym największe skupiska ludności. Stąd obecność ibuprofenu, który jest jednym z najpowszechniej stosowanych leków przeciwzapalnych i przeciwbólowych na świecie, z kolei diklofenak jest powszechnie wykorzystywany w weterynarii.

Aby ostatecznie potwierdzić skuteczność sorbentu MA-BDDE w izolacji wybranych niesteroidowych leków przeciwzapalnych z wody przeprowadzono serię analiz z wykorzystaniem opracowanej procedury badawczej jako matryce stosując próbki wody z różnych źródeł z dodatkiem wzorca. Wyniki tych badań przedstawiono w tabeli 6.

Tab. 6. Zestawienie odzysków analitów po ekstrakcji próbek wody z dodatkiem wzorców.

Analit	**Odzyski [%] (RSD [%]; n = 3)**			
	Brda	**Wisła**	**Woda destylowana**	**Woda kranowa**
Aspiryna	80 (13,8)	n.d.	n.d.	92 (5,3)
Ketoprofen	92 (8,1)	88 (3,3)	99 (3,7)	99 (6,3)
Naproksen	98 (8,7)	93 (4,8)	88 (7,8)	96 (4,5)
Diklofenak	96 (6,1)	101 (6,0)	93 (6,3)	92 (5,2)
Ibuprofen	72 (9,3)	86 (10,1)	79 (7,6)	83 (9,3)

Uzyskane wyniki oscylują blisko 100% odzysku dla większości analitów. Wyraźnie ilustruje to wysoką zdolność sorbentu MA-BDDE do adsorpcji badanych związków z próbek wody. Spośród analizowanych NLPZ-ów najniższe odzyski odnotowano dla ibuprofenu, którego zdesorbowano między 72 a 86% początkowej zawartości. Spowodowane to jest słabszą zdolnością roztworu kwasu octowego do uwalniania tego związku z powierzchni sorbentu w porównaniu do pozostałych analitów (tabela 4).

7. PODSUMOWANIE

W toku rozprawy doktorskiej zaprezentowano cykl czterech publikacji skupiających się na badaniu właściwości nowych materiałów porowatych i ocenie możliwości wykorzystania ich w charakterze sorbentów do izolacji ksenobiotyków z matryc środowiskowych. Opisane zostało zastosowanie magnetycznych materiałów spinelowych do izolacji jonów strontu Sr(II) oraz organicznych związków polarnych i niepolarnych, a także dendrymeru MA-BDDE osadzonego na nośniku krzemionkowym do ekstrakcji wybranych farmaceutyków z wody. Przedstawiono opracowane do tego celu proste i skuteczne metody analityczne. Zarówno sorbenty spinelowe jak i kopolimer MA-BDDE z powodzeniem zastosowane zostały w nowych procedurach ekstrakcyjnych wykorzystujących technikę dyspersyjnej ekstrakcji do fazy stałej. Zgodnie z przewidywaniami, zastosowane sorbenty okazały się znacznie skuteczniejsze w ekstrakcji organicznych związków jonowych, takich jak kwas salicylowy czy NLPZ-y oraz jonów nieorganicznych. Brak wystarczająco silnych oddziaływań jonowych, π-π czy van der Waalsa uznano za główną przyczynę słabej zdolności badanych materiałów do adsorpcji wybranych WWA, które poddano próbom ekstrakcji w charakterze przykładowych związków niejonowych.

Badania opisane w prezentowanych publikacjach dowiodły skuteczności zastosowanych materiałów w izolacji związków jonowych z wodnych próbek środowiskowych. Wykorzystane procedury analityczne opracowane na potrzeby oznaczenia wybranych analitów charakteryzowało niskie zapotrzebowanie na odczynniki i nakłady pracy, jak również skorzystanie z aparatury pomiarowej dostępnej w dowolnym laboratorium analitycznym. Można więc uznać je za przyjazne środowisku oraz niewymagające znacznych nakładów finansowych.

Kontynuacja badań opisanych w niniejszej pracy obejmować powinna dalsze badania nad sorbentem MA-BDDE w celu określenia jego zdolności do adsorpcji szerszego wachlarza ksenobiotyków. Kolejnym aspektem wartym uwagi jest zastosowanie sorbentu o zmodyfikowanej strukturze. Najprostszym przykładem byłoby przygotowanie materiału polimerowego opartego na innych komonomerach, ale też wykorzystanie innego materiału w charakterze rdzenia. Przykładowo mógłby to być nośnik węglowy, taki jak grafen czy nanorurki.

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9. STRESZCZENIE

Nowe materiały sorpcyjne do izolowania ksenobiotyków organicznych i nieorganicznych z matryc środowiskowych

mgr inż. Piotr Ścigalski

Słowa kluczowe: ekstrakcja, chromatografia, ochrona środowiska, ekoanalityka

Ciągły rozwój gospodarczy pociąga za sobą stałe zwiększanie się ilości substancji antropogenicznych uwalnianych do środowiska naturalnego w wyniku działalności człowieka. Ksenobiotyki te, pochodzące z każdej gałęzi przemysłu i rolnictwa wywierają negatywne skutki zakłócając delikatną równowagę obecną w każdym ekosystemie, ale też zagrażając zdrowiu ludzi zamieszkujących skażony region.

Za główne źródło zanieczyszczeń wód naturalnych uznaje się ścieki komunalne i przemysłowe. Stosunkowo duże ilości ścieków nadal pozostają nieoczyszczone – dotyczy to tych pochodzących z górnictwa, ale też części ścieków uwalnianych przez przemysł, a mianowicie zakłady metalurgiczne, farbiarskie czy wytwarzające środki ochrony roślin. Większość oczyszczalni ścieków komunalnych znajduje się w pobliżu dużych skupisk ludzkich natomiast często brakuje ich na obszarach wiejskich, skutkując uwalnianiem zanieczyszczeń bezpośrednio do środowiska. Poważne zagrożenie dla czystości wód powierzchniowych stanowi również rolnictwo uprawiane na szeroką skalę. Środki ochrony roślin z pól uprawnych jak i farmaceutyki stosowane w hodowli zwierząt wypłukiwane są z opadami atmosferycznymi z pól i pastwisk i spływają wprost do rzek i jezior. W celu wykrywania tego typu zagrożeń, a następnie podejmowania kroków mających im przeciwdziałać, konieczny jest ciągły, wiarygodny monitoring czystości wody w rzekach. Dlatego też nieprzerwanie prowadzone są badania nad opracowywaniem nowych technologii i materiałów mogących posłużyć do izolacji i oznaczenia stale rosnącego szeregu zanieczyszczeń antropogenicznych.

Prezentowane opracowanie opiera się na opisie cyklu czterech publikacji przedstawiających badania nad nowymi materiałami mogącymi znaleźć zastosowanie jako sorbenty w ekstrakcji zanieczyszczeń z wodnych próbek środowiskowych. Przedstawiono zastosowanie magnetycznych materiałów spinelowych do izolacji jonów strontu Sr(II), kwasu salicylowego i WWA, a także polimeru MA-BDDE osadzonego na nośniku krzemionkowym

do ekstrakcji wybranych farmaceutyków. Zgodnie z przewidywaniami, zastosowane sorbenty okazały się znacznie skuteczniejsze w ekstrakcji związków jonowych.

Badania opisane w przedstawionych publikacjach dowiodły skuteczności zastosowanych materiałów w izolacji związków jonowych z wodnych próbek środowiskowych. Niskie zapotrzebowanie na odczynniki chemiczne i nakłady pracy wykorzystanych procedur analitycznych, takich jak izolacja analitów techniką dSPE czy rozdział i oznaczenie przy użyciu układu HPLC z detektorami UV-Vis i FLD pozwala na zakwalifikowanie ich jako metod przyjaznych środowisku.

10.ABSTRACT

New sorptive materials for organic and inorganic xenobiotics isolation from environmental matrixes

MSc Eng. Piotr Ścigalski

Key words: extraction, chromatography, environmental protection, ecoanalysis

Constant economic growth results in continuous increase in the amounts of anthropogenic substances being released into the natural environment as a result of human activity. Those xenobiotics originating from every branch of industry and agriculture disturb delicate balance established in every ecosystem, but also pose a threat to the health of the human population living in the contaminated area.

Waste water, both industrial as well as communal, is considered to be the greatest source of natural surface water contamination. Relatively large amounts of wastewater remains untreated, in particular effluents from mining, but also industrial waste from metallurgic, dyeing and pesticide plants. Communal wastewater treatment plants are usually located in the vicinity of large population centres, while their relative scarcity in rural areas might lead to wastes being released directly to the environment. Large scale agriculture also poses a serious danger to natural waters. Crop protection products, such as fungicides, herbicides or pesticides, as well as pharmaceutical products employed in animal husbandry are being washed from fields and pastures with precipitation and flow down directly to rivers. In order to find these threats and effectively counteract them a constant reliable monitoring of surface natural waters is necessary. To that end continuous research to develop new technologies and materials for isolation and identification of the constantly growing family of anthropogenic contaminants.

In this work a cycle of four publications showing the research into new materials that have potential to be used as sorbents in the extraction of contaminants from environmental water samples is presented. Utilization of magnetic spinel materials in isolation of Strontium Sr(II) ions, salicylic acid and polycyclic aromatic hydrocarbons was shown, as well as the use of MA-BDDE polymer immobilized on silica core in the extraction of select non-steroid anti-inflammatory drugs. As expected these materials proved much more effective in isolating ion compounds from water.

Studies described in the presented publications have shown high effectiveness of utilized materials in isolation of ionic compounds from natural water samples. Analytical procedures employed, such as dSPE isolation and quantitative determination with an HPLC system with UV-Vis and FLD detection were characterized by low chemical reagent and manual labour requirements, confirming their status as environmentally friendly.

11. DOROBEK NAUKOWY AUTORA

11.1. Publikacje naukowe

1. **Piotr Ścigalski**, Przemysław Kosobucki, *Dendrimer Coated Silica as a Sorbent for Dispersive Solid-Phase Extraction of Select Non-Steroidal Anti-Inflammatory Drugs from Water,* Molecules (2024), 29, 380, https://doi.org/10.3390/molecules29020380, punktacja MNiSW: 140, *Impact Factor* 4.2
2. **Piotr Ścigalski**, Przemysław Kosobucki, *Nanomateriały opracowane na potrzeby dyspersyjnej ekstrakcji do fazy stałej, część 1 – modyfikacje materiałów klasycznych* Wiadomości Chemiczne (2022), 76, 1-2
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4. Tetiana Tatarchuk, Mariana Myslin, Ivan Mironyuk, Przemysław Kosobucki, **Piotr Ścigalski**, Volodymyr Kotsyubynsky, *Removal of Congo Red dye, polar and non-polar compounds from aqueous solution using magnesium aluminate nanoparticles*, Materials Today: Proceedings (Elsevier), 2021, 35, 4, 518-522,
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   punktacja MNiSW: 100, *Impact Factor* 3.

11.2. Rozdziały w monografiach naukowych

1. Anna Pollok, Przemysław Kosobucki, Waldemar Studziński, **Piotr Ścigalski,** *Sposoby zagospodarowania żużli i popiołów powstałych poprzez termiczne przekształcenie opadów komunalnych*, rozdział w książce pt. „Nauka niejedno ma imię…" tom VII, Wydawnictwa Uczelniane Uniwersytetu Technologiczno-Przyrodniczego, Bydgoszcz 2019.

11.3. Udział w konferencjach naukowych

1. **Piotr Ścigalski**, Przemysław Kosobucki, Renata Gadzała-Kopciuch, *Zastosowanie dendrymerycznego sorbentu MA-BDDE w dyspersyjnej ekstrakcji do fazy stałej parabenów i estradiolu z wody*, poster, 66. Zjazd Naukowy Polskiego Towarzystwa Chemicznego, 15 – 20.09.2024, Poznań.
2. **Piotr Ścigalski**, Przemysław Kosobucki, *Zastosowanie wysokosprawnej chromatografii cieczowej i nowego sorbentu hybrydowego do izolacji i oznaczania zanieczyszczeń farmaceutycznych w wodzie*, komunikat, XIV Konferencja Naukowa „Chromatografia Jonowa i Techniki Pokrewne 2024", 8 – 10.04.2024, Katowice.
3. **Piotr Ścigalski**, Przemysław Kosobucki, *Detection of non-steroid anti-inflammatory drugs in water using dendrimer-coated silica as sorbent*, komunikat, Baltic University Programme Symposium 2023, 7.11.2023, konferencja zdalna.
4. **Piotr Ścigalski**, Przemysław Kosobucki, *Charakterystyka i zastosowanie kopolimeru porowatego na nośniku krzemionkowym do izolacji farmaceutyków z wody*, komunikat, 65. Zjazd Naukowy Polskiego Towarzystwa Chemicznego, 18 – 22.09.2023, Toruń.
5. **Piotr Ścigalski**, Przemysław Kosobucki, *Kopolimer porowaty na nośniku krzemionkowym jak sorbent w dyspersyjnej ekstrakcji do fazy stałej niesteroidowych*

leków przeciwzapalnych z wody, poster, 65. Zjazd Naukowy Polskiego Towarzystwa Chemicznego, 18 – 22.09.2023, Toruń.

6. Maria Kowalska, Alicja Gackowska, Waldemar Studziński, **Piotr Ścigalski**, *Badanie zawartości wybranych metali ciężkich w próbkach pobranych z terenów placów zabaw*, poster, 65. Zjazd Naukowy Polskiego Towarzystwa Chemicznego, 18 – 22.09.2023, Toruń.
7. **Piotr Ścigalski**, Przemysław Kosobucki, *Dendrymerycznie modyfikowana krzemionka jako sorbent w ekstrakcji niesteroidowych leków przeciwzapalnych*, komunikat, 64. Zjazd Naukowy Polskiego Towarzystwa Chemicznego, 11 – 16.09.2022, Lublin.
8. **Piotr Ścigalski**, Przemysław Kosobucki, *Dendrimer coated silica as a sorbent for dispersive solid-phase extraction of non-steroidal anti-inflammatory drugs from water,* komunikat, Zero Waste Technologies 1st International Conference, 9.06.2022, Bydgoszcz.
9. **Piotr Ścigalski**, Przemysław Kosobucki, *Badanie zdolności sorpcyjnych spinelowego materiału porowatego na bazie magnezu otrzymanego metodą samozapłonu zol-żel*, komunikat, E-Zjazd Zimowy Sekcji Studenckiej Polskiego Towarzystwa Chemicznego, 19.12.2020, konferencja zdalna.
10. **Piotr Ścigalski**, Marta Worzakowska, Katarzyna Księżniak, Izabela Bukowska-Śluz, Wiesław Rudź, *Synteza i charakterystyka estrów geraniolu*, poster, 5th International seminar on modern polymeric materials for environmental applications, 15 – 17.05.2013, Kraków.
11. **Piotr Ścigalski**, Barbara Gawdzik, Marta Worzakowska, *Method of synthesis of digernyl esters*, poster, 13th Belgian Organic Synthesis Symposium BOSS XIII, 15 – 20.07.2012, Leuven, Belgia.

12.ZAŁĄCZNIKI

12.1. Kopie artykułów naukowych stanowiących cykl publikacji rozprawy doktorskiej

molecules

MDPI

Review

Recent Materials Developed for Dispersive Solid Phase Extraction

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Academic Editors: Ewa Kłodzińska and Muhammad Ajmal Shah
Received: 29 September 2020; Accepted: 20 October 2020; Published: 22 October 2020

Abstract: Solid phase extraction (SPE) is an analytical procedure developed with the purpose of separating a target analyte from a complex sample matrix prior to quantitative or qualitative determination. The purpose of such treatment is twofold: elimination of matrix constituents that could interfere with the detection process or even damage analytical equipment as well as enriching the analyte in the sample so that it is readily available for detection. Dispersive solid phase extraction (dSPE) is a recent development of the standard SPE technique that is attracting growing attention due to its remarkable simplicity, short extraction time and low requirement for solvent expenditure, accompanied by high effectiveness and wide applicability. This review aims to thoroughly survey recently conducted analytical studies focusing on methods utilizing novel, interesting nanomaterials as dSPE sorbents, as well as known materials that have been only recently successfully applied in dSPE techniques, and evaluate their performance and suitability based on comparison with previously reported analytical procedures.

Keywords: dispersive solid phase extraction; novel sorbents; nanomaterials; environmental samples; food samples

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1. Introduction

The constant increase in the quality of life observed in recent years and decades requires corresponding growth of economy and industry, resulting in increased emissions of potentially harmful substances, such as pesticides, pharmaceuticals, heavy metals and more, collectively known as xenobiotics, into the natural environment. As our understanding of these substances and their effect on the environment and human health grows, restrictions are being put in place to control their release, prompting the need to develop suitable measurement methods, allowing monitoring of their presence in the environment and aiding the industry in reducing polluting emissions.

Numerous precise analytical methods have been developed to this end, many of them consisting of a chemical species separation achieved usually through the means of a wide variety of chromatographic techniques, namely gas chromatography (GC) and liquid chromatography (LC), the latter now mostly employed in its high performance iterations such as HPLC (high pressure liquid chromatography) and UPLC (ultrahigh pressure liquid chromatography), as well as electrophoretic techniques, such as capillary zone electrophoresis (CZE). Target quantification can be carried out based on the analyte type and utilizes one or more of many diverse detection techniques, from atomic emission (AES) or absorption spectroscopy (AAS) in the case of metal ions, to mass spectrometry (MS), to ultraviolet (UV), fluorescence (FL) or visual range (Vis) spectrophotometry for organic compound determination.

However accurate and quick a method should be, samples arriving at the laboratory can rarely be analyzed without any preparation. Environmental samples often exhibit complex matrixes containing many particulate and chemical interferents, rendering them unsuitable for immediate analysis [1–3]. Nearly every sample needs to be subjected to treatment aimed at separating the analyte from the matrix, allowing for reliable analysis. For more complex samples, this can necessitate the employment of multiple complicated procedures, in which case the sample pre-treatment becomes the bottleneck of the entire analytical process [1,2,4]. As measurement becomes faster and more accurate, the drive to develop effective, simple, selective, rapid, reliable and green clean-up and pre-concentration techniques is as strong as ever.

One of the oldest and most simple pre-concentration methods still in wide use is liquid–liquid extraction (LLE). This technique, however, carries some inherent disadvantages that can make it expensive or impractical in application: it is time-consuming and labor-intensive while also requiring large volumes of organic solvents, often highly toxic themselves [1–3].

Solid phase extraction (SPE) enjoys significant advantages over LLE as it largely manages to avoid many of its drawbacks. It requires much lower amounts of solvents, takes less time and is less complex to operate, while providing better effectiveness and selectivity and also being easier to automate and combine with other pre-treatment or analytical procedures. SPE with its modifications and iterations, such as solid phase microextraction (SPME), stir bar sorptive extraction (SBSE), matrix solid phase dispersion (MSPD) or ion-exchange solid phase extraction (IE-SPE), has rightfully become one of the most widely used sample preparation techniques for solid or liquid samples [1–3,5].

Dispersive solid phase extraction (dSPE) is an iteration of the SPE technique that has surged in popularity since 2003, when it was reported by Anastassiades et al. as an effective clean-up procedure in pesticide extraction from produce. In this very approachable method, the solid sorbent is applied directly into the volume of a liquid sample solution without the need for prior sample preparation, and the whole procedure relies entirely on shaking and centrifugation. This simple approach ensures high contact surface between sorbent and sample, allowing for the extraction equilibrium to be reached quickly. The resulting method is rapid and proven to be effective, and considering the very low amounts of sorbent and solvent required, it can be viewed as a more environmentally friendly method than standard solid phase extraction [2,5,6].

dSPE quickly found recognition as a valuable complement to the QuEChERS (quick, easy, cheap, efficient, rugged, safe) clean-up procedure, resulting in the development of CSN EN 15,562 and AOAC 2007.01 official standards for QuEChERS-dSPE pesticide determination methods. Most commonly used commercially available kits developed in accordance with these standards include typically one or more of three sorbents for the dSPE step: graphitized carbon black (GCB), primary-secondary amine (PSA) and octadodecyl-bonded silica (C18). However, new materials are being investigated as suitable for dSPE as the range of perceived potential applications for the technique broadens [2,7]. As shown in Figure 1, materials put to use as sorbents exhibit various functional structures, which can be further modified in order to achieve the highest possible effectiveness and selectivity of the extraction process.

The aim of this review article is to take a closer look at new and interesting materials that have been reported over the last couple years as having potential for application in dispersive solid phase extraction as sorbents. A survey of recently published literature revealed a large interest in exploring the possibilities of dSPE application and improving its efficiency by utilizing newly developed nanomaterials and techniques. In this work, we focused on the most recent reports on novel or modified classical sorbents applied in dSPE procedures and subjected the proposed analytical methods to critical evaluation based on the obtained results and validation parameters.

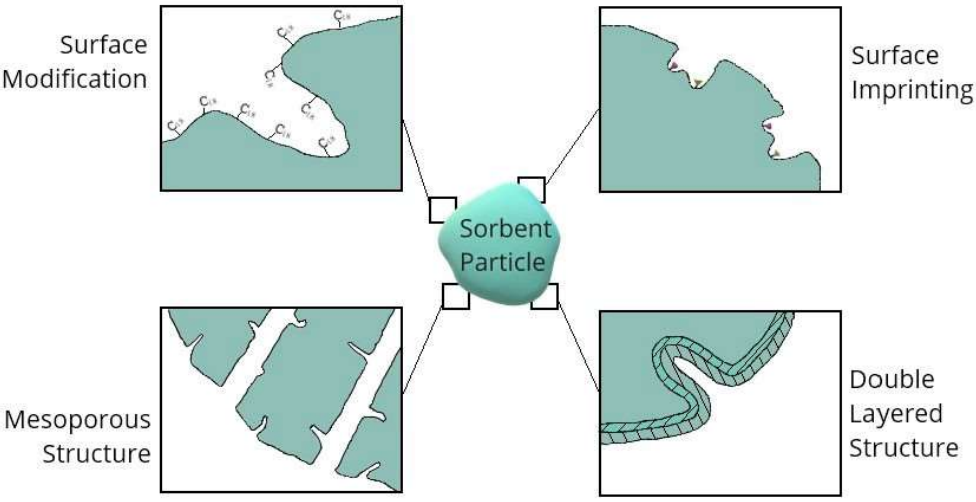

Figure 1. Examples of basic functional structures of SPE sorbents**.**

2. Sorbents Based on Silica

Silica in various forms is one of the oldest and most widely used sorbents in solid phase extraction, typically used in normal phase procedures based on adsorption [1]. Its drawbacks include its limited pH tolerance and singular sorption mechanism, stemming from a lack of diverse surface functional groups. It is, however, an easy to synthesize, cheap and rigid material, with good resistance to shrinking and swelling, and the ease with which it can be modified offsets its disadvantages to a significant degree. In addition to this, mesoporous silica adds the benefit of having an organized, ordered internal structure containing uniformly distributed mesopores [8–11]. Recent attempts to take advantage of the ease with which standard silica can be modified have provided unclear results. Papers describe the immobilization of complex amine-based organic moieties on the surface of the silica carrier and the application of obtained sorbents in the dSPE procedure for the extraction of rare earth elements [12] and phosphoproteins [13]. While the materials show desirable qualities such as high selectivity toward analyte or good reusability, it is difficult to properly evaluate the potential of the proposed methods with no precise numerical data presented. In contrast, a study by Fuh et al. on silanized silica modified with a lauryl methacrylate-based copolymer, used as a sorbent in the dSPE-HPLC-UVD process for the determination of trace herbicide content [14], presented good results, closely comparable to literature data (Table 1). An additional advantage of the method is the remarkably low sample size required; however, the overall precision may suffer from the distinctively limited linear range.

Mesoporous silica has been recognized for carrying similar potential, as a number of commercially available materials, such as MCM (Mobil Composition of Matter), HMS (Hexagonal Mesoporous Silica) and MSN (Mesoporous Silica Nanoparticle), have been modified with quaternary ammonium salts and amines. The obtained sorbents were used in analytical procedures to detect endocrine disrupting compounds (EDC) [15], polyphenols [9,16], as well as synthetic dyes in various food and environmental samples. Results of these studies, gathered and displayed in Table 1, were in all cases comparable or better than cited literature data, while also benefitting from the advantages of dSPE pre-treatment and employing relatively common detection systems, such as HPLC devices coupled with MS or diode array detectors (DAD), proving the high applicability of the proposed methods as well as the rich potential of mesoporous silica as a base for a dSPE sorbent.

Table 1. Silica-based sorbents.

Material	Analyte	Sample Matrix	Linear Range ($\mu g\ L^{-1}$)	Sensitivity [a] ($ng\ L^{-1}$)	Recoveries (%)	Detection Method	Ref.
SiO_2-BPHA	rare earth elements	aqueous solution	-	-	-	ICP-OES	[12]
NIPAAm-*co*-ABTA$_{0.35}$@SiO_2	α-casein	food	-	-	-	HPLC-DAD	[13]
LMA-HEDA@SiO_2	herbicides	environmental	0.1–4	27–53	80.1–97.9	HPLC-UVD	[14]
QTA-MCM-48	EDC	environmental	0.005–0.5	1.2–2.6	95.4–104	HPLC-FLD	[15]
HMS-RPC8-SAX2	polyphenols	food	-	1–560	70–101	UHPLC-MS/MS	[9]
HMS-C18	polyphenols	food	0.02–100	10–50	48–103	UHPLC-MS/MS	[16]
SBA-15/Met	Cd, Ni, Pb	food, environmental	0.0025–10	1–2	97.9–101.5	GFAAS	[10]
SBA-15/CCMet	Cd, Pb	food, environmental	0.001–15	0.2, 0.5	96.4–101.9	GFAAS	[17]
MSN-NH_2	synthetic dyes	food	0.45–1000	0.10, 0.30	80.0–116.8	HPLC-DAD	[11]
IL-WFOMS	plant growth regulators	herbal	0.05–22.5 [b]	0.003–0.008 [b]	77.6–98.3	HPLC-FLD	[8]

[a] LOD (limits of detection) values; [b] $\mu g\ kg^{-1}$; BPHA: *N*-benzoyl-*N*-phenylhydroxylamine; ICP-OES: inductively coupled plasma optical emission spectrometry; NIPAAm-*co*-ABTA$_{0.35}$: poly[(*N*-isopropylacrylamine-*co*-4- (3-acryloythioureido) benzoic acid)$_{0.35}$]; LMA-HEDA: poly(lauryl methacrylate-*co*-1,6-hexanediol ethoxylate diacrylate); QTA-MCM-48: quaternary ammonium-Mobil Composition of Matter-48; HMS-RPC8-SAX2: Hexagonal Mesoporous Silica dual-functionalized with n-octyl and anion exchange groups; SBA-15/Met: Santa Barbara Amorphous-15/metformin; GFAAS: graphite furnace atomic absorption spectrometry; CCMet: cyanoric chloride-metformin; IL-WFOMS: ionic liquid-functionalized ordered mesoporous silica.

A study that seems to fully embrace this potential focused on applying mesoporous silica SBA-15 modified with metformin to isolate heavy metal ions from food samples [10,17]. When compared to literature data, the proposed method exhibited results close to those achieved using a much more expensive inductively coupled plasma–mass spectrometry (ICP-MS) analysis, confirming its very good efficiency. Great effectiveness of the sorbent itself was proven, with calculated enrichment factor (EF) reaching values as extraordinarily high as 1800. The greatest disadvantage of the method appears to be the more complex operating procedures when compared to other dSPE techniques, as it introduces an additional clean-up step of either surfactant-assisted dispersive liquid–liquid microextraction (SA-dLLME) or ultrasound-assisted emulsification microextraction (UA-EME), as well as a relatively complicated sorbent preparation process.

An equally complex material, combining the characteristics of ionic liquids and mesoporous silica, was the subject of an interesting study focused on the determination of plant growth regulators (PGR) in a herb widely used in traditional Chinese medicine [8]. Laborious sorbent preparation appears to be the greatest issue with the method; however, the operating procedure is similar to the standard dSPE technique and enjoys its benefits, and it obtained results exceeding any data used for reference.

3. Sorbents Based on Magnetic Nanoparticles

In recent years, the application of magnetic nanoparticles (MNPs) as sorbents in dSPE procedures has drawn much attention. These materials exhibit good dispersibility and high surface area to volume ratio, and their super-paramagnetic nature makes them easy to isolate from the matrix by an external magnetic field, without retaining residual magnetization. Because of its physicochemical properties, magnetite (Fe_3O_4, iron oxide) is the most widely used in dSPE. In order to protect the material from oxidation and prevent the formation of agglomerates, it is often coated with organic or inorganic coatings, which in turn opens up the option of MNP modification and functionalization [18–20].

The majority of recent studies on MNP-based sorbents reported their extraction methods to be highly accurate, with recovery values close to 100% (Table 2). The most notable exception was described in a series of papers by Hernández-Borges et al., presenting the results of studies on magnetite coated with poly(dopamine) (Fe_3O_4@pDA), applied as a dSPE sorbent for the determination of phthalic acid esters (PAE) in sand and water, as well as mycotoxins in dairy product samples [20–22]. Despite the fairly low precision of the extraction process, the employed analytical procedures were highly sensitive, with obtained values comparable to or better than reported in any cited reference.

The highest extraction accuracy with MNP-based sorbent was reported in a study on the determination of arsenic speciation analysis in water, using poly(methacrylic acid) (PMAA) coated magnetite particles [23]. The sorbent, denoted as M-PMA, proved incredibly stable, showing no significant loss of sorption capabilities after up to 25 sorption–desorption cycles. The sensitivity of the method, employing a hybrid generation microwave plasma atomic emission spectrometry (HG-MP-AES) detection system, marginally falls behind only the most effective analytical procedures. While this is the case for most of the recently reported analytical procedures making use of MNP-based dSPE sorbents, a method for trihalomethane (THM) determination [24] proposed by Farhadi et al. yielded unremarkable results. Here, magnetite nanoparticles were coated with zein, a protein found in maize, which allowed very accurate extraction when applied as a sorbent. Using headspace thermal desorption (HSTD) followed by GC coupled with a micro electron capture detection (MECD) system, however, provided THM detection with sensitivity noticeably lower than in referential literature.

Table 2. Magnetic nanoparticle-based sorbents.

Material	**Target Analyte**	**Sample Matrix**	**Linear Range ($\mu g\ L^{-1}$)**	**Sensitivity [a] ($ng\ L^{-1}$)**	**Recoveries (%)**	**Detection Method**	**Ref.**
GO-Fe_3O_4	tamsulosin hydrochloride	biological	0.5–50	170	98.0–101.4	HPLC-UVD	[18]
Fe_3O_4@pDA	mycotoxins	food	20–400	290–4800, 0.41–5.82 [b]	77–120	HPLC-MS/MS	[20]
Fe_3O_4@pDA	phthalic acid esters	environmental	0.5–500	9–20 [c]	71–120	GC-MS/MS	[21]
Fe_3O_4@pDA	phthalic acid esters	environmental	0.1–250	1.38–3.19 [c] 0.020–4.0 [b] [c]	70–120	GC-MS/MS	[22]
M-PMA	As	environmental	0–100	2.98–9.95	99–102	HG-MP-AES	[23]
Zein@Fe_3O_4	trihalomethanes	environmental	0.5–100	100–360	96.68–101.2	GC-MECD	[24]
Fe_3O_4@PVA	antibiotics	food	20–4000 [b]	0.913–1.23 [b]	82.9–100.7	HILIC-MS/MS	[25]
SAC-MNP	Pb	food	30–250	10,000	102.6–106.6	SQT-FAAS	[26]
SAC-MNP	EDC	environmental	1–1000	0.28–10,000	95.3–107.8	GC-MS	[27]

[a] LOD values; [b] $\mu g\ kg^{-1}$; [c] LOQ (limits of quantification) values; GO: graphene oxide; pDA: poly(dopamine); PVA: poly(vinyl alcohol); HILIC: hydrophilic interaction liquid chromatography; SAC: stearic acid coating; SQT-FAAS: slotted quartz tube flame atomic absorption spectrometry.

4. Sorbents Based on Molecularly Imprinted Polymers

Molecularly imprinted polymers (MIPs) have received broad recognition and found widespread application in residue detection techniques, considered one of the most selective phases applied in SPE methods. Their preparation includes a copolymerization reaction of a functional monomer, capable of interacting with the target analyte, with a crosslinker in the presence of a template, that is either the target analyte or its close derivative. After the reaction, template molecules are removed from the structure, leaving a site on the surface that is complementary in size, shape and chemical functionality to the target analyte. This ensures very high specificity and selectivity of MIPs, sought after in extraction procedures, and prompts their denomination as synthetic antibodies [1,2,28,29].

MIP materials recently applied as sorbents in dSPE procedures generally fulfil the expectation of high selectivity, whether the target analytes are metal ions [19,30,31], polyaromatic hydrocarbons (PAHs) [28] or cephalosporin antibiotics [32]; however, other parameters of these analyses varied (Table 3). Good selectivity was also confirmed for a methacrylic acid (MAA)–ethylene glycol dimethacrylate (EGDMA) copolymer sorbent with dual templates (dt-MIP), designed for the simultaneous separation of two different fluoroquinolones (FQ), norfloxacin (NOR) and enrofloxacin (ENR) [33], as the sorbent showed much higher affinity toward targets than their structural analogues. Utilizing the dSPE technique with the HPLC-DAD system allowed us to carry out analyte determination with parameters better or comparable to the cited reference; however, the sorbent itself exhibited relatively low sorption capacity.

Out of the proposed MIP dSPE procedures, there was one sorbent that did not meet the selectivity expectation. This was reported by Wang et al., who synthesized hydrophilic molecularly imprinted microspheres (HMIMs) using hydroxypropyl methacrylate as a functional monomer and EGDMA as crosslinker in the presence of azoxystrobin fungicide as target template [29]. HMIM selectivity was investigated by carrying out extraction from a mixed solution of three fungicides, including azoxystrobin, which was absorbed in only marginally higher amounts. Moreover, a similar test was performed using a non-imprinted polymer and the obtained results were also comparable. It is worth noting, however, that in a procedure utilizing LC-UV detection, HMIM allowed for target determination in vegetables with good sensitivity within a very wide concentration range.

Table 3. Molecularly imprinted polymer-based sorbents.

Material	**Target Analyte**	**Sample Matrix**	**Linear Range (μg L^{-1})**	**Sensitivity [a] (ng L^{-1})**	**Recoveries (%)**	**Detection Method**	**Ref.**
Fe_3O_4@Cr(VI)IIPs	Cr	environmental	4–140	29,000	96.1–99.2	FAAS	[19]
Pb-IIP	Pb	food	3–900	700	96.0–104.0	FAAS	[30]
Ag-IIP	Ag	environmental	0.5–600	90	96.2–105.7	FAAS	[31]
MMIP	PAH	environmental	0.002–50	1–100	4.5–97	GC-MS/MS	[28]
GO-MIP	cefadroxil	environmental	40–6000	10,000	72.5–104.8	UPLC-DAD	[32]
dt-MIP	fluoroquinolones	environmental	1–200	220, 360	80.9–101.0	HPLC-DAD	[33]
HMIM	azoxystrobin	food	100–10,000 [b]	0.324 [b]	85.93–88.89	HPLC-UVD	[29]
PD-MMIP	PD, resveratrol	medicine	10–10,000	2500, 3500	91.8–102.2	HPLC-DAD	[34]

[a] LOD values; [b] μg kg^{-1}; IIP: ion imprinted polymer; MMIP: magnetic molecularly imprinted polymer; PD: polydatin.

5. Sorbents Based on Carbon

Due to its large surface area, high adsorption capacity as well as outstanding chemical, mechanical and thermal stability and relatively low preparation cost, carbon in different forms has seen wide application in xenobiotic removal from the environment. As these properties are valued for materials used in separation techniques, it is only natural for different carbon allotropes to attract considerable attention as potential SPE sorbents. In fact, as mentioned earlier, graphitized carbon black is one of the sorbents currently utilized and distributed with the QuEChERS standard procedure kits as a sorbent for the dSPE clean-up step [6,35–37].

Carbon forms investigated as sorbents range from allotropes, such as carbon nanotubes (CNTs), graphene and graphite, to modified carbon structures, known as activated carbon (AC). The latter can be produced through thermal and chemical activation of either natural or synthetic material with high carbon content within its structure, including some types of waste—for instance, waste tires [35]. Biomaterials are also being investigated as potential precursors for AC, and these include almond and walnut shells, orange peels and others. The type of precursor used, as well as the applied activation method, greatly impacts the physicochemical properties and characteristics of the obtained material [35,38]. To this end, Ebrahimi et al. reported a study on an AC material based on cherry stones [38] that was applied in the dSPE of copper followed by flame atomic absorption spectrometry (FAAS) detection. The activation process included both chemical and thermal steps, and to further improve the material's sorption capacity, it was subjected to acidic and microwave modifications. Extraction efficiency, illustrated with enrichment factor EF reaching a value of 100, proved to be better than in any of the reported SPE studies used as a reference, as was the overall method sensitivity, displayed in Table 4. The method's applicability was evaluated by carrying out the extraction from spiked milk, macaroni and rice samples, which yielded highly accurate recoveries, and the acid and microwave modified activated carbon (AMM-AC) sorbent, exhibited satisfactory reusability, showing no significant decrease in effectiveness for up to six sorption cycles. The proposed method appears to be a strong competitor for copper determination; however, it has a potentially severe drawback, as the selectivity test revealed the sorbent's low tolerance for the presence of Co^{2+}, No^{2+} and Pd^{2+} ions in the matrix, which needs to be taken into account. A study investigating the applicability of chemically activated, tire waste-originated AC deposited on the surface of polyacrylonitrile (PAN) nanofibers as a dSPE sorbent [35] shows its good ability to extract fluoroquinolones, allowing for high detection sensitivity when paired with the HPLC-DAD system. The method yielded excellent recovery values and the reusability test showed that the material can be utilized efficiently for up to ten times, after which threshold a sharp decline in sorptive properties is observed.

5.1. Graphite and Graphene

Graphite is a natural, crystalline carbon allotrope with a hexagonal internal structure. It found wide use in chromatography and solid phase extraction as it exhibits a large surface area and therefore high adsorption capacity, has good mechanical, electric and thermal resistance and conductivity and appears to be nearly inert chemically. These remarkable properties, however, are amplified in recently discovered material initially derived from graphite, graphene, which could be described as a single layer of graphite, an essentially two-dimensional sheet of hexagonally arranged carbon atoms that is just one atom thick. As the carbon rings forming the structure exhibit aromatic properties, it possesses a large delocalized π-electron system, making it possible to enter strong interactions with other aromatic compounds. Additionally, graphene derivatives, such as graphene oxide (GO), can be readily modified to employ additional functionalization to further adjust the sorption performance of the material [39,40].

As graphene has a tendency for irreversible aggregation that diminishes its sorptive properties, studies have been carried out to alleviate this problem through its immobilization or modification [36,39–43]. Although the provided literature reference was very limited, remarkable sensitivity and good accuracy were obtained when applied to real samples, as well as good sorbent reusability, attesting to the high potential of the proposed methods and sorbents (Table 4). An interesting method proposed by El-Wekil et al. saw the use of cobalt hydroxide nanoparticles (CHNPs) as sorbents complementary to reduced graphene oxide (rGO) in the dSPE procedure [44]. CHNP addition inhibited graphene aggregation and therefore ensured the high surface area of the sorbent, as well as decreasing its binding affinity towards the surfactant, polyethylene glycol (PEG) 6000, used in a cloud point extraction (CPE) system, via the formation of rGO-CHNPs hydrogen bonds. This method was proven to be highly tolerant towards potentially interfering compounds and ions and the calculated sensitivity and accuracy placed it among the most effective methods cited from the literature. In addition, the sorbent reusability test showed no significant drop in signal intensity for up to six sorption cycles.

Some studies reported the application of graphitic carbon nitride as the base for a novel dSPE sorbent. Mesoporous graphitic carbon nitride (MCN) was used in the enrichment of sulfonamides in a column-assisted extraction procedure (CA-dSPE) designed for easier separation of the dispersed sorbent [45]. A series of extraction procedures, namely SPE, dSPE and pipette-tipped SPE (PT-SPE), using the MCN sorbent, was carried out for reference; however, none of the standard methods yielded better or even comparable sulfonamide extraction results than CA-dSPE. The proposed method utilizing HPLC-DAD analysis showed good sensitivity and recovery while also requiring very little solvent for analysis when compared to the reference data, and the sorbent itself also showed good reusability. A method for phenoxy carboxylic acid (PCA) compound screening was developed with the use of “velvet-like” graphitic carbon nitride (V-g-C_3N_4) as a sorbent [46]. The employment of the direct analysis in real time (DART) ionization technique coupled with an MS detector resulted in achieving remarkable sensitivity, much higher than in both the comparative HPLC-UVD analysis and the cited literature, while requiring application of as little as 1 mg of the sorbent. Considering the fact that the material preparation is not complicated, this method’s biggest drawback appears to be its relatively low extraction accuracy and the complexity and cost of the DART apparatus.

5.2. Carbon Nanotubes

Carbon nanotubes (CNTs) are an allotropic form of carbon related to fullerene and graphene. Similarly to fullerene, they form three-dimensional structures composed of carbon atoms ordered in a hexagonal grid; however, they form tubules instead of cages. Single-wall carbon nanotubes (SWCNTs) can be visually described as a graphene sheet rolled into a tube, and multi-wall carbon nanotubes (MWCNTs) consist of multiple SWCNTs nested one over another.

Recent years have seen a significant rise in the importance of these materials, as their remarkable and unique electrical, mechanical and chemical properties have garnered them much attention. CNTs show good thermal and chemical stability, which, combined with their high adsorption capacity, ability to enter into π-π interactions with aromatic compounds as well as the relative ease with which they can be modified, opens up exciting possibilities for their application. While they have already found wide use in other separation techniques, such as standard SPE or SBSE, only recently have carbon nanotubes begun to gain popularity as sorbents in dSPE procedures [4,47,48]. A series of works published by Paszkiewicz et al. describe the performance of several MWCNT types as dSPE sorbents in analytical procedures determining different analytes, including PAHs [4,47], heavy metals [4] and various pharmaceuticals [48,49]. Theoretical and analytical tests saw studies on both modified MWCNTs and unmodified tubes of varied shapes, lengths and diameters. Great results obtained even by coupling the dSPE technique with standard procedures, such as GC-MS or LC-MS (Table 4), show the very high potential of MWCNTs as sorbent materials. Their flexibility in this role was perfectly highlighted in a separate study, where modified MWCNTs intercalated with magnetite nanoparticles were used together with CTAB surfactant to collect gaseous PAHs from marine diesel engine emissions [50]. All sixteen investigated PAHs were captured in the aqueous solution, including the heaviest ones, such as chrysene and indeno(1,2,3-cd)pyrene, and extracted using OH-MMWCNTs@CTAB, with satisfactory recovery, which allowed for detection with high sensitivity using the GC-MS system.

Recently, MWCNTs have also been investigated as a component for "bucky gels", a novel type of material combining the properties of ionic liquids and nanomaterials. Utilizing carbon nanotubes as a nano component is a way of inhibiting their aggregation while also increasing their dispersibility in water. Such a material can be applied as a sorbent in the dSPE procedure, as was reported in a paper focusing on chromium determination in water [51]. In a follow-up study, the development of a magnetic bucky gel (MBG) based on choline chloride, a hydrophilic deep eutectic solvent (DES), is described, again using MWCNTs [52]. The obtained material was applied as a dSPE sorbent in the determination of chlorine pesticides utilizing a GC-MECD system. Comparison with the reference reveals the remarkable sensitivity of the proposed method, better than in any of the cited studies. Its additional benefits include the exceptionally fast extraction process, which is reported to only take few seconds, as well as the excellent target enrichment (EF values found within 305–335 range), with the relatively wide recovery range appearing as the only notable disadvantage.

Table 4. Carbon-based sorbents.

Material	**Target Analyte**	**Sample Matrix**	**Linear Range (µg L^{-1})**	**Sensitivity [a] (ng L^{-1})**	**Recoveries (%)**	**Detection Method**	**Ref.**
AMM-AC	Cu	food	0.8–180	310	95.7–103.6	FAAS	[38]
AC-PAN	antibiotics	waste	-	50–200	98–103	HPLC-DAD	[35]
ACF	pesticides	food	-	1.14–5.89 [b]	70–120	GC-ECD, GC-MS/MS	[53]
GO@SiO$_2$	phytohormones	food	0.5–50	30,000–50,000	98.1–118.4	HPLC-UVD	[39]
GO@SiO$_2$	melatonin, tryptophan	food	0.25–500	50,000–100,000	89.1–114.8	HPLC-DAD, UPLC-MS/MS	[36]
3D-Mag-CMGO	disperse dyes	waste	5–1000	500–2480	70–109	UFLC-MS/MS	[41]
3D-Mag-CMGO	disperse dyes	environmental	0.005–5	0.17–10.2	80.0–112	UFLC-MS/MS	[42]
3D-Mag-CMGO	pharmaceuticals	environmental	0.001–0.5	0.034–0.63	78.0–109	UFLC-MS/MS	[43]
tri-BuA-rGO	pesticides	food	1–500 [b]	0.33–16.5 [b]	72.1–120.5	UHPLC-MS/MS, GC-MS/MS	[40]
rGO-CHNPs	velpatasvir	biological	0.5–45	40	97.96–103.0	CPE-FLD	[44]
G/Sep	ryboflavin	food	80–700	3000	95–104	FLD	[54]
G/Sep	PAH	waste	0.39–45	96–830	95.2–100.2	HPLC-FLD	[37]
MCN	sulfonamides	environmental	0.09–200	20–50	82.3–110.5	HPLC-DAD	[45]
V-g-C$_3$N$_4$	PCA	environmental	-	0.5–2	80.12–119.17	DART-MS, HPLC-UVD	[46]
MWCNTs	PAH, Cd, Cr, Pb	environmental	0.01–50	3–30	80.7–116.1	GC-MS/AAS	[4]
MWCNTs	PAH	environmental	-	-	-	GC-MS	[47]
MWCNTs	pharmaceuticals	environmental	0.02–2.5	1–8	85.99–120.05	LC-MS/MS	[48]
MWCNTs	β-blockers	environmental	0.005–0.5	1	80.2–135.7	GC-MS, LC-MS/MS	[49]
QA-Mag-CCNTs	perchlorate	biological	0.01–1 [b]	0.00249 [b]	85.2–107	UFLC-MS/MS	[55]
PEG-CNT-MNP	*Z*-ligustilide	herbal	-	-	98.9	HPLC-DAD, HPLC-MS/MS	[56]
M-BG	Cr	environmental	0.4–40	100	94.4–106	FO-LADS	[51]
DES-MBG	pesticides	environmental	0.0002–2	0.03–0.27	80–119	GC-MECD	[52]
OH-MMWCNTs @CTAB	PAH	engine exhaust	0.02–1	9–100	72.65–96.54	GC-MS	[50]

[a] LOD values; [b] µg kg^{-1}; ACF: activated carbon fibers; CMGO: magnetite-graphene oxide composite; tri-BuA: tri-butylamine; Sep: sepiolite; PCA: phenoxy carboxylic acid; QA-Mag-CCNTs: quaternary ammonium modified magnetic carboxylic carbon nanotubes; FO-LADS: fiber optic linear array detection spectrophotometry; CTAB: cetylthrimethylammonium bromide.

6. Sorbents Based on Layered Double Hydroxides

Layered double hydroxides (LDHs) belong to a class of synthetic anionic clays formed by stacked layers of double hydroxides of divalent and trivalent cations with hydrated anions dispersed between them. A unique property of these materials compared to other sorbent types is their high solubility in acid, which led to the development of extraction methods in which the desorption step is replaced entirely by LDH-based sorbent dissolution, thus reducing the expenditure of organic solvents. An additional benefit of replacing desorption in the analytical procedure is minimizing analyte loss, leading to highly accurate recovery [57,58].

In recent years, there have been several reports on studies investigating LDH materials as dSPE sorbents in analytical procedures aimed at the determination of heavy metals, such as cadmium, cobalt or lead. The accuracy of the extraction process was as high as expected and, in addition, most LDHs showed very good selectivity as well, even when tested with as many as 20 potentially interfering inorganic ions [59]. Many of the studies also report the sensitivity of the proposed methods to be comparable to or better than in the cited literature; however, the provided results are noticeably worse than in other papers mentioned in this review, particularly those using silica or carbon-based sorbents (Table 5).

While most of the studies employed a FAAS detection system, an attempt at chromium(VI) determination with fluorescence, using Mg-Al mixed hydroxide as the dSPE sorbent, was reported [60]. The method showed good selectivity; however, the fluorescence detection sensitivity was poor, even when using a novel probe, while also being applicable in only a narrow concentration range.

Table 5. Layered double hydroxide-based sorbents.

Material	Target Analyte	Sample Matrix	Linear Range (μg L^{-1})	Sensitivity [a] (ng L^{-1})	Recoveries (%)	Detection Method	Ref.
BCS-LDH	Fe	food, environmental	0.5–100	400	99.04–102.3	UV/Vis	[59]
Mg-Al-AHDNA-LDH	Cd, Co, Cr, Ni, Pb	biological	2–725	600–2400	95–102	FAAS	[61]
LDH-APDC	Cr	biological	8–640	2400	96–101	FAAS	[57]
LDH-ALA	Cr	environmental	20–700	7100	97.67–110.08	FAAS	[58]
DAMP-CuNCs	Cr	environmental	116–812	36,000	101.6–106.9	FLD	[60]

[a] LOD values; BCS: bathocuproine disulfonic acid; AHDNA: 4-amino-5-hydroxyl-2,7-naphthalendisulfonic acid; APDC: ammonium pyrrolidine dithiocarbamate; ALA: L-alanine; DAMP-CuNCs: 4,6-diamino-2-mercaptopyrimidine-coated copper nanoclusters.

7. Sorbents Based on Metallic Organic Frameworks

Porous coordination networks, also known as metallic organic frameworks (MOFs), are crystalline organic–inorganic hybrid materials, formed by metal ions or clusters and organic bridging ligands. Their most notable properties, including high specific surface area, porosity easily tuneable by linker choice and the fact that they are readily modifiable, brought significant attention towards a wide spectrum of industrial and scientific applications. They have already found use in catalysis, drug delivery and energy storage, as well as separation techniques [62–64].

One of the more common types of MOF researched recently appears to be zeolitic imidazole frameworks (ZIF), networks based on various metals with imidazolate ligands. A zinc-histamine-based ZIF-8 material showed remarkable efficiency in organophosphorus pesticide extraction [64], as enrichment factors calculated for the analytes were found between 801 and 914, and it retained its high effectiveness for up to eight sorption cycles. Analyte determination was carried out using a gas chromatograph coupled with a flame ionization detector (GC-FID) system, and the proposed method allowed for sensitivity better than in any study cited for reference; however, the narrow applicable concentration range is a noticeable disadvantage (Table 6). In another study, Ghani proposed using a ZIF based on cobalt (ZIF-67) as a precursor in the dSPE procedure with hierarchical Ni-Co LDH (HLDH) sorbent forming in situ [65]. The method additionally retains the benefits of LDH sorbents as HLDH is easily dispersed in 8% trifluoroacetic acid, thus reducing solvent use and analyte loss, resulting in high accuracy. The method proved to be more effective at bisphenol A (BPA) extraction than dSPE with a standard Ni-Co LDH sorbent performed for comparison and also showed good sensitivity when coupled with a HPLC-UVD system.

A copper-based MOF utilizing benzene-1,3,5-tricarboxylic (BTC) moieties as ligands was used as a precursor for a material designed to combine the properties of metallic organic frameworks and graphitic carbon [62]. The final product was characterized as porous octahedron graphitic carbon cages with metallic copper and applied as a dSPE sorbent for the extraction of fluoroquinolones, achieving good target enrichment. Comprehensive selectivity tests showed high tolerance in the presence of glucose, fructose and vitamins, as well as Fe^{3+}, Cu^{2+}, Ca^{2+}, K^{+}, Cl^{-} and NO_3^{-} ions; however, the sorbent retained only 80% of its sorption effectiveness after just four extraction cycles. Comparing the analytical performance of the proposed dSPE-HPLC-UV method with literature data shows exceptional sensitivity, greatly exceeding values reported in any of the cited studies.

Table 6. Metallic organic framework-based sorbents.

Material	Target Analyte	Sample Matrix	Linear Range (μg L^{-1})	Sensitivity [a] (μg L^{-1})	Recoveries (%)	Detection Method	Ref.
Cu@graphitic carbon cages	fluoroquinolones	food, environmental	0.1–500 1–500 [b]	0.018–0.042 0.61–1.76 [b]	81.3–104.3	HPLC-UVD	[62]
carboxylated ZIF-8	methamphetamine	biological	50–2500	10	99.83	HPLC-UVD	[63]
zinc-based MOF	pesticides	environmental	0.1–100	0.03–0.21	91.9–99.5	GC-FID	[64]
HLDH	bisphenol A	environmental	0.5–200	0.12	92–97	HPLC-UVD	[65]
NH_2-MIL-101	bisphenols	environmental	0.05–200	0.016–0.131	90.8–117.8	HPLC-FLD	[66]
UiO-66	insecticides	environmental	10–500	0.02–0.4	73.7–119.0	HPLC-MS/MS	[67]
Fe_3O_4@Fe-BTC	blood lipid regulators	environmental	585–15,400	170–467	86.7–99	HPLC-UV/Vis	[68]
MOF-5	thiols	environmental	0.118–276	0.0016–0.0031	86.6–98.5	HPLC-FLD	[69]

[a] LOD values; [b] μg kg^{-1}; MIL: Material Institute Lavoisier; UiO: Universitete I Oslo.

8. Sorbents Based on Porous Polymers

Porous polymers based on organic crosslinked resins form beads of uniform diameter with regular pore sizes. The properties of the material depend on the monomers used and the parameters of the polymerization reaction, allowing for high control over the final product and reliability of the process. Their advantages over other porous materials include inherent functional diversity and physicochemical stability, especially against water, while exhibiting very high surface areas. These remarkable properties granted polymers wide application in catalysis, gas storage and photoluminescence, among others, and their structural uniformity makes porous polymers excellent packing materials, commonly used in column-based separation techniques [1,70,71].

Recently, there has been also a growing interest in investigating their applicability in the dSPE technique (Table 7), including a study focusing on a series of materials using poly(styrene-divinylbenzene) (PS-DVB) copolymer or silica cores modified with N-vinyl pyrrolidon (NVP), 1H,1H,7H-dodecafluoroheptyl methacrylate (DMFA) or both [6]. All of the obtained materials were investigated as sorbents for flavonoid extraction. P-N-F (PS-DVB-NVP-DMFA) showed the highest sorption capacity of both quercetin and pyrocatechin and was therefore selected for further study. When combined with the HPLC-UV/Vis detection system, the procedure yielded very good sensitivity; however, reported target recoveries were relatively low.

The potential for porous polymers as sorbents of choice is illustrated by research focusing on polyethyleneimine (PEI), a weak polymeric anion exchanger, in a direct comparison with PSA regarding applicability for the simultaneous extraction of multiple pesticides and matrix clean-up of QuEChERS extracts [71]. In most cases, PEI performance appears to be similar or better, including much more accurate target recoveries as well as more effective fatty acid clean-up. In addition, a calculation of material cost per sample suggests PSA to be nearly five times more expensive to use than PEI.

Table 7. Polymer-based sorbents.

Material	Target Analyte	Sample Matrix	Linear Range (mg L^{-1})	Sensitivity [a] (μg L^{-1})	Recoveries (%)	Detection Method	Ref.
PEI	pesticides	food	-	-	91–105	TLC, LC-MS	[71]
PANI-NaY	pesticides	food, environmental	0.05–50	1–310	64–128	HPLC-DAD	[72]
dPPA	food colorants	food	100–50,000 [b]	0.035–0.055 [b]	94.3–102	FASI-CE-C^{4}D	[73]
CDP	quinolones	environmental	0.025–5	2.67–5.50	95.47–103.3	HPLC-UVD	[74]
P-N, P-N-F, Si-N, Si-N-F	pyrocatechin, quercetin	food	1–400	50, 80	78.06–83.63	HPLC-UV/Vis	[6]

[a] LOD values; [b] μg kg^{-1}; TLC: thin layer chromatography; PANI-NaY: NaY zeolite coated with polyaniline; dPPA: dispersive powder polyamide; FASI-CE-C^{4}D: capacitively filed amplified sample injection capillary electrophoresis-coupled contactless conductivity detector; CDP: cyclodextrin-based polymer.

9. Other Novel Sorbents of Note

Various materials have been thoroughly researched as sorbents applicable to the dSPE procedure that do not necessarily belong to any of the types more commonly investigated. One such material is molybdenum disulfide (MoS_2), a transition metal dichalcegonide forming two-dimensional sheets of sulfide atoms with molybdenum trapped between them. Reports describing the application of MoS_2 for sulfonamide determination in the dSPE procedure coupled with capillary zone electrophoresis (CZE) [75,76] yielded somewhat disappointing results, showing low recovery accuracy and sensitivity (Table 8). A composite of molybdenum disulfide and carbon dot (MoS_2/CD) used to extract flame retardants [77] produced results much closer to data reported in referential studies and also substantially exceeded the performance of unmodified MoS_2 and CD. The composite was also shown to be reusable for up to seven extraction cycles.

As metal oxides are known to exhibit high selectively towards cis-diol moieties, reports describe medical studies focusing on the determination of ribose conjugates in biological fluids that employ a dSPE clean-up step with CeO_2 as a sorbent [78,79]. The selectivity of the sorbent was confirmed by performing the extraction of four standard ribonucleosides from a solution of potentially interfering 2′-deoxynucleosides; however, target recoveries from real samples were low. Additionally, labeling analytes with a pair of stable isotope labeling (SIL) reagents significantly improved the sensitivity of the HPLC-MS/MS detection system, allowing for successful identification of 50 potential ribose conjugates in each study.

Table 8. Other notable sorbents.

Material	Target Analyte	Sample Matrix	Linear Range (μg L^{-1})	Sensitivity [a] (μg L^{-1})	Recoveries (%)	Detection Method	Ref.
PEG@MoS$_2$	sulfonamides	food	300–30,000	30–200	61.80–110.91	CZE-DAD	[75]
MoS$_2$	sulfonamides	environmental	500–50,000	50–120	73.20–111.51	CZE-DAD	[76]
MoS$_2$/CD	flame retardants	environmental	1–100	0.01–0.06	80–91	HPLC	[77]
CeO$_2$, ZrO$_2$	ribose conjugates	biological	-	0.16–1.59 [b]	78.5–97.5	HPLC-MS/MS	[78]
CeO$_2$	ribose conjugates	biological	-	4.11–18.09 [b]	34.0–55.9	UHPLC-MS/MS	[79]
[C$_{16}$MIM]Br-AL	insecticides	environmental	1–500	0.14–0.21	70.6–97.8	HPLC-DAD, HPLC-UVD	[80]
[C$_{12}$MIM]Br-ATP	pyrethroids	environmental	2–500	0.3–0.6	90.28–107.56	HPLC-DAD	[81]
TFA-TAPB	NAC	environmental	100–50,000	30–90	84.0–112.3	HPLC-DAD	[82]
N-Mag-COF	disperse dyes	textile	0.5–200 [c]	0.021–0.058 [c]	72.2–107	UFLC-MS/MS	[83]

[a] LOD values; [b] pg L^{-1}; [c] μg kg^{-1}; [C$_{16}$MIM]Br: 1-hexadecyl-3-methylimidazolium bromide; AL: alkalized luffa sponge fibers; [C$_{12}$MIM]Br: 1-dodecyl-3-methylimidazolium bromide; ATP: attapulgite; TFA: 2,3,5,6-tetrafluoroterephthalaldehyde; TAPB: 1,3,5-tris(4-aminophenyl)benzene; NAC: nitroaromatic compounds; N-Mag-COF: N-doped magnetite-covalent organic framework composite.

10. Summary and Conclusions

The necessity to determine trace amounts of numerous xenobiotics present in environmental samples containing varied and complex matrixes commands the drive to search for increasingly sensitive and selective methods of detection, as well as pre-treatment procedures that diminish the negative sample matrix effect. Among many known and widespread extraction methods used for analyte concentration prior to qualitative or quantitative analysis, dispersive solid phase extraction is a relatively new development of the classic SPE technique. In recent years, a significant increase in interest in dSPE can be observed, as this remarkably simple, rapid and effective technique finds use in a growing number of applications.

Articles surveyed for the purpose of this review presented studies on a wide variety of samples ranging from environmental soil and water samples to fresh produce, grain, herbs and meat, to processed food products, to biological and medical samples as well as pharmaceutical products. The reach of the analyzed xenobiotics was similarly broad, including heavy metal and rare earth metal ions, various pesticides, pharmaceuticals and their metabolites, PAHs, dyes, flame retardants and others. Procedures described in these studies were also varied in their utility, with some methods designed for the highly selective extraction and detection of a particular chemical, while others were refined to carry out a simultaneous determination of dozens of compounds of a specific type. This proves the high adaptability of the dSPE technique and suggests that the scope of possible applications for which this method is suitable will further increase in the future.

Nanomaterials based on various carbon allotropes, such as graphene or carbon nanotubes, are currently the most popular research subject, with only recently over twenty papers published. Several other sorbent types were also broadly investigated as suitable for dSPE—for instance, standard and mesoporous silica, magnetite-based nanoparticles, metallic organic frameworks and others.

There is a strong trend of modifying previously known, classical sorbents to acquire hybrid materials. The goal is to create sorbents combining the properties of two or more different materials such as carbon-based nanoparticles, MNPs and polymers. This multifunctional sorbent could then be applied for the extraction of multiple analytes; thus, it is essential to ensure that it retains most of the effectiveness of its parent materials. In parallel, a lot of attention is given to highly specialized sorbents such as MIPs, focusing on extracting particular compounds with extremely high efficiency. As research further refines and improves sorbent properties, focusing on extracting either multiple targets from complex matrixes or a selected few analytes with very high efficiency appear to be the two most prominent paths for the application of dSPE as a pre-treatment technique in the future.

What needs highlighting is that, in the majority of the presented studies, procedures utilizing these novel sorbents in dSPE produced very good results. In some cases, the precision and sensitivity of the analysis competed with the most accurate methods reported to date, while most have traded some small measure of analytical performance for the remarkable operating simplicity, greatly shortened process time and lower solvent, as well as sorbent and sample amount requirements. This implies that the popularity of dSPE as a standard sample pre-treatment procedure should grow, especially in large, high-throughput laboratories dealing with large amounts of samples, where decreased cost and analysis time would matter most, since the trade-off in analytical performance is often minimal, if any at all.

At the same time, as more sorbents and improvements to the technique itself are developed, its advantages over other extraction procedures may very well outweigh any negatives.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

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Environmental Science and Pollution Research (2020) 27:26681–26693
https://doi.org/10.1007/s11356-020-09043-1

RESEARCH ARTICLE

Adsorption of Sr(II) ions and salicylic acid onto magnetic magnesium-zinc ferrites: isotherms and kinetic studies

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Received: 20 January 2020 / Accepted: 23 April 2020

Abstract

Magnetic magnesium-zinc spinel ferrite $Mg_{1-x}Zn_xFe_2O_4$ (where $x = 0.4$, 0.6, and 0.8) was investigated as adsorbent for the efficient removal of Sr(II) ions and salicylic acid (SA) contaminants from aqueous medium. The characterization of ferrites was carried out using XRD, VSM, BET, SEM, and EDS. The surface charge of magnetic adsorbents was measured by the drift method. The determination of SA and Sr(II) ion concentrations in the solution phase was carried out by UFLC and complexometry, respectively. It was shown that varying of the Zn(II) content affected the adsorption capacities of magnesium-zinc ferrites. The increasing of zinc content from $x(Zn^{2+}) = 0.4$ to $x(Zn^{2+}) = 0.6$ increased the adsorption of Sr(II) ions from 50 to 65 mg/g, and then it was decreased to 36 mg/g for the sample with $x(Zn) = 0.8$. The $Mg_{0.4}Zn_{0.6}Fe_2O_4$ sample demonstrated the maximum adsorption capacity of 74 mg/g. The adsorption isotherm for Sr(II) was fitted by the Dubinin-Radushkevich, Langmuir, Freundlich, and Sips models. The adsorption kinetics of Sr(II) was analyzed by PFO, PSO, and Elovich models. The adsorption kinetics of SA was also investigated. It was demonstrated that the $Mg_{0.2}Zn_{0.8}Fe_2O_4$ sample exhibited 90% removal of salicylic acid from the water solutions. The results demonstrated that magnetic Mg-Zn ferrites with spinel structure are good sorbents for the removal of SA and Sr(II) ions from aqueous solution.

Keywords Magnezium-zinc ferrites · Adsorption · Strontium · Salicylic acid · Magnetic adsorbent

Introduction

Magnetic materials are increasingly used in various scientific and technological processes (Sharma et al. 2017; Kothawale et al. 2019; Satheeshkumar et al. 2019; Tsay et al. 2019; Hua et al. 2020). The use of such materials in adsorption processes makes them possible to significantly simplify the complicated procedure for separating powdered adsorbents from solution using an external magnetic field (Tatarchuk et al. 2017, 2019a, d; Deepty et al. 2018). One of the environmental problems is the contamination of territories with radionuclides, originated from nuclear power plants. A characteristic feature of all nuclear power facilities is the presence of radiation sources, which under certain conditions can lead to negative effects on humans and the environment. Strontium and cesium are the often identifed species in water and soils close to the nuclear plant facilities. Strontium has high toxicity due to its ability to actively engage in the biological cycle of substances. Strontium is an analog of calcium and easily enters the metabolic processes of animals and humans (Alby et al. 2018).

One of the most promising routes for the strontium removal is adsorption technology due to its simplicity of equipment design, low energy consumption, accessibility, and high effectiveness (Ainscough et al. 2017; Mironyuk et al. 2019a, b; Mohanraj et al. 2019). Advantages of adsorption are that it allows the separation of selected compounds from solutions

Responsible editor: Tito Roberto Cadaval Jr

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(Ng et al. 2018; Mohanraj et al. 2019; Zhang et al. 2020). The design and operation of adsorption equipment are relatively simple. The adsorption demonstrates high performance and favorable speed and is insensitive to toxic substances (Mohamed et al. 2020). In addition, adsorbed compounds can be recovered by desorbing agents, leaching, biological processes, and heat treatment. The use of adsorption processes is especially relevant when large volumes of liquid radioactive waste have to be cleaned (Faisal et al. 2020). For example, in the aftermath of accidents at nuclear facilities (during the release of radioactive substances into the environment), the decommissioning of nuclear power plants, the reclamation of places, contaminated by acts of nuclear terrorism, etc. adsorption processes are avaiable for this purposes. In such case, the use of magnetic adsorbents is very attractive (Reddy and Yun 2016; Tatarchuk et al. 2019e).

Non-magnetic cations are often introduced into the spinel structure in order to enhance the magnetic properties of spinels (Alla et al. 2018). For example, Mg^{2+} ions can be introduced into non-magnetic zinc ferrite in order to raise magnetic properties and to get stronger magnetically controlled samples. Such systems are widely studied. Magnesium-zinc ferrites with chemical formula $Mg_{1-x}Zn_xFe_2O_4$ ($x = 0.4–0.7$) were obtained by the hydrothermal method (Tsay et al. 2019). The spinel-type core-shell Zn-Mg-Fe microspheres were synthesized by the solvothermal method and tested as photocatalysts in the degradation of 1,2-dichlorobenzene gas (o-DCB) under the sunlight (Hu et al. 2019). The solution combustion route followed by sintering has been used to magnesium-zinc ferrites with chemical formula $Mg_{1-x}Zn_xFe_2O_4$ (x = 0.00…1.00, step 0.25) and crystallite sizes in the range of 47–80 nm (Choodamani et al. 2016). The $Mg_{1-x}Zn_xFe_2O_4$ nanoparticles (x = 0–0.9) with quasispherical morphology and average core diameter about 15 nm for magnetic hyperthermia applications were obtained by the sol-gel method (Reyes-Rodríguez et al. 2017). The magnesium-zinc ferrites can be obtained by other methods: auto combustion method (John and Mathew 2019), microwave-assisted sol-gel combustion method (Gore et al. 2018), co-precipitation (Zaki et al. 2015; Sharma et al. 2016; Liu et al. 2019), electrospinning technique (Ghazi et al. 2018), plasma spray (Liu et al. 2014), etc. The studies on the use of spinel ferrite nanoparticles to purify water and wastewater from organic and inorganic contaminants have proven their benefits (Kefeni et al. 2017). In particular, magnetic spinel nanoparticles are very stable and can be regenerated and reused over several cycles without losing their properties (Tatarchuk et al. 2019b). The presence of magnetic properties allows for the effective separation of solid and liquid phases under the impact of an external magnetic field, bypassing the process of filtration and/or centrifugation.

Magnetic materials based on nanoscale iron oxides are also widely used in the field of concentration and separation of various emerging contaminants from water mediums (Li 2014; Rodriguez-Narvaez et al. 2017; Sophia and Lima 2018). Among them is the salicylic acid as emerging pollutant, which is contained in the wastewater of the pharmaceutical industry and causes an urgent environmental problem (He et al. 2015). Salicylic acid and salicylates, as well as its esters (methyl salicylate) and other synthetic derivatives, have a pronounced anti-inflammatory effect (Arshadi et al. 2017). As a result, salicylic acid derivatives are widely used in medicine: sodium salicylate, salicylamide, and acetylsalicylic acid (aspirin)—as antipyretic, anti-rheumatic, anti-inflammatory, and painkillers; phenyl salicylate—as an antiseptic; and para-aminosalicylic acid—as a specific anti-tuberculosis drug. The production of these substances contributes to their contamination into the environment, mainly the aquatic environment. Salicylic acid is toxic in large doses. Thus, the removal of salicylic acid and its derivatives from the wastewater of the pharmaceutical industry is an urgent problem (Karunanayake et al. 2017; Xiao et al. 2017; Ghezzi et al. 2018; Martín et al. 2018).

In this study, we presented the results of the use of magnetic spinel ferrites with chemical composition $Mg_{1-x}Zn_xFe_2O_4$ (where x = 0.4, 0.6, and 0.8) for the removal of Sr(II) ions and salicylic from aqueous medium. Isotherm and kinetic studies for the removal of these two pollutants were also performed.

Experimental

Sample synthesis

Mg-Zn ferrites were obtained by auto-combustion sol-gel method as described in our earlier report (Tatarchuk et al. 2019c). It was noticed that the combination of fuels (urea and β-alanine) makes it possible to carry out low-temperature synthesis of spinel ferrites without additional heat treatment. In brief, the precursors were magnesium nitrate $Mg(NO_3)_2 \cdot 6H_2O$, zinc acetate $Zn(CH_3COO)_2 \cdot 2H_2O$, and ferric nitrate $Fe(NO_3)_3 \cdot 9H_2O$ (the nitrates used as oxidizers). The mixture of alanine $C_3H_7NO_2$ and urea $CO(NH_2)_2$ was used as reductant and fuel. In propellant chemistry, the total valence of the metal salts precursors must be balanced by the valence of the complexing agent (fuel). The charges of the chemical elements were taking into account (V(C)= +4; V(H) = +1; V(O) = −2; V(N) = 0; V(Me) = + 2 or + 3 (for Me(II) or (Me(III) respectively)) and the calculated results are shown in Table 1. The nitrates of metals were incorporated into a distilled water and stirred for half an hour. Then the fuel mixture was

Table 1 Total valences of the reagents

Reagent	Chemical formula	Calculations	Total valance
Magnesium nitrate	$Mg(NO_3)_2$	$1\times(+2)+2\times(1\times(0)+3\times(-2))$	− 10
Zinc acetate	$Zn(CH_3COO)_2$	$1\times(+2)+2\times(1\times(+4)+3\times(+1)+1\times(+4)+2\times(-2))$	+ 16
Iron(III) nitrate	$Fe(NO_3)_3$	$1\times(+3)+3\times(1\times(0)+3\times(-2))$	− 15
Alanine	$C_3H_7NO_2$	$3\times(+4)+7\times(+1)+1\times(0)+2\times(-2)$	+ 15
Urea	CH_4N_2O	$1\times(+4)+4\times(+1)+2\times(0)+1\times(-2)$	+ 6

introduced into the solution. After homogenization, the mixture was heated until the gel-sol formation. The further heating caused ignition reaction. The obtained samples (in powder form) were hand-crushed with a pestle.

Characterization methods

X-ray diffraction analysis was carried out on the STOE STADI P diffractometer ($CuK_{\alpha 1}$ radiation, $15 \leq 2\theta \leq 130°$ with a step of 0.015°). The XRD patterns were refined by the Rietveld method using the pseudo-Voigt profile function using FullProf.2k (version 5.60). The morphological peculiarities of the ferrites were determined using REMMA-102-02 scanning electron microscopy (SEM) (JCS SELMI, Ukraine). The specific surface area of samples was estimated by N_2 adsorption-desorption isotherms using surface area analyzer Quantachrome Autosorb, Nova 2200e, at temperature 77 K. Magnetic properties were checked using vibrating sample magnetometer (VSM) at room temperature under an applied field of ± 3 Tesla.

Adsorption studies

pH_{PZC} determination (pH-drift method)

Initially, 0.1 M solutions of sodium chloride with different pH values were prepared. The pH was adjusted by adding a hydrochloric acid solution ($pH < 7$) or sodium hydroxide ($pH > 7$). Then, 75 mg of sample was added to 15 mL of each solution. The solutions were shaken at room temperature for 4 h and left for 24 h to establish equilibrium pH. The final pH was measured using a pH meter and ΔpH was plotted against pH_o and then pH_{PZC} was calculated.

Adsorption of Sr(II) ions

The adsorption of Sr(II) ions was investigated under static conditions by shaking 100 mg adsorbent with 5 mL Sr(II) solution of different concentrations: 0.001 to 0.1 M (87.6 to 8760 mg/L, respectively) for 6 h at 22 °C. The $SrCl_2$ (Khimreaktyvy, Ukraine) was taken as source of Sr(II) ions. It was previously established that 6 h was sufficient to establish adsorption equilibrium in the system. The solutions were then decanted by magnetic separation, sampled, and the equilibrium concentration of Sr(II) was determined by a complexometric method (Harris 2007). The adsorption capacity was calculated by the following Eq.(1):

$$q_e = \frac{(C_o - C_e)\cdot V}{m} \tag{1}$$

where C_o and C_e are initial and equilibrium concentrations (mg/L) of Sr(II), respectively; m is the mass of adsorbent (g), and V is volume of strontium chloride solution (L).

Adsorption of salicylic acid

Salicylic acid (POCh, Gliwice, Poland) solution was first prepared in methanol (Merck, Darmstadt, Germany) due to its high solubility in methanol and then diluted in DMW from initial concentration of 100 mg/mL to 160.5 ng/mL. After that, sorbent (10 ± 0.2 mg) was placed in a separate centrifuge tube with 5 mL of the salicylic acid solution and mixed for 24 h using a mechanical shaker IntelliMixer (Elmi, Latvia). After 1, 2, 5, 10, and 24 h, the process was interrupted and a sample of 200 μL was withdrawn for liquid chromatography analysis, carried out on a Shimadzu UFLC Prominescence System (Shimadzu, Kyoto, Japan). The chromatograph consisted of a LC-20AB solvent delivery system equipped with a Rheodyne injection valve with a 20-μL loop, a fluorescence detector set at 332 and 450 nm, and a LC-Solution system software. Chromatographic separation was achieved at room temperature on a Supelco Discovery HS C18 (Supelco, Bellefonte, USA) column with the dimensions 4.6 mm I.D., 150 mm length, and 5 μm particle size. The efficiency of SA elimination from water solutions was estimated using Eqs.(1) and (2):

$$\%Removal = \frac{C_0 - C_e}{C_0} \times 100\% \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentrations of SA (μg/L), respectively.

Results and discussion

Adsorbents characterization

The deep characterization of magnesium-zinc ferrites has been already described in our previous paper (Tatarchuk et al. 2019c). It was shown that they have porous structure so they can be used as adsorbents for environmental remediation. Here, we reported the adsorption properties of three magnetic samples $Mg_{1-x}Zn_xFe_2O_4$ (x= 0.4, 0.6, 0.8) toward Sr(II) ions and salicylic acid. The phase composition of the ferrite samples was identified by the XRD phase analysis (Fig. 1a). All diffraction peaks in the range of 15° to 130° belong to single spinel phase and corresponded to cubic spinel structure with space group Fd3m. The cell constants are shown in Table 2. The average crystallite size of the $Mg_{1-x}Zn_xFe_2O_4$ samples was computed using Scherer formula (3):

$$D = \frac{0.9 \cdot \lambda}{\beta_{1/2} \cdot \cos\theta} \quad (3)$$

where D is average crystallite size, β is line broadening in radians (FWHM) obtained from $\beta_{1/2} = [(\beta_{\mathrm{measured}})^2 - (\beta_{\mathrm{instur}})^2]^{1/2}$, θ is Bragg angle, and λ is X-ray wavelength ($\lambda = 0.1546$ nm). The average crystallite size of the magnesium-zinc ferrite nanoparticles changed from 31 to 39 nm and are shown in Table 2.

It is known that the physicochemical characteristics of the adsorbent are primarily influenced by its texture and surface chemistry. The specific surface area of ferrite adsorbents was calculated using BET method (Fig. 1b). The results are presented in Fig. 1b which demonstrated that the samples have relatively small specific surface area from 6 to 11 m^2/g.

The vibrational sample magnetometry was used to characterize the magnetization of the magnesium-zinc ferrites (the applied magnetic field up to 3 kOe) and results are shown in Fig. 1c. The magnetic parameters (saturation magnetization M_S, remanence M_r, coercivity H_C) for $Mg_{1-x}Zn_xFe_2O_4$ samples are listed in Table 2. The saturation magnetization values were 40.1, 25.1, and 5.1 emu/g for $Mg_{0.6}Zn_{0.4}Fe_2O_4$, $Mg_{0.4}Zn_{0.6}Fe_2O_4$, and $Mg_{0.2}Zn_{0.8}Fe_2O_4$ samples, respectively. Thus, the substitution of Mg(II) ions by Zn(II) ions decreased the magnetization of ferrites. The remanence

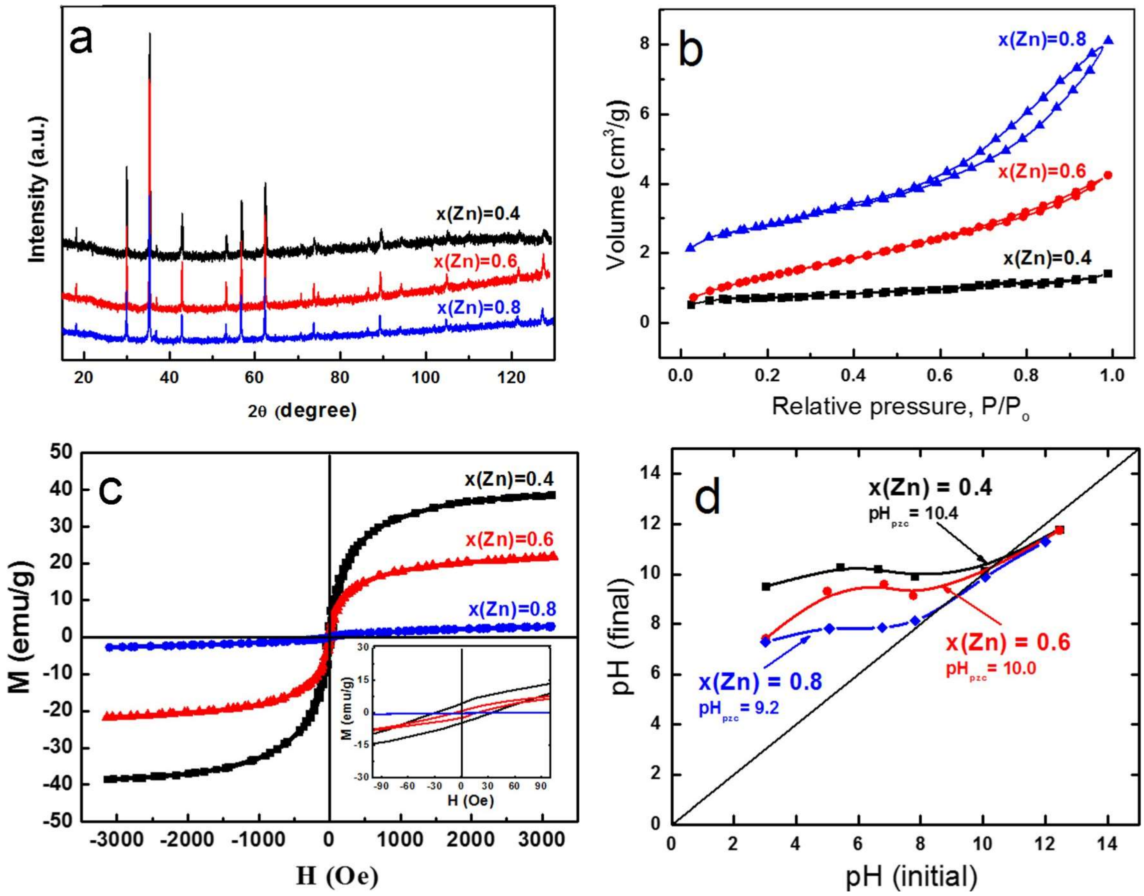

Fig. 1 a The XRD patterns of $Mg_{1-x}Zn_xFe_2O_4$ (x = 0.4, 0.6, 0.8) samples [reprinted from Tatarchuk et al. 2019c, Copyright (2019), with permission from Elsevier]; b BET; c magnetization (M_S) versus applied magnetic field (H) of the $Mg_{1-x}Zn_xFe_2O_4$ samples at room temperature; d pH_{PZC} of $Mg_{1-x}Zn_xFe_2O_4$ (x= 0.4, 0.6, 0.8) samples

Table 2 The lattice parameter (a_{exp}), crystallite size (D_{XRD}), specific surface area (S_{BET}), and magnetic properties (saturation magnetization M_S, remanence M_r, coercivity H_C) for $Mg_{1-x}Zn_xFe_2O_4$ samples

$x(Zn^{2+})$	a_{exp}, nm	D_{XRD}, nm	S_{BET}, m^2/g	M_S, emu/g	M_r, emu/g	M_r/M_S	H_C, Oe	μB, exp
0.4	0.8405	31	6	40.1	4.70	0.118	32.6	1.55
0.6	0.8418	39	7	25.1	1.14	0.045	9.2	1.01
0.8	0.8427	38	11	5.1	0.03	0.006	2.5	0.21

magnetization was decreased from 4.7 to 0.03 emu/g with increase in Zn content. The coercivity value was also decreased from 32.6 to 2.5 Oe with increase in Zn content. The magnitudes of experimental magnetic moment were estimated from Eq. (4):

$$\mu_B = \frac{M_S \cdot M}{5585} \tag{4}$$

where M_S is saturation magnetization of the sample (emu/g) and M is molecular mass of the sample (mol/g). The experimental magnetic moments μ_{exp} are presented in Table 2. It can be seen that the increase in Zn content decreased the magnetization, but samples were still magnetic. The magnetic parameters confirmed the possibility of magnetic separation of magnesium-zinc ferrites after wastewater treatment.

Acid-base parameters are often used to describe the surface of solids, since their values indicate the presence of acid and basic Lewis and Bronsted centers directly involved in surface reactions. The acid-base parameter is a universal physicochemical characteristic of the solid surface, which depends on the material nature, synthesis method, chemical composition, the impurities of nature, and amount on the surface, etc. In this regard, we tried to trace the change in the acid-base state of the ferrite surface in order to identify the common peculiarities in the formation of acid-base surface centers. One of the methods for studying of acid-base surface properties is “drift pH method,” which allows to get the point of zero charge (pH_{PZC}) parameter. For this purpose, the values of $\Delta pH = pHo - pHi$ were calculated and the curve ΔpH vs. pHo was drawn. The pH_{PZC} was determined at the crossing of the curve with the axis (x) (Fig. 1d). In Fig. 1d, the dependence of the pH_{PZC} vs. Zn(II) content for the magnetic samples is shown. The values of the point zero charges (pH_{PZC}) indicated that at a pH lower than the pH_{PZC}, the surface of the adsorbent was positively charged and adsorption of the anions took place on it. At higher pH, the surface has negative charge and the cation adsorption more preferably occurred on it. The points of zero charge for the studied magnetic samples was 10.4, 10.0, and 9.2 for $Zn_{0.4}Mg_{0.6}Fe_2O_4$, $Zn_{0.6}Mg_{0.4}Fe_2O_4$, and $Zn_{0.8}Mg_{0.2}Fe_2O_4$, respectively (Fig. 1d). The SEM of adsorbents showed that the structures of magnetic samples are represented by a large number of pores of 0.5-2 μm on their surfaces (Fig. 2). The results, which are presented in Fig. 2, indicated the difference in the porous structure of magnesium-zinc ferrite powders. Figure 2 shows the macropores that were represented by recesses with a spherical shape and a diameter of 0.5 to 2 μm. It can be seen that in $Zn_{0.6}Mg_{0.4}Fe_2O_4$ sample, there were pores with the smallest size (approximately 0.5 μm) compared to the pore sizes in the $Zn_{0.4}Mg_{0.6}Fe_2O_4$ and $Zn_{0.8}Mg_{0.2}Fe_2O_4$ samples.

Adsorption of Sr(II): isotherm modeling and kinetics

The adsorption capacity of magnetic adsorbents toward Sr(II) ions was determined from adsorption isotherms (Fig. 3). The isotherm at constant temperature relates the amount of adsorbed compound to the amount of absorbate in the equilibrium solution. The shape of the isotherm reflects the intensity of adsorption and the attraction between the adsorption and adsorbent. Isotherms can provide qualitative information about the adsorption process, as well as indicate the proportion of surface coverage. The adsorption activity of ferrite samples was studied in a batch mode in the aqueous solutions, containing Sr(II) ions. The data showed that $Mg_{0.4}Zn_{0.6}Fe_2O_4$ sample had the highest adsorption capacity which was 65 mg/g. The experiments showed that changes in the zinc content affected the adsorption efficiency of Sr(II) ions on the adsorbents surface. Figure 3 shows that the increasing of zinc content from $x = 0.4$ to $x = 0.6$ increased the adsorption of Sr(II) ions from 50 to 65 mg/g, and then the adsorption capacity was decreased to 36 mg/g for the sample with $x = 0.8$. This was due to the change in the morphological and structural properties of the adsorbent surface. It can be seen from Fig. 2 that sample $x(Zn) = 0.6$ showed the surface with smallest pores and has particles with the biggest crystallite sizes (Table 2). It could also be seen that observed adsorption was due to the presence of specific active sites on the adsorbent surface, able to react with adsorbate (Sr(II)), and does not determine by the specific surface area (Table 2).

The attempts were made to apply some of adsorption models (Langmuir, Freindlich, Dubinin-Radushkevich, and Sips) in order to quantify the main characteristics of the interaction of Sr(II) ions with ferrite nanoparticles. Nowadays, the two approaches can be used to determine adsorption parameters: non-linear regression (Dotto et al. 2012; Marques et al. 2018) and linearization (Tran et al. 2017). The linearization was used to determine adsorption parameters in the present work. The Langmuir model is based on the concept of a monomolecular layer of adsorbed particles formed due to the short-range nature of surface forces. The Langmuir

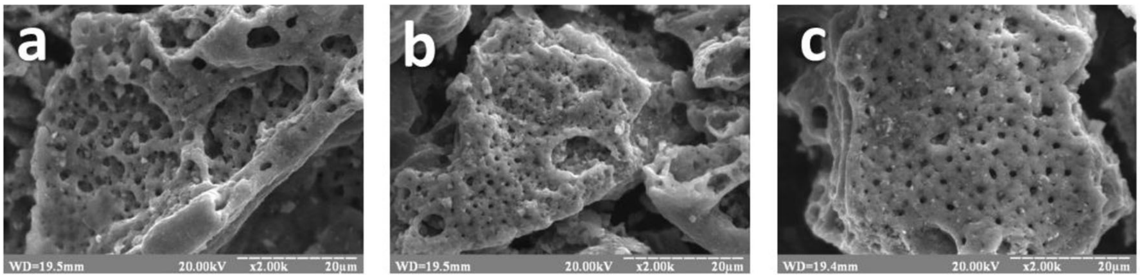

Fig. 2 SEM of magnesium-zinc ferrite samples (magnification × 2000): a $Zn_{0.4}Mg_{0.6}Fe_2O_4$; b $Zn_{0/6}Mg_{0/4}Fe_2O_4$; c $Zn_{0/8}Mg_{0/2}Fe_2O_4$

isotherms are based on physical assumptions that all surface states have the same adsorption energies, that atoms do not interact with each other, and that only one atom or molecule can accommodate on one surface center. The change in energy during adsorption or desorption is the same (Tran et al. 2017). The Langmuir equation in the linear form can be expressed as Eq. (5):

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max}K_L} \tag{5}$$

where q_e (mg/g) is adsorption capacity, q_{max} (mg/g) is the maximum adsorption capacity, C_e (mg/L) is the strontium amount at equilibrium, and K_L (L/mg) is a Langmuir constant. The parameters q_{max} and K_L were obtained from a plot of C_e/q_e vs. C_e. The separation factor R_L (dimensionless constant characterizing the Langmuir isotherm) was computed by Eq. (6):

$$R_L = \frac{1}{1 + K_L C_0} \tag{6}$$

where R_L is a constant separation factor (dimensionless) of the solid-liquid adsorption system, K_L is the Langmuir equilibrium constant, and C_o (mg/L) is the initial Sr(II) concentration (Tran et al. 2017). R_L is related to the nature of adsorbent/adsorbate interaction and isotherm type: unfavorable ($R_L >$ 1), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

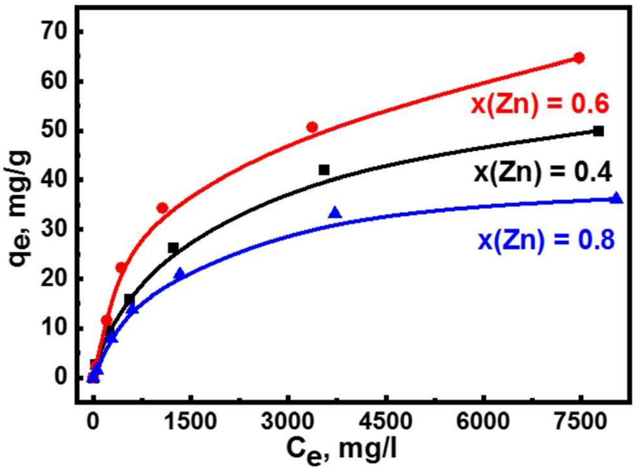

Fig. 3 Isotherms of Sr(II) adsorption onto $Mg_{1-x}Zn_xFe_2O_4$ samples (x = 0.4; 0.6; 0.8)

In fact, if the surface of the adsorbent is heterogeneous, an interaction takes place between the adsorbed particles, the active centers are not completely independent of each other, etc. All these factors complicate the form of the isotherm equation. The Freundlich model is used to describe the adsorption on a heterogeneous surface and there is no saturation zone on the Freindlich isotherm. The Freundlich equation in the linear form can be expressed as Eq. (7):

$$\log q_e = n \log C_e + \log K_F \tag{7}$$

where q_e (mg/g) is the equilibrium adsorption capacity; C_e (mg/L) is the equilibrium concentration of Sr(II); K_F ((mg g^{-1})(mg L^{-1})$^{-1/nF}$) is Freundlich constant; and $1/n_F$ is the heterogeneity factor.

The Langmuir and Freundlich models are widely used, but they do not explain the adsorption mechanism. To study the mechanism of the adsorption process, we verified the equilibrium data using the Dubinin-Radushkevich (D-R) isotherm model. The D-R model does not imply surface homogeneity and is used to differentiate the chemical and physical adsorption. The Dubinin-Radushkevich model determines the nature of adsorption and can be used to calculate the average free adsorption energy. The linear form of the Dubinin-Radushkevich model can be expressed as Eq. (8):

$$\ln q_e = -K_{DR} \cdot R^2 T^2 ln^2 \; 1 + C_e^{-1} \; + \ln q_{DR} \tag{8}$$

where q_{DR} (mol/g) is the adsorption capacity, K_{DR} (mol^2/kJ^2) is a constant related to the adsorption energy, R is the gas constant ($R = 8314 \times 10^{-3}$ kJ/(mol × K)), T is the temperature (in Kelvin), q_e (mg/g) is the equilibrium adsorption capacity, and C_e (mg/L) is the equilibrium concentration of Sr(II). The parameters q_{DR} and K_{DR} were obtained from a plot of $\ln q_e$ versus $R^2 T^2 ln^2 \; 1 + C_e^{-1}$. The slope and intercept were equal to -K_{DR} and ln(q_{RD}), respectively.

Thus the mean adsorption energy E (kJ/mol) was calculated using Eq. (9):

$$E = \frac{1}{\sqrt{2K_{DR}}} = \frac{1}{\sqrt{-2slope}} \quad (9)$$

The value of K_{DR} allows one to make a conclusion about the nature of the interaction forces between strontium ions and active surface centers of the adsorbents in order to answer the question whether the binding of strontium ions to the ferrite surface is a physical process or a chemical process. It is believed that if the value of E is higher than 8 kJ/mol, the adsorption process is chemosorption and if this value is less than 8 kJ/mol, the adsorption process has physical nature.

The Sips model is based on the Langmuir equation, but takes into account the attractive forces between the adsorbate molecules. The Sips equation has three parameters and it combines the Freundlich and Langmuir equations. The linear form of the Sips equation can be written as Eq. (10):

$$\ln\left(\frac{q_{ms}}{q_e}-1\right) = -\ln K_s - \frac{1}{n_S}\ln C_e \quad (10)$$

where q_e (mg/g) is the Sr(II) amount adsorbed at equilibrium, q_{ms} (mg/g) is the maximum adsorption capacity, C_e (mg/L) is the adsorbate concentration at equilibrium, K_S (L/mg) is the Sips equilibrium constant, and n_S is the Sips parameter. The difference between the Sips and Langmuir equations lies in the additional parameter n_s. It can be considered as a parameter that characterizes the system's heterogeneity and it comes from either adsorbent or adsorbate or a combination of both. The Sips model describes the adsorption processes in a wider range of concentrations compared to Freundlich model.

The linearized forms of Langmuir, Freindlich, Dubinin-Radushkevich, and Sips models are presented in Fig. 4. The calculated model parameters as well as the correlation coefficients are presented in Table 3.

The values of the correlation coefficients (R^2) obtained from linearized forms of isotherm showed that the adsorption of Sr(II) ions by magnetic ferrite nanoparticles was best described by the Langmuir model. The Langmuir equation describes localized adsorption. Therefore, it can be assumed that Sr(II) ions were quite strongly fixed on the ferrite surface due to chemical interactions. The maximum theoretical adsorption capacities of magnesium-zinc ferrite, obtained from Langmuir model, were 57, 74, and 43 mg/g for $x = 0.4$, $x = 0.6$, and $x = 0.8$ samples, respectively. The adsorption energy (E) obtained from Dubinin-Radushkevich isotherm model can define adsorption processes. The calculations showed that the values of the adsorption free energy was 10.1-11.3 kJ/mol (Table 3), which indicated the chemical interaction of the adsorbate with the adsorbent. Thus, the adsorption of Sr(II) ions on the ferrite surface was chemosorption in nature. For the sample with $x = 0.6$, the Sips model described adsorption most accurately. Since the Sips model is a combination of the Langmuir and Freindlich models, the application of this model to the obtained experimental results indicated the surface heterogeneity of the synthesized materials on the one hand, and monolayer

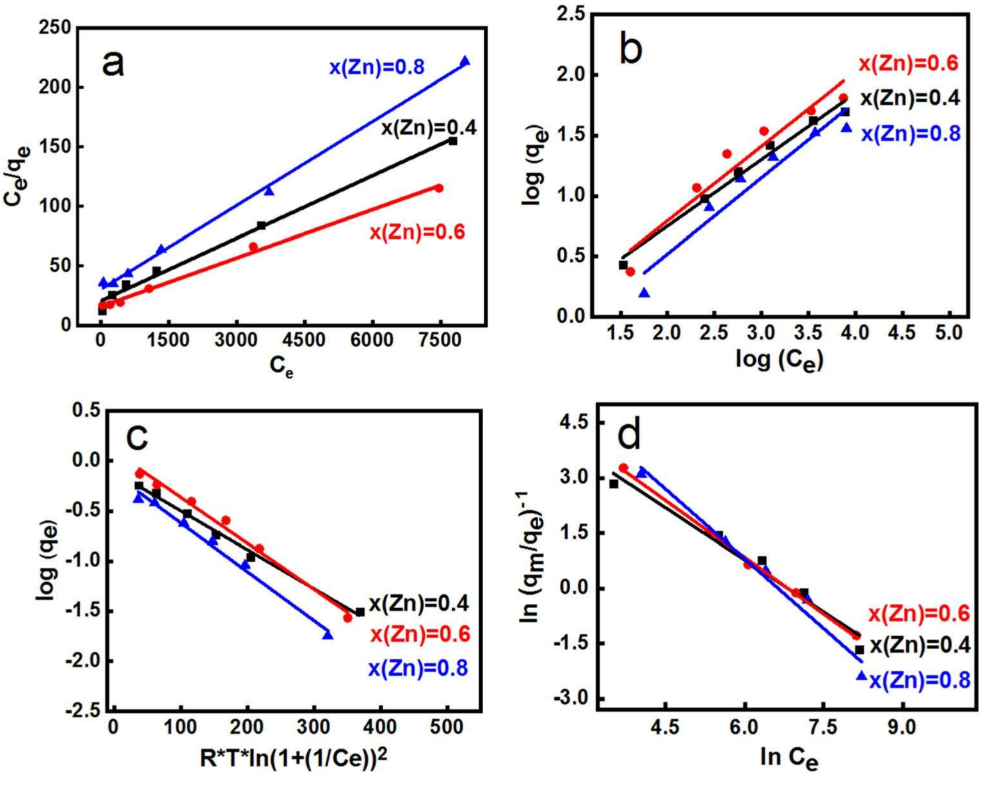

Fig. 4 The linear forms of a Langmuir, b Freundlich, c Dubinin-Radushkevich, and d Sips isotherm models for Sr(II) uptake by $Mg_{1-x}Zn_xFe_2O_4$ samples

Table 3 The parameters of different adsorption models for Sr(II) uptake onto $Mg_{1-x}Zn_xFe_2O_4$ magnetic samples

Parameter	Sample		
	x(Zn) = 0.4	x(Zn) = 0.6	x(Zn) = 0.8
q_{exp}, mg/g	50	65	36
Langmuir isotherm model			
q_{max}, mg/g	57	74	43
K_L	0.0008	0.0008	0.0008
R_L	0.1186	0.1185	0.1288
R^2	0.991	0.996	0.997
Freundlich isotherm model			
K_F, (mg g^{-1})(mg L^{-1})$^{-1/nF}$	0.45	0.36	0.18
n	0.549	0.616	0.630
R^2	0.983	0.932	0.931
Dubinin-Radushkevich isotherm model			
q_m, mg/g	79	96	77
K_{DR}	0.0039	0.0046	0.0049
E, kJ/mol	11.3	10.4	10.1
R^2	0.994	0.989	0.989
Sips isotherm model			
K_s, L$^{1/n}$/mg$^{1/n}$	621	1102	4304
$1/n$	0.944	1.027	1.261
R^2	0.967	0.998	0.976

adsorption on the other hand. It should be noted that there is no correlation of q_{max} with the specific surface area of synthesized materials. Hence, it can be assumed that the nature of the active centers of adsorbents contributed to the effective adsorption of Sr(II) ions on magnetic adsorbents. The spinel ferrite nanoparticles contain surface-active cations, which could attract the Sr(II) ions. Based on the anti-structural modeling (see below), the magnesium ions were the ones that were interacted with Sr(II) ions.

The rate at which thermodynamic equilibrium is reached in equilibrium is usually described by kinetics. The adsorption process continues until equilibrium is reached. Adsorption, physical or chemical, involves the mass transfer of the adsorbent from solution to the surface of the adsorbent. The adsorption kinetics of magnesium-zinc ferrites are presented in Fig. 5. The results showed that the synthesized ferrites effectively adsorb Sr(II) ions. It can be seen that the time necessary to reach adsorption equilibrium was approximately 3 h. A further increase in adsorption time to 5 h does not lead to a significant change in the concentration of Sr(II) in the solutions. The adsorption under static conditions proceeds at a high rate for the first 30 min and reaches its maximum value after 180 min. The increase in the Zn content from 0.4 to 0.6 mol leads to a noticeable change in the adsorption activity, but the further increase in zinc content from 0.6 to 0.8 mol significantly slowed down the adsorption process.

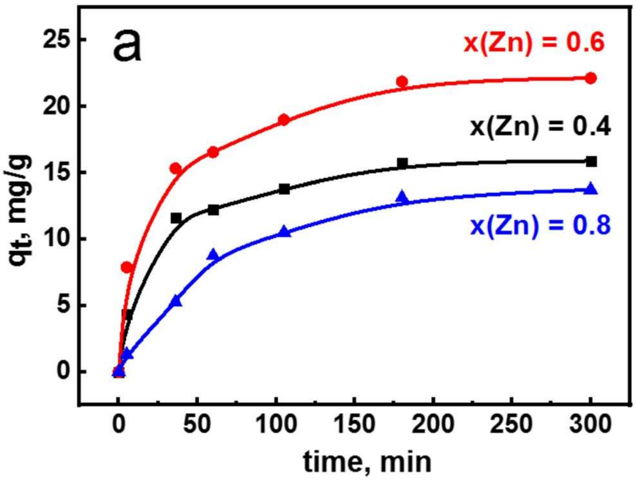

Fig. 5 Kinetic of Sr^{2+} adsorption onto magnetic $Mg_{1-x}Zn_xFe_2O_4$ samples

In this study, experimental data was compared with various kinetics models, including pseudo-first-order, pseudo-second-order, intra-particle diffusion, and Elovich models. The kinetic curves were drawn in corresponding coordinates: log($q_e - q_t$) versus t (min) for pseudo-first-order; t/q_e versus t (min) for pseudo-second-order; q_t versus $t^{1/2}$ for interparticle diffusion interaction model; and q_t versus ln(t) for Elovich model, where q_e is equilibrium amount of Sr^{2+} (mg/g) and q_t is amount of Sr^{2+} (mg/g) at time t, min. The plots of these models are shown in Fig. 6 and the parameters of all kinetic models are given in Table 4. The highest values of correlation coefficient R^2 for pseudo-second-order model mean that the adsorption process depends not only on the constant of the adsorption rate but also on the initial concentration of Sr(II) ions. The sample $Mg_{0.4}Zn_{0.6}Fe_2O_4$ was the most active adsorbent and the PSO rate constant h has the highest value in comparison to the other samples.

To confirm the presence of Sr(II) ions on the adsorbents surface, magnetic samples were analyzed by the energy-dispersion analysis after Sr(II) adsorption. Figure 7 shows the SEM and EDX spectrum of $Mg_{0.4}Zn_{0.6}Fe_2O_4$ and $Mg_{0.2}Zn_{0.8}Fe_2O_4$ samples after adsorption process. The selected samples were washed with distilled water after adsorption of Sr(II) ions, and dried in air. It can be seen that Sr(II) ions were present on the sample surface. The porous structures of adsorbents were still without significant changes.

The surface of any material can be largely inhomogeneous due to the existing various crystallographic planes, atoms, the presence of structural defects (vacancies, dislocations, etc.), the presence of various functional groups, and also physically and chemically adsorbed impurities. The formation of structural defects on the surface leads to the formation of active surface centers with different energies. This determines the possibility of physical and/or chemical adsorption of various molecules, as well as the reactivity of compounds, i.e., surface chemistry. Antistructural model (Kumar et al. 2018;

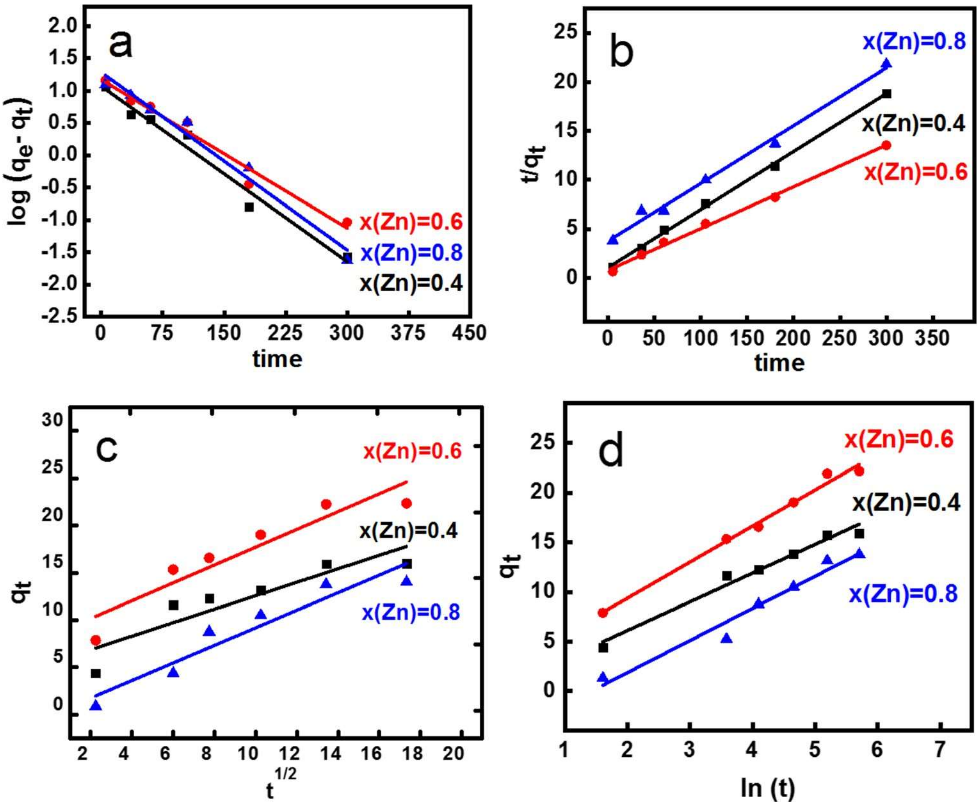

Fig. 6 The a pseudo-first, b pseudo-second, c intra-particle diffusion, and d Elovich kinetic models for Sr(II) adsorption onto $Mg_{1-x}Zn_xFe_2O_4$ samples

Table 4 The parameters of pseudo-first, pseudo-second, intra-particle diffusion, and Elovich kinetic models for Sr(II) uptake onto $Mg_{1-x}Zn_xFe_2O_4$ magnetic adsorbents

Parameters	Sample		
	x(Zn) = 0.4	x(Zn) = 0.6	x(Zn) = 0.8
q_{exp}, mg/g	16	22	14
Pseudo-first-order model			
q_{max}, mg/g	23	24	20
k_1, 1/min	0.035	0.028	0.022
R^2	0.9857	0.9063	0.9391
Pseudo-second-order model			
q_{max}, mg/g	17	24	18
k_2, 1/min	0.0030	0.0022	0.0007
h, mg/(g min)	0.88	1.26	0.24
R^2	0.9962	0.9962	0.9655
Intra-particle diffusion model			
c, mg/g	5.47	8.29	0.195
k_i, mg/(g min$^{1/2}$)	0.7112	0.9417	0.9054
R^2	0.8133	0.882	0.9131
Elovich model			
α, mg/(g min)	3.183	6.230	0.723
β, g mg	0.347	0.271	0.295
R^2	0.9694	0.9862	0.9267

Prabukanthan et al. 2018; Rajesh Kumar et al. 2018; Theerthagiri et al. 2019) gives a better comprehension on the lattice defects formation and the types of surface active centers:

$$\left[Mg_y^{2+}Zn_x^{2+}Fe_{1-x-y}^{3+}\right]_A \left[Mg_{1-x-y}^{2+}Fe_{1+x+y}^{3+}\right]_B \left[O_4^{2-}\right]_O + \left[V''\right]_A \left[V'''_2\right]_B \left[O_4^{\cdot\cdot}\right]_O \rightarrow \left[Mg_y^{\times}Zn_x^{\times}Fe^{\cdot}_{1-x-y}\right]_A \left[Mg'_{1-x-y}Fe^{\times}_{1+x+y}\right]_B \left[O_4^{\times}\right]_O$$

where ● is an excess positive charge; ′ is an excess negative charge; V is a cationic/anionic vacancy; A and B are indices of cationic tetrahedral and octahedral positions, respectively, and O is anion position in the spinel lattice.

During the interaction of Sr(II) with the sorbent surface, the partial adsorption of Sr(II) occurred at certain active centers. From Table 5, we can see that the increase of zinc content led to decrease of concentration of negatively charged defect centers Mg'_B and positively charged defect centers $Fe^{\cdot}_A$. Anti-structural modeling gives us new and clear information about active centers: Zn^{2+}_A, Mg^{2+}_A, and Fe^{3+}_B were not active centers (due to their effective zero charge), while Fe_A^{3+} and Mg_B^{2+} were active centers in the adsorption, catalytic, or other processes in "solid/gas" or "solid/liquid" systems. This is the reason that Sr(II) ions were better adsorbed on the samples with $x = 0.4$ and $x = 0.6$ due to higher content of negatively charged active defects Mg'_B.

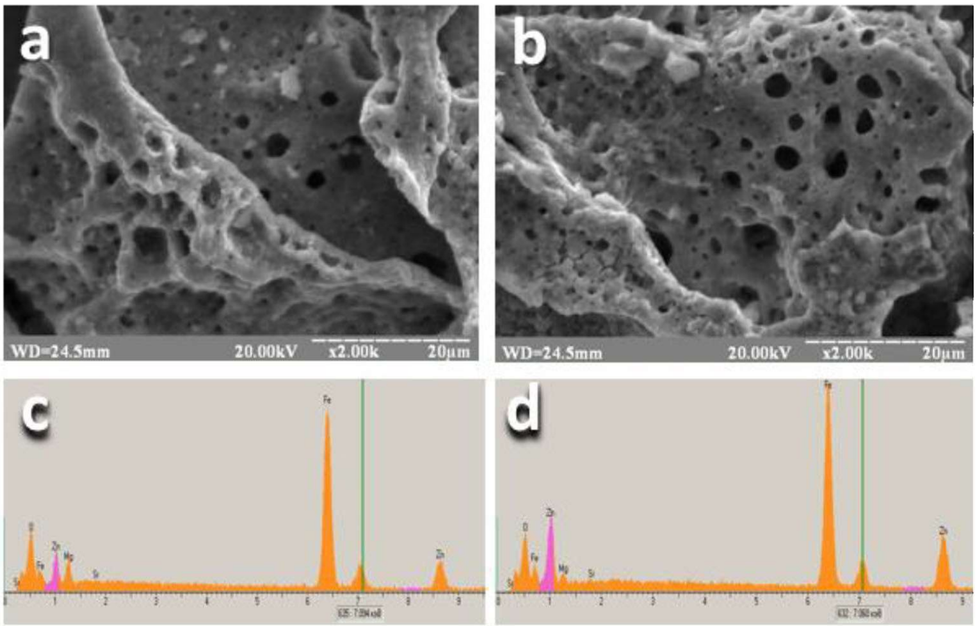

Fig. 7 a,b SEM and c,d EDX spectra of a,c $Mg_{0.4}Zn_{0.6}Fe_2O_4$ and b,d $Mg_{0.2}Zn_{0.8}Fe_2O_4$ after Sr(II) adsorption

Adsorption of salicylic acid

The adsorption kinetics of salicylic acid was investigated at 24 h in order to find the equilibrium time for achieving the maximum adsorption capacity of magnesium-zinc ferrites. The kinetic curves are shown in Fig. 8a. As can be seen from Fig. 8a, the adsorption equilibrium for $Mg_{0.6}Zn_{0.4}Fe_2O_4$ sample was reached in 5 h and for $Mg_{0.2}Zn_{0.8}Fe_2O_4$, it was reached in 10 h. However, for the $Mg_{0.4}Zn_{0.6}Fe_2O_4$ sample, the equilibrium was established after 24 h. The adsorption capacity was increased with increasing the Zn content and more time was required for saturation of adsorbent surface.

The three kinetic models were involved in order to explain the adsorption mechanism of salicylic acid on magnesium-zinc ferrites: pseudo-first-order, pseudo-second-order, and Elovich models. PFO and PSO models were describing the physical adsorption, while the Elovich model describes some cases of heterogeneous chemosorption. The linearized forms of kinetic models are presented on Fig. 8b-d. The calculated model parameters as well as the correlation coefficients are described in Table 6.

For the sample with $x = 0.4$, the adsorption kinetics was well fitted by a pseudo-second-order model due to the better values of R^2 (0.999) and the estimated values of the adsorption capacity were also close to those obtained experimentally. For the samples with $x = 0.6$ and $x = 0.8$, the adsorption kinetics was fitted by a pseudo-first-order model, since R^2 was 0.949 and 0.992, respectively. The adsorption rate (h) was calculated from the values of the second-order rate constant which were equal to 0.496 and 0.435 μg/(g·min) for samples with $x = 0.4$ and $x = 0.8$, respectively. The sample with $x = 0.6$ has the lowest $h = 0.127$ μg/(g min). The rate constants (k_2) were 0.63, 0.03, and 0.06 μg/(g min) for magnesium-zinc ferrites with $x = 0.4$, 0.6, and $x = 0.8$, respectively. It means that for $Mg_{0.4}Zn_{0.6}Fe_2O_4$ sample, the rate constant k_2 has the lowest value. The rate constant for $Mg_{0.6}Zn_{0.4}Fe_2O_4$ sample was ten times higher than that of $Mg_{0.2}Zn_{0.8}Fe_2O_4$ sample and 20 times higher than that of $Mg_{0.4}Zn_{0.6}Fe_2O_4$ sample. As magnesium-zinc ferrite samples were fitted better by pseudo-second-order model, it can be concluded that the adsorption process was chemosorption. The negatively charged octahedral magnesium ions attract the SA molecules (based on the anti-structure modeling (Table 5)). It is advisable to use $Mg_{0.2}Zn_{0.8}Fe_2O_4$ sample for fast removing of salicylic acid from the water solutions. The parameters of the Elovich model are important for understanding the kinetics mechanism, for example, the constant α is the initial adsorption rate, and the constant β characterizes desorption process. The initial adsorption rate has the lowest value for $Mg_{0.4}Zn_{0.6}Fe_2O_4$ sample and the highest value for $Mg_{0.6}Zn_{0.4}Fe_2O_4$ sample. The desorption constant β was decreased from 0.242 to 0.054 g/μg

Table 5 Donor and acceptor active centers on the magnesium-zinc ferrite surface

$x(Zn^{2+})$	Chemical formula	Crystaloquasichemical composition
0.4	$Mg_{0.6}Zn_{0.4}Fe_2O_4$	$Mg^{\times}_{0.134}Zn^{\times}_{0.4}Fe^{\bullet}_{0.466\,A}\,Mg'_{0.466}Fe^{\times}_{1.534\,B}\,O^{\times}_{4\,O}$
0.6	$Mg_{0.4}Zn_{0.6}Fe_2O_4$	$Mg^{\times}_{0.114}Zn^{\times}_{0.6}Fe^{\bullet}_{0.286\,A}\,Mg'_{0.286}Fe^{\times}_{1.714\,B}\,O^{\times}_{4\,O}$
0.8	$Mg_{0.2}Zn_{0.8}Fe_2O_4$	$Mg^{\times}_{0.072}Zn^{\times}_{0.8}Fe^{\bullet}_{0.128\,A}\,Mg'_{0.128}Fe^{\times}_{1.872\,B}\,O^{\times}_{4\,O}$

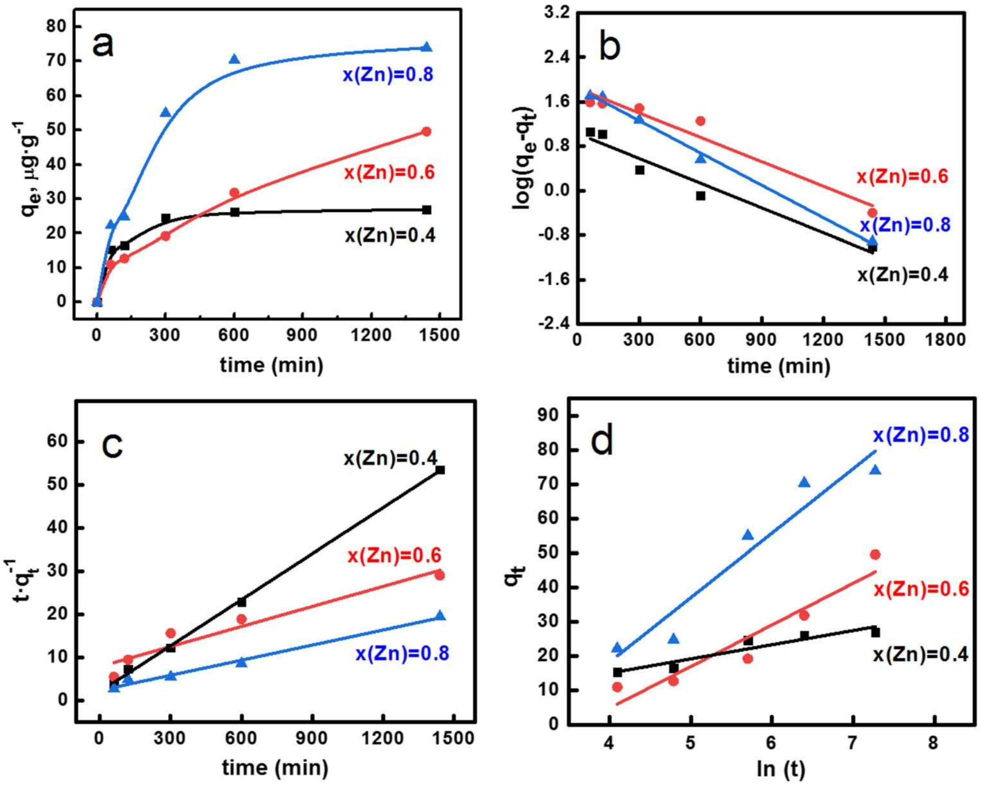

Fig. 8 a Adsorption kinetics of salicylic acid onto magnesium-zinc ferrites (conditions: temperature 298 K; adsorbent dosage 10 mg; volume 5 mL; concentration of salicylic acid 160.5 ng/mL, pH 7.0); b Pseudo-first-order kinetic model; c Pseudo-second-order kinetic model; d Elovich kinetic model

with increasing zinc content. This was in a good agreement with the experimental data of the adsorption capacity. In addition, the removal rate of $Mg_{0.2}Zn_{0.8}Fe_2O_4$ sample toward SA was maintained above 90% after 24 h (Fig. 9). It can be concluded that uptake of salicylic acid molecules occurred on the surface of the magnetic sorbents due to hydrogen bonds appearing among the OH^- groups of salicylic acid and the H^+ ions of the ferrites.

Table 6 The parameters of kinetic models for the salicylic acid uptake onto $Mg_{1-x}Zn_xFe_2O_4$ surface

Parameters	x(Zn) = 0.4	x(Zn) = 0.6	x(Zn) = 0.8
q_{exp}, μg/g	27	50	74
Pseudo-first-order kinetic model (PFO)			
q_{max}, μg/g	11	69	70
k_1, min^{-1}	0.0032	0.0035	0.0044
R^2	0.951	0.949	0.992
Pseudo-second-order kinetic model (PSO)			
q_{max}, μg/g	28	65	86
k_2, μg/(g min)	0.63	0.03	0.06
h, μg/(g min)	0.496	0.127	0.435
R^2	0.999	0.925	0.987
Elovich kinetic model			
α, μg/(g min)	2.89	0.33	0.91
β, g/μg	0.242	0.082	0.053
R^2	0.888	0.906	0.926

Conclusion

The magnetic spinel ferrite $Mg_{1-x}Zn_xFe_2O_4$ (where x = 0.4; 0.6 and 0.8) was tested for the removal of Sr(II) ions and SA as emerging contaminant from water medium. The structure of magnetic samples was characterized by XRD; the morphology and surface were characterized by SEM, BET, and pH_{pzc}; magnetic properties were characterized by VSM. The samples exhibited good affinity toward Sr(II) due to strong adsorbent-adsorbate interactions in the wide concentration range. It was

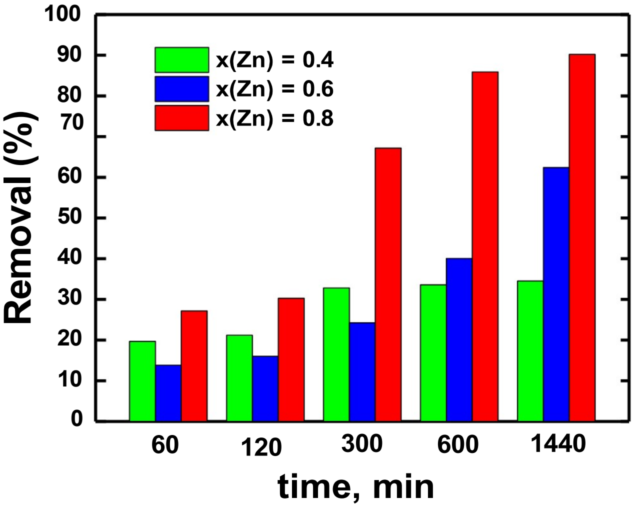

Fig. 9 Removal (%) of salicylic acid by $Mg_{1-x}Zn_xFe_2O_4$ samples

concluded that the adsorption of Sr(II) ions on the ferrite surface was due to chemosorption. The spinel ferrite nanoparticles contain surface-active cations, which could attract the Sr(II) ions. Based on the anti-structural modeling, it was noted that magnesium ions were the one which were interacted with Sr(II) ions. The maximum theoretical adsorption capacities of magnesium-zinc ferrite, obtained from Langmuir model, were 57, 74, and 43 mg/g for $x = 0.4$, $x = 0.6$, and $x = 0.8$ samples, respectively. The adsorption of SA was 90% onto $Mg_{0.2}Zn_{0.8}Fe_2O_4$ sample after 24 h. The adsorption of SA molecules involves the hydrogen bonds, which were formed between the hydroxyl groups of salicylic acid and the H^+ ions of the ferrite surface. The studies of the Sr(II) and SA adsorption are important for the development of the adsorbent for industrial applications and environmental applications.

Funding information The Ministry of Education and Science of Ukraine (project number 0118U000258) financially supported this research work. One of the authors (Mu. Naushad) is grateful to the Researchers Supporting Project number RSP-2019/8, King Saud University, Riyadh, Saudi Arabia for the financial support.

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Materials Today: Proceedings 35 (2021) 518–522

Contents lists available at ScienceDirect

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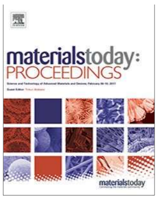

Removal of Congo Red dye, polar and non-polar compounds from aqueous solution using magnesium aluminate nanoparticles

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ARTICLE INFO

Article history:
Received 19 September 2019
Accepted 8 October 2019
Available online 8 November 2019

Keywords:
Magnesium aluminate
Spinel
Adsorption
Dye
Aromatics

ABSTRACT

Magnesium aluminate nanoparticles were prepared by the sol–gel autocombustion method using mixture of alanine and urea as a fuel. The sample was characterized using XRD, FE-SEM, EDS, and IR spectroscopy. XRD analysis confirmed the formation of single-phase spinel compound with average particle size of 28 nm estimated from FE-SEM analysis. IR spectrum revealed the stretching vibration of M_A-O and M_B-O bonds at 517 and 691 cm^{-1} respectively. The adsorption process of Congo Red dye on the spinel surface was studied under static conditions using UV–Vis spectrophotometry. The maximum equilibrium adsorption capacity obtained from the Langmuir model was calculated 24.5 $mg \cdot g^{-1}$. In addition, the salicylic acid and mixture of polyaromatic hydrocarbons as polar and nonpolar compounds, respectively, were used to investigate the adsorption properties of $MgAl_2O_4$ by liquid chromatography (UFLC) analysis. The results suggest that the magnesium aluminate can be used as efficient adsorbent for anionic dyes and polar compounds due tothe presence of active centers on its surface.

Selection and peer-review under responsibility of the scientific committee of the XVII International Freik Conference on Physics and Technology of Thin Films and Nanosystems.

1. Introduction

Magnesium aluminate $MgAl_2O_4$ is an inorganic coordination polymer, which is involved into large number of experimental and theoretical studies. Materials based on magnesium aluminate have excellent mechanical, optical, and refractory properties, chemical resistance to aggressive environments. It is promising to use $MgAl_2O_4$ as a catalyst carrier [1], an inert matrix in nuclear fuel [2], and an insulating material for magnetic coils [3]. High performance characteristics of materials based on magnesium aluminate have shown a great interest in the development of its new synthesis methods.

It is known, that the chemical composition of oxide spinels is expressed by the general formula AB_2O_4 (spinel type 2–3) [4–6]. In the densest cubic packing of oxygen anions 1/8 of all tetrahedral and 1/2 of all octahedral sites is occupied by metal cations. Thus, the spinel unit cell is a cube, which consists of 8 tetrahedral cations (A), 16 octahedral cations (B), and 32 oxygen anions. Each oxygen anion is surrounded by one A and three B cations. The composition of spinels can be described by the formula $\left(M^{2+}_{1-x}M^{3+}_{x}\right)_A\left[M^{2+}_{x}M^{3+}_{2-x}\right]_B O_4$, where × refers to the degree of inversion, which depends fromseveral reasons, such as electron configuration of cations and the differences in the spinel synthesis conditions. There is possible the three types of spinel structure: normal, inverse and mixed, which having different values of the distribution parameter [7–10].

Synthesis methods have a great impact on the morphology and physico-chemical properties of magnesium aluminate. Different methods were used for the synthesis of magnesium aluminate: microwave sintering [11], solid state reaction with mechanical activation [12], gel-casting [13], spark plasma sintering [14–16], etc. Some of those methods are expensive and can not be used in large scale production. Among them the auto-combustion method

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https://doi.org/10.1016/j.matpr.2019.10.012

Selection and peer-review under responsibility of the scientific committee of the XVII International Freik Conference on Physics and Technology of Thin Films and Nanosystems.

has a lot of benefits [17]. The main advantage of sol–gel auto-combustion methods is the small crystallinity of the received materials, the controlled size and shape of particles, small particle sizes (in nanometer range) and lower synthesis temperatures compared with other, in particular, ceramic methods.

The aim of this study is to synthesize magnesium aluminatevia sol–gel auto-combustion method using a mixture of alanine and urea as a reducing agent and fuel. The structure and morphology of aluminate were characterized by XRD, SEM, HR-SEM, EDS and FTIR techniques, and the adsorption of Congo Red dye and polar and nonpolar compounds were carried out to investigate the adsorption properties of $MgAl_2O_4$.

2. Experimental

2.1. Synthesis of magnesium aluminate

The sample of $MgAl_2O_4$ was prepared via sol–gel auto-combustion technique used mixture of alanine and urea as a fuel. $Mg(NO_3)_2\cdot 6H_2O$, $Al(NO_3)_3\cdot 9H_2O$, $C_3H_7NO_2$ and CH_4N_2O were used as starting materials and stoichiometric ratios of metal nitrate/fuel mixtures were used. Nitrates of metals were dissolved in 200 mL of distilled water and magnetically stirred for 30 min, leading to the formation of a homogeneous solution and then mixture of fuels (alanine and urea) was added to the solution and continue to stir at 60 °C for 20 min. After homogenization, the mixture was heated until to transform into a gel while by further heating up to a certain temperature, ignition reaction started from a point and propagated spontaneously. The obtained powders were hand-crushed with a pestle. The typical gases products by reactions are CO_2, N_2 and H_2O.

2.2. Adsorbent characterization

The diffraction patterns was obtained by means diffractometer PANalyticalX'Pert equipped with Cuk$_\alpha$irradiation (k = 0.154 nm). The FE-SEM imaging and EDX analysis of the samples was performed using Dual Beam SEM/FIB Quanta 3D FEG microscope by FEI (USA) equipped with EDAX SDD EDX detector system operated at Institute of Physics Jagiellonian University Krakow Poland. The EDX microanalysis was performed for 5 keV of electron energy. FTIR spectra were recorded by SPECORD spectrophotometer in the range 4000 – 300 cm^{-1}by mixing the powdered samples with KBr in 1:100 ratio.

2.3. Removal of Congo Red dye

The adsorption studies were carried out at temperature 293 K and neutral pH. Aqueous solutions of Congo Red dye (20 mL) with certain concentration 10; 25; 50; 75; 100 mg/L were mixed with 20 mg of magnesium aluminate powder during 24 h. The equilibrium concentrations of Congo Red dye were determined with spectrophotometer ULAB 102-UV at 500 nm. The adsorption capacity, q_e (mg/g), was calculated as follows:

$$q_e = \frac{(C_o - C_e)\cdot V}{m} \tag{1}$$

where, q_e is the adsorption capacity (mg/g), C_o and C_e are the initial and the equilibrium dye concentrations (mg/L), m is the adsorbent mass (g) and V is the sample volume (L).

2.4. Removal of polar and nonpolar compounds

In the adsorption process a polar (salicylic acid, POCh, Gliwice, Poland) and nonpolar (mixture of polyaromatic hydrocarbons, Ultra Scientific, Agilent) compounds was used. Model solutions were prepared with following concentrations (Table 1).

Table 1
The characterization of polar and non-polar aromatic compounds.

	Compounds	Abbreviation	Concentration [ng/ml]
Polar	Salicylic acid	SA	144.73
Nonpolar	Fluoranthene	FLT	105.38
	Benzo[a]fluoranthene	B(a)F	125.82
	Benzo[k]fluoranthene	B(k)F	111.46
	Benzo[a]pyrene	B(a)P	110.72
	Benzo[ghi]perylene	B(g,h,i)P	77.13
	Indeno[1,2,3-cd]pyrene	IP	117.41

The prepared solutions in different concentrations were placed in centrifuge tube, and 80 ± 0.3 mg of the adsorbent was added to the solution. The system was mixed using a mechanical shaker (IntelliMixer, Elmi, Latvia) for 1 and 30 min. After this time the resulting mixture was centrifuged.

Liquid chromatography (UFLC) analysis enabled precise determination of the quantity of analytes in the filtrate after the adsorption process.

Nonpolar compounds (PAHs) analyses were performed on a Shimadzu UFLC Prominescence System (Shimadzu, Kyoto, Japan) which consisted of a LC-20AB solvent delivery system equipped with a Rheodyne injection valve with a 20 1L loop, a fluorescence detector set at 365 and 470 nm, and an LC-Solution automation system software. Chromatographic separation was achieved isocratically at 30 °C on an Supelcosil LC-PAH (Supelco, Bellefonte, USA) column with the dimensions 4.6 mm I.D, 250 mm length, and 5 1m particle size. The mobile phase was an methanol:aceton (95:5, v/v) with a flow rate of 1.0 mL/min.

Polar compound (SA) analyses were performed on a Shimadzu UFLC Prominescence System (Shimadzu, Kyoto, Japan) which consisted of a LC-20AB solvent delivery system equipped with a Rheodyne injection valve with a 20 1L loop, a fluorescence detector set at 332 and 450 nm, and an LC-Solution automation system software. Chromatographic separation was achieved isocratically at 30 °C on anSupelco Discovery HS C18 (Supelco, Bellefonte, USA) column with the dimensions 4.6 mm I.D, 150 mm length, and 5 1m particle size. The mobile phase was an 0,1% acetic acid: methanol:acetonitrile (50:30:20, v/v/v) with a flow rate of 1.0 mL/min.

For both analysis, before the analysis, a calibration curve was prepared to enable calculation of the analytes concentrations in the filtrate. All analysis were performed in triplicate.

The results obtained using UFLC analysis were used for calculations relating to the efficiency of the process of removal of analytes from aqueous solutions. The following formula was used:

$$\%RemoVal = \frac{C_0 - C_e}{C_0}\, x100\% \tag{2}$$

whereC_0 and C_e are respectively the initial and equilibrium concentrations of analytes (ng/mL).

3. Results and discussion

3.1. X-ray diffraction analysis

The X-ray diffraction pattern of the magnesium aluminate is depicted in Fig. 1a. The planes (1 1 1), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1), (4 4 0), (5 3 1), (6 2 0), (5 3 3), (4 4 4), (5 5 1), (6 4 2), (5 5 3), (8 0 0) correspond to the spinel cubic symmetry and diffraction peaks indicate that $MgAl_2O_4$ has regular crystallinity. The lattice parameter a = 0.8083 nm, oxygen parameter u = 0.376 and lattice volume V = 0.528 nm^2. The average

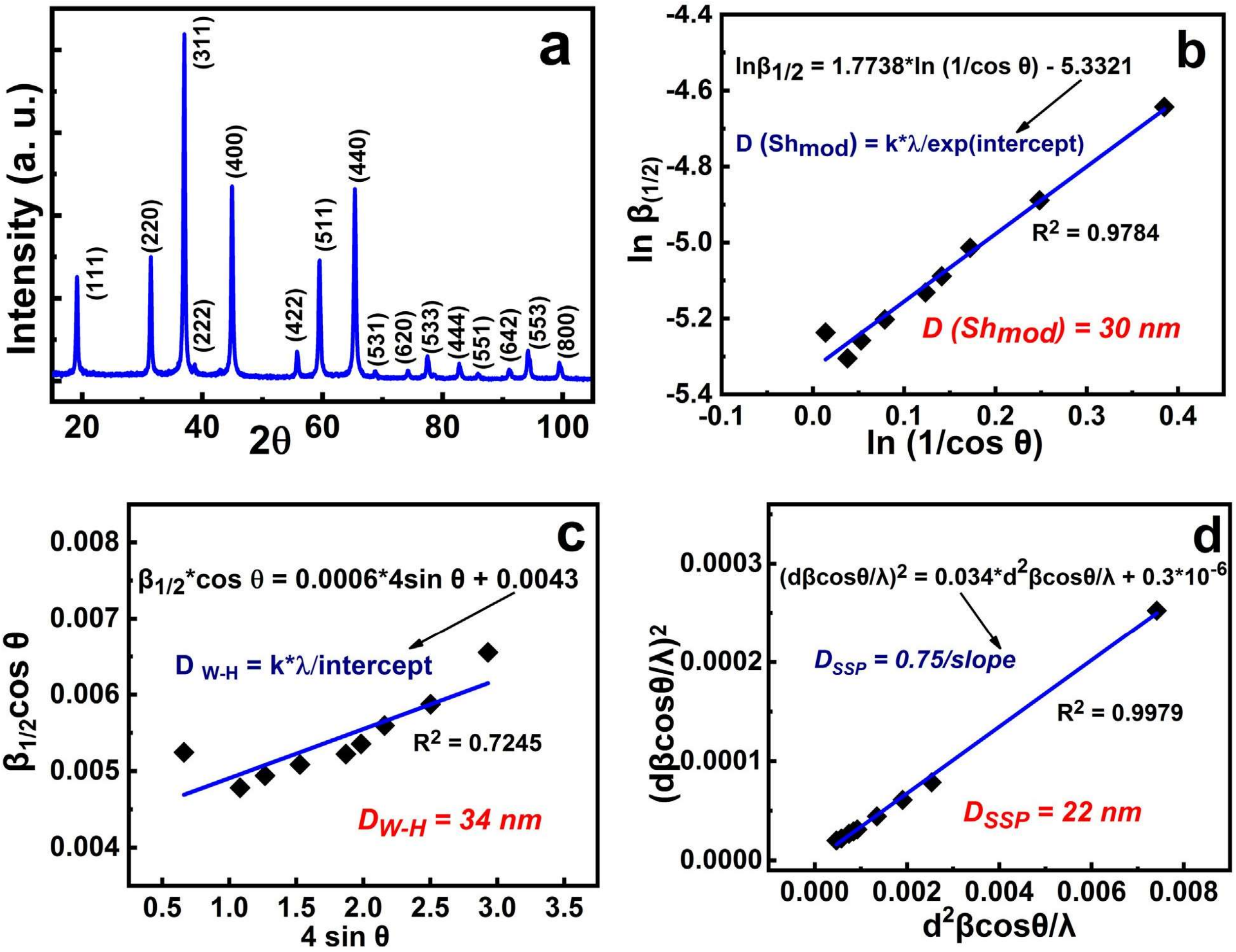


Fig. 1. (a) X-ray diffraction pattern of $MgAl_2O_4$ NPs and the calculations of crystallite size by (b) modified Scherer's method, (c) Williamson-Hall (W-H) method, and (d) size-strain plot method (SSP).

crystallite size of the NPs was calculated using modified Scherer's method [18], Williamson-Hall (W-H) method [19], and size-strain plot method (SSP) [20,21] and the results are depicted in Fig. 1b-d. It can be seen that the size of crystallites lies in the nanoscale region and very close to result, obtained from FE-SEM (Section 3.3). In addition, the average crystallite size of $MgAl_2O_4$ nanoparticles calculated from modified Scherer's method, Williamson-Hall (W-H) method and size-strain plot method (SSP) is highly correlated.

3.2. IR spectroscopy

In order to confirm the presence of tetrahedral and octahedral sublattices in the $MgAl_2O_4$ its structure was also examined by IR spectroscopy. IR spectroscopy is very useful techniques used to identify inorganic materials and surface functional groups [22–26]. Fig. 2 shows IR spectrum of $MgAl_2O_4$. It can be seen that there are two main absorption bands at 517 and 691 cm^{-1}, related to octahedral metal–oxygen and tetrahedral metal–oxygen stretching vibration respectively. The adsorption bands at 1384 cm^{-1}can be assigned to C–O group. The adsorption bands at 3442 cm^{-1} attributed to the vibrations of O–H groups of water.

3.3. Field emission scanning electron microscopy

The morphological analysis of magnesium aluminate was carried out by means FE-SEM. As can be seen from Fig. 3a, the $MgAl_2O_4$ NPs have annonspherical shape. The size of the $MgAl_2O_4$ NPs, determined using FE-SEM, practically coincide with the average crystallite size D, calculated from the corresponding X-ray diffraction pattern (Fig. 1b–d). The size distribution histogram of the particles is depicted in Fig. 3c, and the arithmetic mean value of D was about ~28 nm. The desired chemical composition of spinel was confirmed by EDS analysis (Fig. 3c), which proved that there are only Mg, Al and O elements in stoichiometric amounts (Fig. 3d).

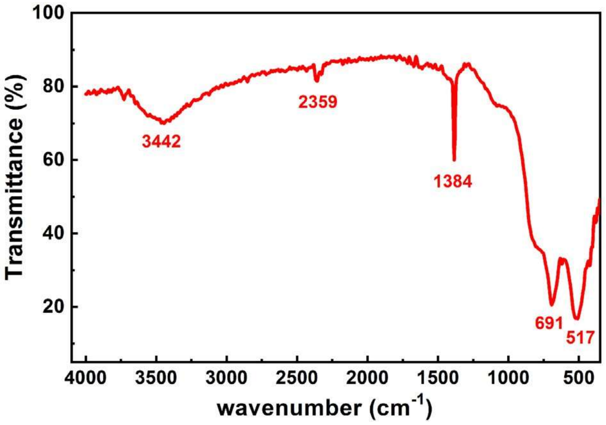
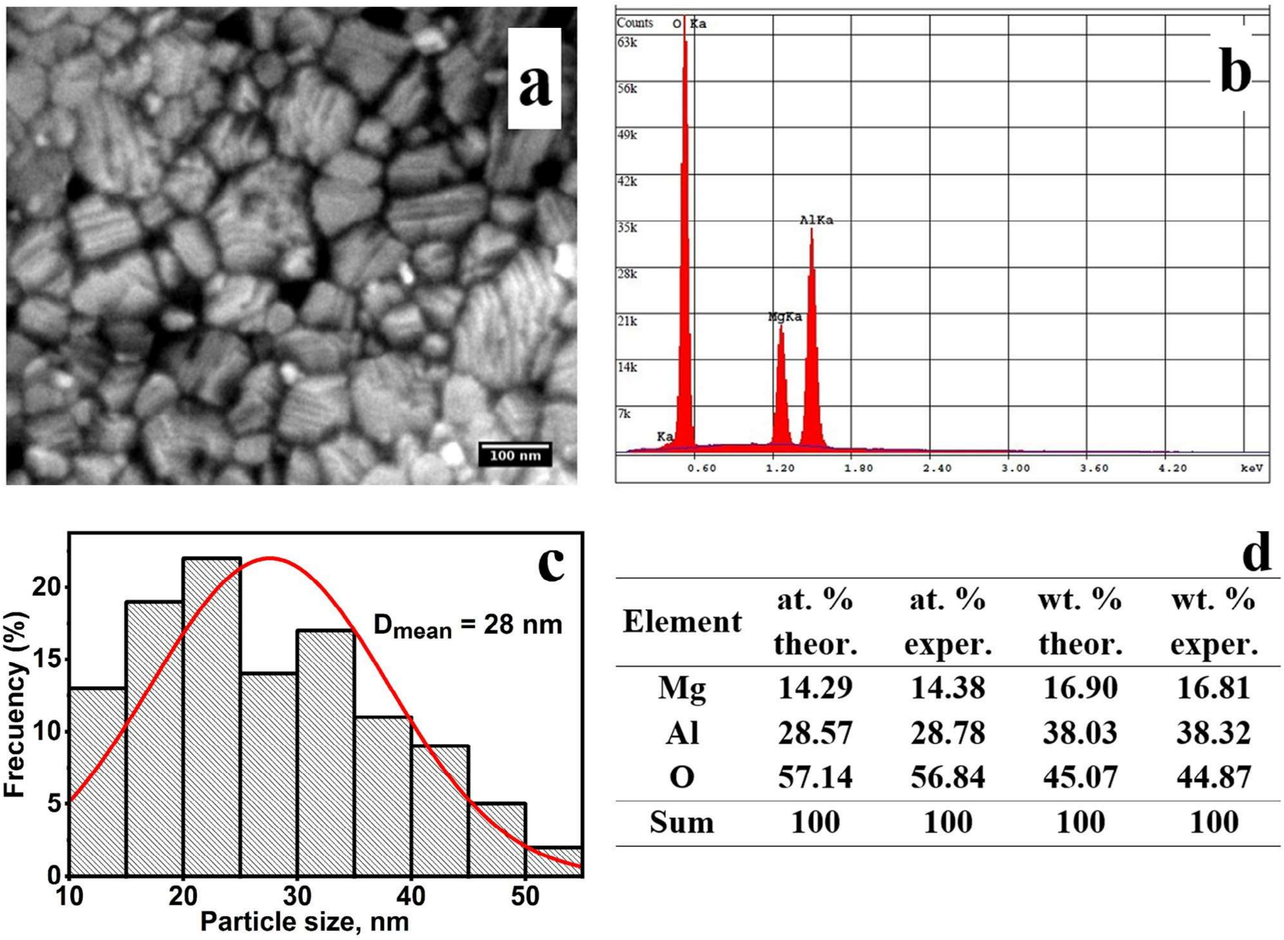


Fig. 2. IR spectrum of magnesium aluminate nanoparticles.



Element	at. % theor.	at. % exper.	wt. % theor.	wt. % exper.
Mg	14.29	14.38	16.90	16.81
Al	28.57	28.78	38.03	38.32
O	57.14	56.84	45.07	44.87
Sum	100	100	100	100

Fig. 3. (a) FE-SEM, (b) EDS, (c) particle size distributions of magnesium aluminate NPs, and (d) atomic and weight percentage(theoretical and experimental) of elements.

3.4. Adsorption of Congo Red dye

The adsorption study at constant temperature has been conducted for the removal of Congo Red (CR) dye from aqueous medium and is shown in Fig. 4a. The maximum adsorption capacity of magnesium aluminate for CR is q_{exp} = 23 $mg\cdot g^{-1}$.In order to investigate the adsorption mechanism of CR onto adsorbent surface the experimental data were analyzed using Langmuir and Freundlich adsorption isotherms (Fig. 4b and c). Langmuir isotherm model has been used to study the monolayer adsorption capacity, while the Freundlich isotherm model describes multilayer adsorption and adsorption on heterogeneous surfaces [27]. The constants of Langmuir and Freundlich models for Congo Red adsorption on $MgAl_2O_4$ adsorbent together with the correlation coefficients (R^2) are shown in Table 2. It was found that Langmuir isotherm model fits experimental data better (R^2 = 0.9983) than Freundlich isotherm model (R^2 = 0.9885). The calculated value of q_{max} = 24.5 $mg\cdot g^{-1}$ is in a good agreement with experimental obtained q_{exp}. A separation factor R_L has also been estimated using formula $R_L = 1/(1 + K_LC_o)$, where K_L (L/mg) is the Langmuir constant, C_o (mg/L) is the initial dye concentration. The factor R_L is in the range $0 < R_L < 1$ (R_L = 0.07) what means that adsorbent is favorable for Congo Red adsorption [28]. Therefore, the results indicated homogenous nature of the spinel surface and monolayer adsorption. The obtained constants of the Freundlich model are displayed in Table 2. The magnitude n less than 1 thus adsorption of Congo Red by spinel surface is favorable [29]. The

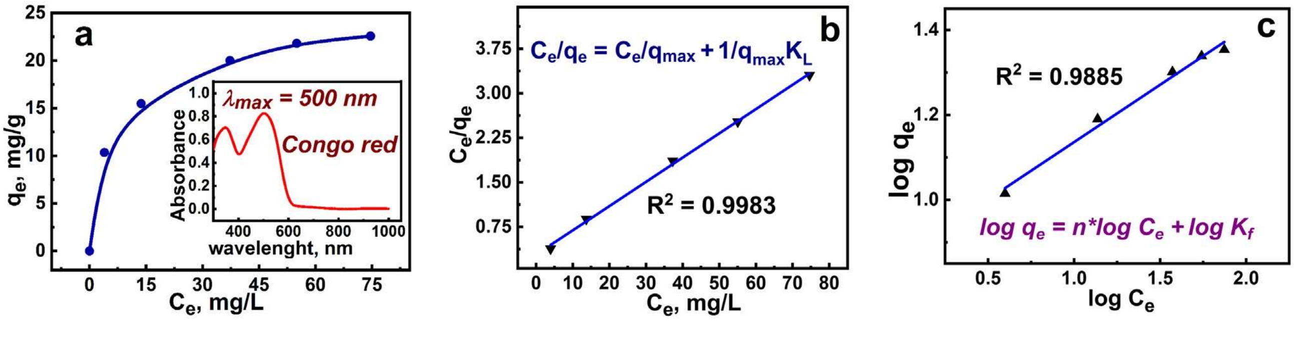


Fig. 4. (a)Equilibrium adsorption isotherm of Congo Red dye on the magnesium aluminate (conditions: V = 20 mL, m_{ads} = 20 mg, pH = 7, T = 25 °C, time 24 h) (Inset: absorbance spectra of Congo Red dye); (b) Langmuir isotherm model; (c) Freundlich isotherm model. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Langmuir and Freundlich constants for Congo Red adsorption on $MgAl_2O_4$ adsorbent.

Isotherm model	R^2	Parameters		
Langmuir model	0.998	$q_{max} = 24.5\ mg\cdot g^{-1}$	$K_L = 0.14$	$R_L = 0.07$
Freundlich model	0.989	–	$K_F = 7.35$	n = 0.27

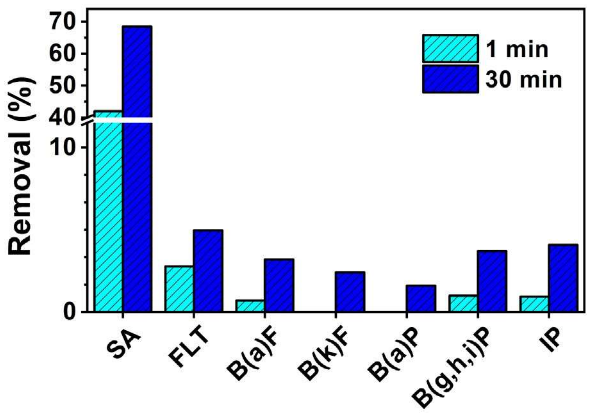


Fig. 5. Efficiency of removal of polar and nonpolar organic compounds.

Freundlich constant $K_F = 7.35$ also suggests a good adsorption capacity for magnesium aluminate powder.

3.5. Adsorption of polar and nonpolar compounds

In this study, it was decided to use the magnesium aluminate material for the adsorption of compounds with different properties (polar and nonpolar) from aqueous systems. The results confirmed that the initial adsorption process takes place very slowly regardless of the properties of compounds, with a high adsorption capacity for salicylic acid (polar) of almost 70% after 30 min of adsorption. For selected polyaromatic hydrocarbons (nonpolar compounds) with a low adsorption capacity of almost 5%, after the same time (Fig. 5). It is result of polar properties of magnesium aluminate. Probably electrostatic interactions (ionic) are responsible for adsorption.

In summing up the results of the experiments, it can be stated that the efficiency of the process of adsorption of salicylic acid or PAHs on the synthetic adsorbent magnesium aluminate is significantly influenced by the properties of examinated species. It was only pilot study, full kinetic study, isotherm and desorption procesess are necessary in further investigations.

4. Conclusions

The magnesium aluminate spinel NPs has been synthesized by autocombustion sol–gel method with urea and alanine as fuel and reducing agents. The NPs composition and crystallite sizes were analyzed using X-ray diffraction, field-emission scanning electron microscopy and IR-spectroscopy. XRD pattern confirms the formation of cubic spinel structure with good crystallinity. The crystallite size was analysed by the modified Scherer, Williamson-Hall and SSP methods and obtained results are in the good agreements with particle size obtained from FE-SEM (28 nm). Magnesium aluminate has been investigated as adsorbents for the extraction of anionic dye Congo Red and polar and nonpolar organic compounds from aqueous solutions. The effect of time on the adsorption activity was studied. The maximum equilibrium adsorption capacity obtained from the Langmuir model was estimated to be 24.5 $mg\cdot g^{-1}$ for CR dye. A high adsorption capacity for salicylic acid (polar compound) of almost 70% after 30 min of adsorption was observed what can be explained due to polar properties of magnesium aluminate and presence of active centers responsible for electrostatic interactions. Studies have shown that the spinel material has sufficient adsorption capacity with respect to anionic dyes and polar compounds and the using of the investigated $MgAl_2O_4$ will expand the range of existing adsorbents.

Acknowledgements

The authors are grateful to the Ministry of Education and Science of Ukraine (Projects Number 0118U000258 and 0117U002408) for their financial support. The TT thankful to Benedykt R. Jany for his support in FE-SEM/EDS analysis carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (contract no. POIG.02.01.00-12-023/08).

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Dendrimer Coated Silica as a Sorbent for Dispersive Solid-Phase Extraction of Select Non-Steroidal Anti-Inflammatory Drugs from Water

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Abstract: Non-steroidal anti-inflammatory drugs (NSAIDs) have been recognized as a potentially serious threat to the natural environment. NSAIDs are popular painkillers, and the main pathway for them to reach natural water is via discharge from wastewater and sewage treatment plants. In order to monitor contamination caused by these drugs, as well as their impact on the environment, a new material based on Silica Gel 60, functionalized with a dendrimeric copolymer of methylamine and 1,4-butanediol diglycidyl ether (named MA-BDDE), was prepared. Initial physicochemical characterization of the MA-BDDE material was carried out using ATR FT-IR spectroscopy as well as solid-state carbon-13 NMR spectroscopy. Its effectiveness at NSAID extraction was evaluated by the application of five select drugs in dispersive solid-phase extraction (dSPE): aspirin, ketoprofen, naproxen, diclofenac and ibuprofen. This was followed by their simultaneous determination using the HPLC-UV/Vis system demonstrating good sensitivity, with limits of detection values within the 63–265 ng mL^{-1} range. A comparison of the sorption capacity of each pharmaceutical with unmodified base silica showed an at least tenfold increase in capacity after modification. Initial MA-BDDE application in a quick, low-waste extraction procedure of those select NSAIDs from spiked surface water samples yielded promising results for its use as a sorbent, as recovery values of analytes adsorbed from various samples were found to exceed 72%.

Keywords: liquid chromatography; solid-phase extraction; environmental protection; trace analysis; pharmaceutical contamination

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Citation: Ścigalski, P.; Kosobucki, P. Dendrimer Coated Silica as a Sorbent for Dispersive Solid-Phase Extraction of Select Non-Steroidal Anti-Inflammatory Drugs from Water. *Molecules* **2024**, *29*, 380. https://doi.org/10.3390/molecules29020380

Academic Editor: Constantinos K. Zacharis

Received: 13 December 2023
Revised: 8 January 2024
Accepted: 9 January 2024
Published: 12 January 2024

1. Introduction

Civilizational advances can often have side effects that negatively impact the natural environment in several ways, one of which is the introduction of new pollutants into natural water resources. The increasing world population and the drive to improve the standard of living around the globe, resulting in constantly growing industrialization and agriculture, are the major reasons behind declining water conditions [1,2].

Pharmaceutical contaminants, including non-steroidal anti-inflammatory drugs (NSAIDs), while playing an important role in the effort to protect human health, have recently been recognized as a growing threat to the natural environment [3,4]. Their trace amounts, as well as those of their metabolites and the products of their biodegradation (hydrolysis and photolysis), have recently been detected in samples of surface and ground natural water and soil [5,6]. Across the world, studies have been conducted within the last decade in order to determine the concentrations of pharmaceuticals in rivers. European rivers were shown to have the lowest NSAID contamination levels. In some regions, particularly those where the employed water treatment technologies were not of the highest quality or did not provide sufficient processing capacity, concentrations of certain drugs in the water were reported to be as high as 100 ng mL^{-1} [7–10].

The following urge to more closely monitor their presence in the environment leads to the identification of main entry pathways responsible for releasing the highest loads of NSAIDs and their derivatives. Due to their incomplete metabolism, some drug amounts are excreted through defecation and urinary systems and remain unchanged. These pharmaceutical residues reach sewage and wastewater treatment plants, yet employed treatment techniques often are not appropriate or efficient enough to treat concentrations present in sewage from hospitals and residential areas. As a result, portions of these drugs pass through wastewater treatment plants unprocessed and are released directly into rivers. Additionally, discharge of only partially treated or untreated effluents from pharmaceutical industries into open areas and streams, as well as the illegal disposal of unused (i.e., expired) drugs, further contributes to the contamination of the environment [11–13].

Non-steroidal anti-inflammatory drugs are a class of therapeutic drugs whose main function is the inhibition of cyclooxygenase enzyme activity responsible for the synthesis of biological mediators involved in inflammation and blood clotting. As such, they are commonly used to prevent blood clotting and combat fever but have also found wide applications as effective painkillers. The effectiveness and wide applicability of NSAIDs, together with their low cost and high availability (often without prescription), make them a preferred medicine of choice in many hospitals and households [6,12]. As a result of NSAID consumption, their demand and production have steadily increased, resulting in higher loads reaching wastewater and sewage treatment plants and, ultimately, the environment. This growing concern recently caused the European Union to re-evaluate its approach to water contamination, as detailed in a communication from the European Commission to the European Parliament and the European Council [14], advising the improvement of environmental monitoring and the assessment of risk posed by pharmaceuticals.

Many accurate analytical methods already developed for this purpose consist of a chemical species separation process. Most commonly used techniques are usually based on chromatographic procedures such as gas chromatography (GC) or liquid chromatography (LC); the latter is now mostly employed in its high-performance iterations, known as HPLC (high-pressure liquid chromatography) and UHPLC (ultrahigh-pressure liquid chromatography), as well as electrophoretic techniques such as capillary zone electrophoresis (CZE). Target quantification in the sample is carried out based on the analyte type using one or more (out of many) diverse detection techniques, which, among others, include atomic emission (AES) and absorption spectroscopy (AAS), in the case of metal ions, and mass spectrometry (MS), ultraviolet (UV), fluorescence (FL) or visual light (Vis) spectrophotometry for organic and inorganic compound determination.

Environmental samples arriving at a laboratory usually need treatment aimed at separating the target analyte due to large amounts of particulate and chemical interferents that render them unsuitable for direct analysis [15,16]. Samples exhibiting more complex matrices require the employment of complicated procedures often containing multiple steps in order to perform accurate analysis, turning the sample pre-treatment into the bottleneck of the entire process [17,18]. As a result, laboratories around the world conduct research in order to find new materials and methods, allowing for more effective, rapid, and green sample clean-up, or to improve upon existing solutions.

Liquid–liquid extraction (LLE) is one of the oldest pre-concentration methods still in wide use, in which mixing a liquid sample with immiscible solvent results in the transfer of the analyte from the sample into the volume of the solvent. This technique is time-consuming and labor-intensive while also requiring large volumes of organic solvents, making it expensive and impractical in application. In more modern solid-phase extraction (SPE), the volume of the sample comes into contact with a solid sorbent material designed to have a strong physical or chemical affinity towards the target analyte, resulting in its adsorption onto the solid surface. SPE is considered to exhibit several crucial advantages over LLE: it requires lower amounts of solvents, time and labor while providing higher effectiveness and selectivity. Additionally, this technique is much easier to automate and integrate with other pre-treatment and analytical procedures, leading to the development of numerous modifications and combinations, such as solid-phase microextraction (SPME), stir bar sorptive extraction (SBSE), matrix solid-phase dispersion (MSPD) or ion-exchange solid-phase extraction (IE-SPE). Solid-phase extraction and its many iterations have now become one of the most widely used sample preparation techniques for both solid and liquid samples [15–18].

In 2003, Anastassiades et al. [19] presented an extremely simple extraction procedure used as a clean-up step in the analysis of pesticide content in agricultural products called dispersive solid-phase extraction (dSPE), where a powdery sorbent was applied directly into the volume of the sample solution and stirred. This allowed quick acquisition of the extraction equilibrium due to the high contact surface between the sorbent and the sample, while requiring only small amounts of solvent. dSPE was therefore introduced as a method that is simple, rapid and effective and generates little waste, resulting in its quick and wide recognition, becoming the base for QuEChERS multiresidue analysis [18,20].

Currently, one of the materials most widely used as a sorbent is silica, typically applied in normal phase procedures based on physical adsorption [16], despite its limited pH tolerance and lack of surface functional groups, resulting in only a singular sorption mechanism, which severely limits possible applications. It is, however, a material that is rigid and easy to synthesize, exhibiting resistance to shrinking and swelling, and the ease with which it can be modified offsets its disadvantages to a significant degree. In addition to this, mesoporous silica exhibits an organized internal structure containing uniformly distributed mesopores, assuring a significantly higher surface area [21,22].

Polymers based on crosslinking organic resins are among the materials most commonly used to modify silica. Their particular properties directly depend on the monomers used for synthesis and parameters of the polymerization reaction, allowing for high reliability of the process and precise control over the final product. Aside from the potential for high surface areas, they offer significant advantages over other materials, such as rich functional diversity and high chemical stability, especially against water. Considering some polymers show relatively weak physical properties that would be offset by immobilizing them on a silica core, both materials complement each other's strengths and weaknesses perfectly, promising a hybrid material of much wider applicability than its constituents [16,23,24].

Among polymers, dendrimers are a unique type of macromolecule carrying highly complex, branched, three-dimensional internal structures with an external surface exhibiting remarkably high functionality. Like most polymers, dendrimer-specific properties are dependent on various combinations of diverse components available for synthesis, as well as on parameters by which the reaction was carried out. It is, therefore, entirely possible to reliably yield a product designed to offer highly specific characteristics such as particle size, chelation ability, stability, etc. [25,26].

This study presents a new porous material consisting of a silica core coated with a dendrimeric copolymer based on methylamine (MA) and 1,4-butanediol diglycidyl ether (BDDE). A quick, low-waste analytical procedure consisting of dSPE NSAID isolation and HPLC-UV/Vis detection was developed and utilized to evaluate the obtained materials' (labeled as MA-BDDE) sorption effectiveness from spiked surface water samples.

2. Results

2.1. Sorbent Characterization

For the purpose of isolating NSAIDs from environmental surface water samples, a hybrid sorbent, named MA-BDDE and consisting of a silica core layered with a dendrimeric copolymer of methylamine and 1,4-butanediol diglycidyl ether, was prepared as described in Section 4. Figure 1 illustrates part of the expected macromolecular structure of the material, showing a binding between the polymer and the silica core, and the first two dendrimeric layers.

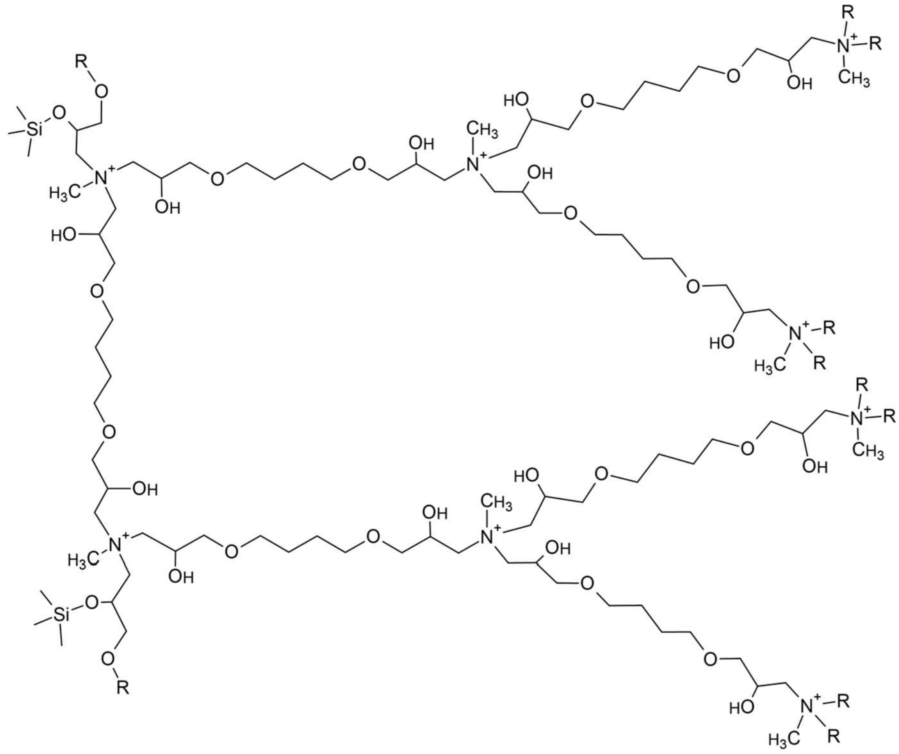

Figure 1. Hypothetical internal structure of the MA-BDDE material.

Initial physicochemical analysis of the obtained material, performed using carbon-13 nuclear magnetic resonance (^{13}C NMR) in solid state as well as Fourier-transformed infrared spectroscopy (FTIR), confirmed the presence of amine and ether groups within the structure. Figures 2 and 3 show solid-state NMR and FTIR spectra, respectively.

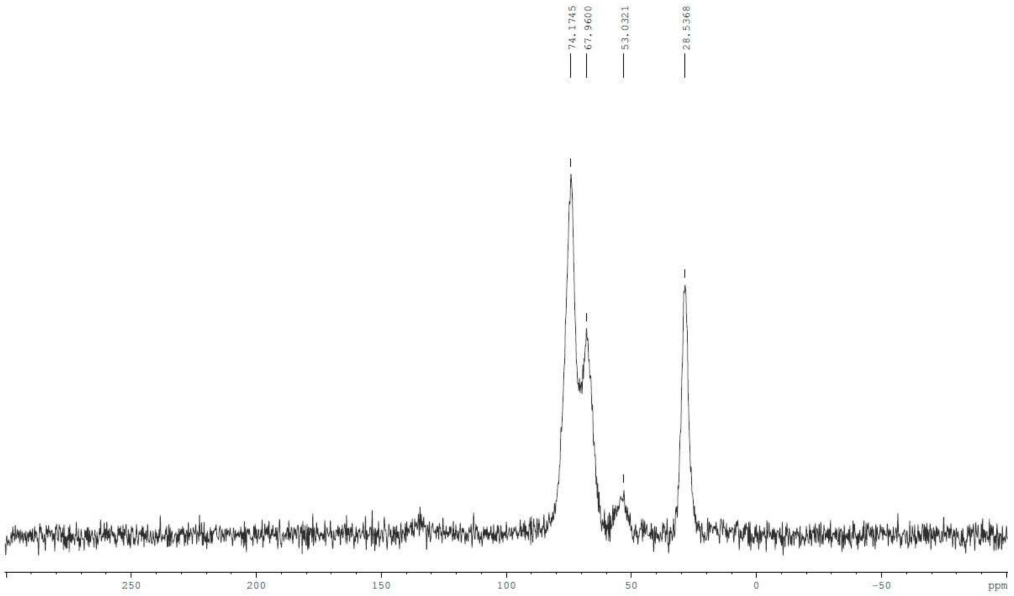

Figure 2. NMR spectrum of MA-BDDE material.

The ^{13}C NMR spectrum exhibits a strong peak at the value of 28.5 ppm, within a shift range where amine nitrogen C–N grouping feedback peaks occur, confirming the presence of these groups within the structure. The other strong signal, a doublet of 68 ppm and 74.2 ppm peaks, is an image characteristic of carbon–hydrogen and hydroxyl carbon–oxygen interactions. The most prominent peak visible on the ATR FTIR spectrum is a signal at a wavelength of 1051 cm^{-1}, associated with the stretching of a single strong alkoxy carbon–oxygen C–O bond. Its width could be attributed to the presence of a second peak at around 1200 cm^{-1}, indicative of an amine C–N bond. Lack of separation between these two peaks is likely the result of the polymeric nature of the material hindering the resolution of the measurement. A broad peak within the 2800–3700 cm^{-1} range is characteristic of a hydroxyl O–H stretch—the lack of any sharp peaks in this area might suggest a lack of nitrogen–hydrogen interactions, implying that virtually every methylamine nitrogen built into the structure of the MA-BDDE material is of the tertiary or quaternary ordinance.

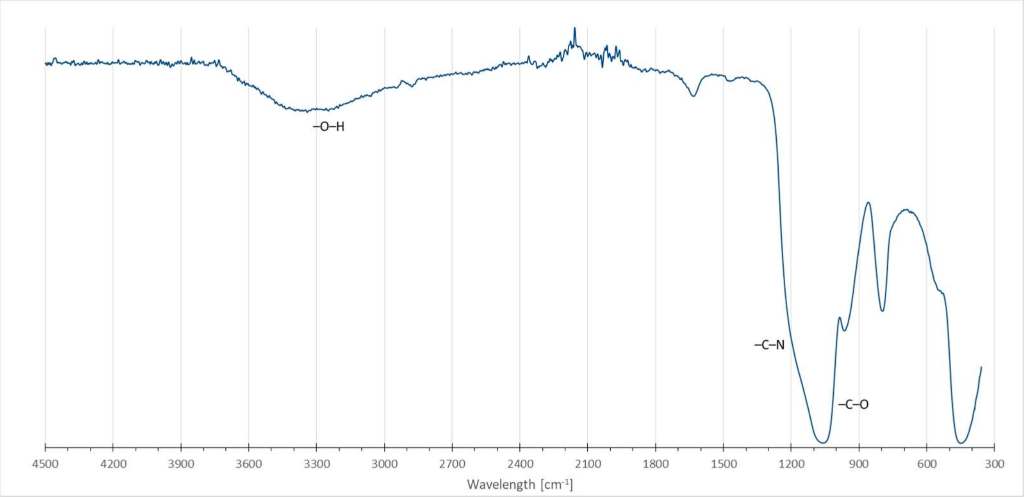

Figure 3. FTIR spectrum of MA-BDDE material.

2.2. HPLC Calibration

Five common NSAIDs were selected in order to evaluate the ability of the MA-BDDE sorbent to isolate organic ionic xenobiotics, namely aspirin (ACA), ketoprofen (KET), naproxen (NAP), diclofenac (DIC) and ibuprofen (IBP). Determination of the samples was carried out using liquid chromatography combined with detection in the visible and ultraviolet light spectrums (HPLC-UV/Vis system). Figure 4 shows a chromatogram obtained during the simultaneous analysis of all five analytes in a standard solution of methanol. Based on absorption spectra obtained for each of the pharmaceuticals, two detection channels were chosen for accurate analyte quantification. The primary channel was set for detection at a wavelength of 220 nm as it provided strong signals for all five compounds. Resolution between ketoprofen and naproxen (peaks 2 and 3 in Figure 4) was not satisfactory; therefore, a secondary channel was introduced for detection at 280 nm allowing for better separation of the signal from ketoprofen. For naproxen, the peak obtained from the primary channel was chosen for analysis, as this strong signal was unaffected by poor resolution, as is reflected by the good linearity value of its calibration curve, as shown in Table 1.

Calibration was performed by using five NSAID solutions at varying concentrations between 0.1 and 2 μg mL^{-1}, and the experiments were performed in replicates of three. The coefficient of determination (R^2) obtained for each analyte, as well as their respective detection (LOD) and quantitation limits (LOQ), are presented in Table 1. LOD and LOQ values were calculated in accordance with the guidelines found in *Analytical method validation: A brief review* [27] as LOD = 3.3 Sa/b and LOQ = 10 Sa/b, where Sa is the standard deviation of the calibration curve intercept, and b is the calibration curve slope.

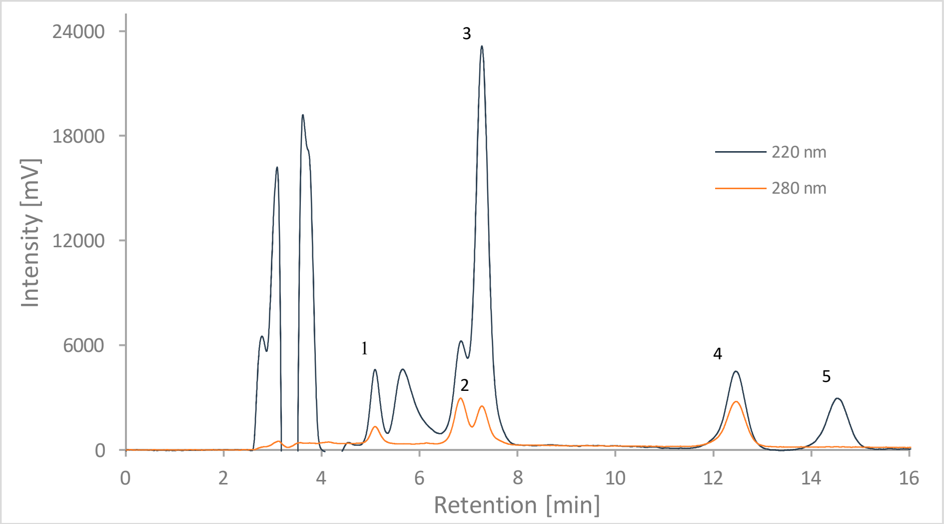

Figure 4. Chromatogram of 1 μg mL^{-1} pharmaceuticals solution. 1—aspirin; 2—ketoprofen; 3—naproxen; 4—diclofenac; 5—ibuprofen.

Table 1. Validation parameters for pharmaceutical HPLC-UV/Vis analysis.

Analyte	R^2	LOD [ng mL^{-1}]	LOQ [ng mL^{-1}]
Aspirin	0.9936	131	396
Ketoprofen	0.9744	265	802
Naproxen	0.9952	114	346
Diclofenac	0.9985	63	191
Ibuprofen	0.9970	89	270

2.3. *Sorption Effectiveness*

Extraction was carried out using the dSPE procedure due to its simplicity and ease of application combined with its effectiveness, as well as low sorbent and solvent expenditure. Table 2 shows the amount of each pharmaceutical absorbed by 1 g of the MA-BDDE sorbent and unmodified silica in simultaneous extraction. Calculation of the equilibrium sorption capacity Q was carried out using the following formula:

$$Q = (C_0 - C_e) \times V/m \quad (1)$$

where C_0 is the initial concentration of the solution (μg mL^{-1}), C_e is the equilibrium concentration (μg mL^{-1}), V is solution volume (mL), and m is sorbent mass (mg). The obtained results clearly show the sorption capacity of the MA-BDDE sorbent has greatly improved over unmodified silica. The lower affinity of the material towards ketoprofen and ibuprofen is also easily noticeable.

Table 2. Sorption capacity of selected pharmaceuticals shown for silica modified with MA-BDDE dendrimer and unmodified silica.

Analyte	Sorption Capacity [mg g^{-1}]	
	MA-BDDE	Silica Gel 60
Aspirin	2.005	0.08
Ketoprofen	1.073	0.11
Naproxen	2.131	0.11
Diclofenac	2.253	0.10
Ibuprofen	1.253	0.06

Initial analysis of the simultaneous extraction process from a mixed solution of 1 μg mL^{-1} reveals that around the 30 min mark, its effectiveness is the highest, while carrying the process past 60 min no longer brings any significant change to the NSAID content in the solution (Figure 5).

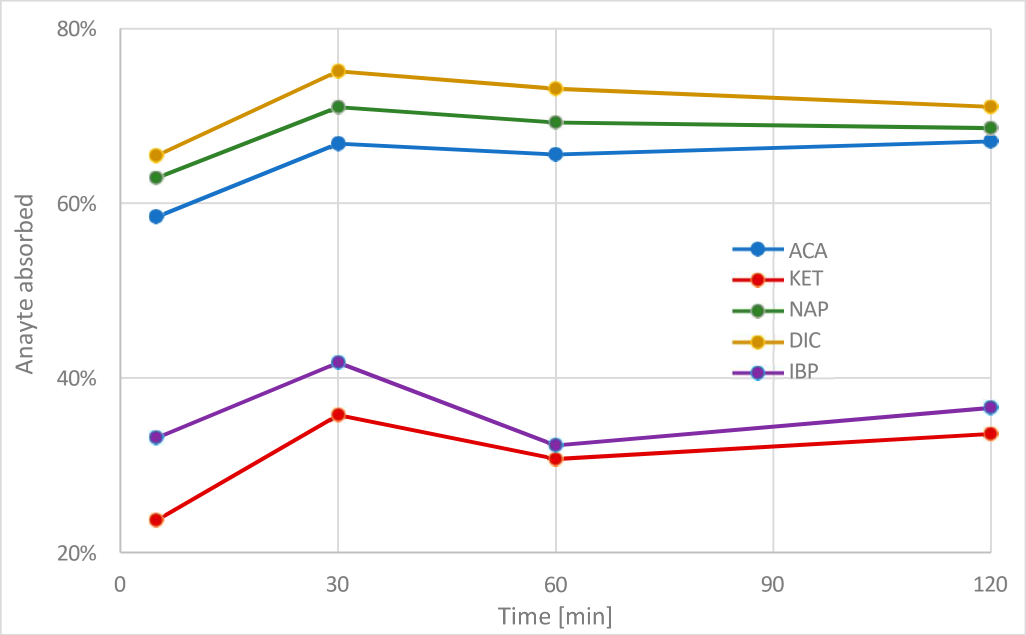

Figure 5. NSAID sorption effectiveness over time.

Desorption from the surface of the MA-BDDE sorbent was carried out using 1% acetic acid solution in methanol and produced very good recovery values (Table 3). In comparison, pure methanol proved to be an inadequate solvent for this purpose. It was noted, however, that during chromatographic analysis, the presence of acetic acid in the injected volume caused the signal corresponding to formic acid present in the mobile phase to shift slightly towards lower values, at times hindering the determination of the amount of aspirin in the sample.

Table 3. Recovery values obtained using methanol and acetic acid solutions as solvents in desorption process.

Analyte	Recovery (%) (RSD (%); *n* = 3)	
	Methanol	**1% HAc ***
Aspirin	22 (8.5)	n.d.
Ketoprofen	4 (5.8)	96 (4.3)
Naproxen	9 (6.8)	103 (14.3)
Diclofenac	12 (6.1)	88 (9.7)
Ibuprofen	26 (11.0)	77 (10.1)

* 1% acetic acid solution in methanol.

2.4. *Environmental Samples*

For the purpose of evaluating the synthesized sorbent and the developed analytical procedure, samples were taken from two rivers: Vistula, a major river in Poland, and its tributary, Brda. Extraction and analysis were performed as described in Section 4 of this article. The results, as shown in Table 4, were unremarkable: while traces of some of the analyzed NSAIDs were found in Vistula River, no peak was observed on a chromatogram obtained from the Brda sample. The most likely explanation is the fact that Vistula is a great river and there are multiple large population centers located within its basin. Discharge from wastewater treatment plants accompanying these towns and cities flows to and eventually ends up in Vistula River waters. In comparison, Brda is a small river with just one city with a population of roughly 340,000 in its vicinity. As such, pharmaceutical contamination of its waters is bound to be much lower and, in this case, NSAID concentration was too low to be detected using our method.

Table 4. NSAID concentrations found in river samples.

Analyte	**Concentration (ng mL^{-1})**	
	Vistula	**Brda**
Aspirin	n.d.	n.d.
Ketoprofen	n.d.	n.d.
Naproxen	n.d.	n.d.
Diclofenac	32.7	n.d.
Ibuprofen	31.6	n.d.

n.d.: not determinated.

In order to definitively confirm MA-BDDE efficiency, a final series of tests was conducted, where extraction was carried out as described on both river water samples as well as distilled and tap water samples, all of which were spiked with a mixed NSAID solution containing 100 µg of each pharmaceutical. Recoveries obtained in this experiment, shown in Table 5, are very similar to the high values displayed in Table 3, proving the high applicability of our sorbent in NSAID isolation from water.

Table 5. NSAID % recovery and standard deviation values (%, $n = 3$) from spiked water samples.

	Brda River	**Vistula River**	**Distilled Water**	**Tap Water**
Aspirin	80 (13.8)	n.d.	n.d.	92 (5.3)
Ketoprofen	92 (8.1)	88 (3.3)	99 (3.7)	99 (6.3)
Naproxen	98 (8.7)	93 (4.8)	88 (7.8)	96 (4.5)
Diclofenac	96 (6.1)	101 (6.0)	93 (6.3)	92 (5.2)
Ibuprofen	72 (9.3)	86 (10.1)	79 (7.6)	83 (9.3)

n.d.: not determinated.

3. Discussion

A novel material consisting of silica coated with dendrimeric copolymer MA-BDDE was successfully synthesized and applied for the extraction of five selected NSAIDs using the dSPE procedure for the first time. The initial characteristic of the material, using solid-state ^{13}C NMR and FT-IR spectroscopy, strongly suggests that both amine and ether groups originating from co-monomers indeed constitute the structure of the obtained material. A remarkable increase in NSAID sorption capacity, when compared to unmodified silica used as a core of the dendrimer, further confirms successful preparation of the sorbent. Results obtained via the HPLC-UV/Vis system show the high effectiveness of the applied nanomaterial in isolating NSAIDs from solutions and water samples, especially in the case of aspirin, diclofenac and naproxen, confirming MA-BDDE's potential for isolating these substances from natural matrixes.

Analysis of the progress of the adsorption process revealed that the equilibrium is reached after an hour into the procedure. This allowed for the development of a dSPE extraction procedure for the isolation of pharmaceuticals from water samples, which is described in detail in Section 4. Using this procedure, the sorbent was applied in the determination of NSAID traces present in natural water samples taken from two rivers. Samples taken from a major river showed ibuprofen and diclofenac contamination most likely originated from large population centers found upstream. Vistula's expansive river basin is also rich in agriculture and animal husbandry, which could also contribute especially to diclofenac contamination. Samples from the Brda River did not contain detectable NSAID traces as it is a much smaller river and lacks significant sources of pharmaceutical contamination in its vicinity. Methanol and an acetic acid solution in methanol were tested as solvents used in desorption, and the latter was chosen due to its very good recovery values despite occasional issues with aspirin detection. Using this eluent after extraction from various water samples spiked with NSAIDs allowed for the recovery of over 72% of the adsorbed analytes.

The performance of the entire analytical procedure developed for this study was compared with results presented in several recently published articles focused on the determination of NSAIDs in water samples from the perspective of the sensitivity of the employed analytical method, as shown in Table 6. As expected, using methods based on mass spectrometry detection, especially coupled with gas chromatography separation, allowed for the detection of much lower concentrations of analytes [28–30]. It is notable that Alinezhad et al. [31] presented results of a study on NSAID determination in water using high-pressure liquid chromatography followed by detection in ultraviolet light with exceptionally good validation parameters obtained. Modification of polyamidoamine dendrimer with magnetic Fe_3O_4 nanoparticles allowed for the employment of a magnetic solid-phase extraction procedure (MSPE). When combined with HPLC-UV detection, it resulted in an analytical method achieving sensitivity values easily comparable to those displayed in studies performing GC-MS analyses. Chen et al. [32], who also reported NSAID detection using a standard HPLC-UV system, presented results showing higher LOD values, which were very close to those obtained by Al-Khateeb and Dahas [33] using a similar detection method while also employing buffered superheated water in an HPLC mobile phase in order to improve mass transfer and analyte diffusion and therefore enhance separation. The displayed sensitivities of these two methods are only slightly higher and still comparable to the parameters of our developed procedure.

Table 6. Comparison of the developed methods' performance with recently reported data.

Analyte	Analytical Method	LOD ($ng\ mL^{-1}$)	Linear Range ($ng\ mL^{-1}$)	Reference
Diclofenac, ibuprofen, ketoprofen, naproxen	FPSE [a]-GC-MS	0.8–5	0.005–0.5	[28]
Phenlacetin, meloxicam, naproxen, diclofenac, carprofen	SPE-UHPLC-MS/MS	0.019–0.041	0.02–5	[29]
Piroxcam, meloxicam, ketoprofen, naproxen, diclofenac, indomethacin, mefenamic acid, tolfenamic acid	MSPE [b]-UHPLC-MS/MS	0.003–0.06	0.02–25	[30]
Naproxen, diclofenac, ibuprofen	MSPE-HPLC-UV	0.05–0.08	0.15–500	[31]
Ketoprofen, naproxen, diclofenac, ibuprofen	SPE-HPLC-UV	2–32	5–500,000	[33]
Ibuprofen, diclofenac, ketoprofen, 4-CAA [c], clofibric acid	dSPE-HPLC-UV	2.9–21.4	10–10,000	[32]
Aspirin, diclofenac, ibuprofen, ketoprofen, naproxen	dSPE-HPLC-UV/Vis	63–265	100–2000	present study

[a]—fabric-phase sorptive extraction; [b]—magnetic solid-phase extraction; [c]—4-chlorophenoxyacetic acid.

4. Materials and Methods

Methylamine (40% aqueous solution) and 1,4-butanediol diglycidyl ether (95%), as well as Silica Gel 60, were provided by Merck KGaA, Darmstadt, Germany. For the purposes of sorbent synthesis, following aqueous solutions were prepared: MA + BDDE (2.8% and 7.2%, respectively), MA (4%) and BDDE (10%). Aspirin (acetic salicyl acid), diclofenac (2-[(2,6-dichlorophenyl)amino]benzeneacetic acid sodium salt), ketoprofen (2-(3-benzoylphenyl)propionic acid), naproxen ((*S*)-(+)-2-(6-methoxy-2-naphthyl)propionic acid) and ibuprofen ((±)-2-(4-isobutylphenyl)propanoic acid) are certified pharmaceutical standards for analysis and were supplied by Merck KGaA, Germany. Pharmaceutical stock solutions in methanol at concentration of 100 mg L^{-1} were prepared and stored in darkness. Methanoic acid (80%) and methanol (HPLC-grade) were provided by Merck KGaA, Germany, and acetonitrile (methyl cyanide; HPLC-grade) was obtained from Honeywell International Inc., Charlotte, NC, USA. Acetic acid (99.5%) was purchased from CHEMPUR.

In order to coat silica with a binding layer of MA-BDDE copolymer, 5 g of silica gel was stirred for 30 min with the MA + BDDE solution at 65 °C. The material was then filtered, washed with deionized water and finally dried. The next two steps consisted of repeating the same procedure, using MA and BDDE solutions (in this order) instead of MA + BDDE solution, to obtain branching co-monomer layers, forming the first layer of dendrimeric MA-BDDE copolymer. Steps involving the use of MA and BDDE solutions were repeated four more times, resulting in five layers of dendrimerically branching MA-BDDE copolymer coating a silica core, which were proven to exhibit the best sorptive properties [34].

Initial physicochemical characterization of the obtained material consisted of infrared spectroscopic analysis with the help of a Bruker Alpha-P Attenuated Total Reflectance (ATR) Fourier Transform InfraRed (FT-IR) spectrometer, as well as carbon-13 nuclear magnetic resonance (^{13}C-NMR) analysis in solid state using Bruker Ascend III 400 MHz (9,4T) spectrometer with an Avance III HD console.

Analyte extraction with MA-BDDE sorbent was carried out utilizing dSPE procedure. Around 5 mg of the sorbent and 15 mL of analyte solution in methanol were placed in a polypropylene centrifugal container that was then shaken at 80 RPM in order to disperse the sorbent within the solution volume. After each dispersion step, containers were placed in a centrifuge and rotated for 20 min at a speed of 4000 RPM. After centrifugation, 100 μL of supernatant was taken out of the container, out of which 20 μL was injected into HPLC apparatus for analysis.

After extraction, sorbent was filtered from the sample and briefly washed with methanol. It was then moved to another centrifugal container, where 10 mL of 1% acetic acid solution in methanol was subsequently added. The container was then shaken at a speed of 80 RPM for half an hour and centrifuged. After centrifugation, 100 μL of supernatant was taken for the purpose of performing HPLC analysis.

Surface water samples taken from Brda and Vistula rivers were first filtrated in order to remove any suspended particles. A total of 100 mL of the filtrate was then placed in flasks with 10 mg of MA-BDDE sorbent and stirred for half an hour. When the extraction phase was finished, the desorption procedure was carried out as described above.

Simultaneous analyte detection was conducted using a SHIMADZU Prominence HPLC-UV/Vis system. Mobile phase consisted of acetonitrile (40% v/v), methanol (30% v/v) and 0.5% formic acid aqueous solution (30% v/v). Separation was carried out with mobile phase flow of 0.5 mL min^{-1} in reverse phase, using Supelco Discovery HS C18 column with dimensions of 15 cm × 4.6 mm × 5 μm at 30 °C. Detection wavelengths of 220 and 280 nm were chosen based on absorption spectra of each analyzed pharmaceutical compound obtained with JENWAY 7315 spectrophotometer.

5. Conclusions

A novel material based on silica coated with a dendrimeric copolymer of methylamine (MA) and 1,4-butanediol diglycidyl ether (BDDE) was successfully synthesized for the first time. The initial characteristic of the material, labeled MA-BDDE, using solid-state ^{13}C NMR and FTIR spectroscopy, confirms the presence of both amine and ether groups originating from co-monomers within the structure. The material was applied as a sorbent in a dispersive solid-phase extraction procedure of select pharmaceuticals from solutions and water samples, showing a good ability to isolate these compounds from natural matrixes. Coupling it with a standard HPLC-UV/Vis detection system created an effective analytical method with sensitivity comparable to most reported methods employing a similar methodology. The utilization of an acetic acid solution for desorption yielded high recovery values.

Small quantities of organic solvents that are required translate directly into equally small volumes of waste produced in the course of the analysis. The entire analytical procedure, from extraction to chromatographic separation and finally to detection, is extremely simple, as well as fast and effective, and does not rely on highly expensive or complex equipment. The liquid chromatograph combined with a UV/Vis detection system used in this study could be considered a standard apparatus that can be found in virtually any analytical laboratory today. As such, our method stands as a valid alternative for NSAID determination in natural water samples.

Author Contributions: Conceptualization, P.K. and P.Ś.; methodology, P.Ś.; validation, P.Ś.; investigation, P.Ś.; writing—original draft preparation, P.Ś.; writing—review and editing, P.Ś. and P.K.; supervision, P.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data generated during this research are presented within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

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12.2. Oświadczenie Autora rozprawy doktorskiej

Z.16.2021.2022

Załącznik nr 3 do
Instrukcji drukowania, gromadzenia, rejestrowania i udostępniania rozpraw doktorskich przez rady naukowe dyscyplin (dyscyplin artystycznych) prowadzących postępowanie w sprawie nadania stopnia naukowego doktora

Oświadczenie Autora rozprawy doktorskiej

mgr inż. Piotr Ścigalski
(tytuł zawodowy, imiona i nazwisko autora rozprawy doktorskiej)

Politechnika Bydgoska im. Jana i Jędrzeja Śniadeckich
Wydział Technologii i Inżynierii Chemicznej
(miejsce pracy/afiliacja)

OŚWIADCZENIE

Oświadczam, iż mój wkład autorski w niżej wymienionych artykułach naukowych stanowiących cykl publikacji rozprawy doktorskiej był następujący*:

1. Tetiana Tatarchuk, Mariana Myslin, Ivan Mironyuk, Przemysław Kosobucki, **Piotr Ścigalski**, Volodymyr Kotsyubynsky, *Removal of Congo Red dye, polar and non-polar compounds from aqueous solution using magnesium aluminate nanoparticles*, Materials Today: Proceedings (Elsevier), 2021, 35, 4, 518-522,
   https://doi.org/10.1016/j.matpr.2019.10.012,
   ilość punktów MNiSW: 0, Impact Factor 0

   Wykonane zadania przez Doktoranta w ramach artykułu:
   a) opracowanie metodyki ekstrakcji i oznaczenia zawartości kwasu salicylowego oraz wielopierścieniowych węglowodorów aromatycznych
   b) wykonanie ekstrakcji i oznaczenia zawartości kwasu salicylowego oraz wielopierścieniowych węglowodorów aromatycznych
   c) opis przebiegu ekstrakcji i oznaczenia zawartości kwasu salicylowego oraz wielopierścieniowych węglowodorów aromatycznych

2. Tetiana Tatarchuk, Mu. Naushad, Jolanta Tomaszewska, Przemysław Kosobucki, Mariana Myslin, Hanna Vasylyeva, **Piotr Ścigalski**, *Adsorption of Sr(II) ions and salicylic acid onto magnetic magnesium-zinc ferrites: isotherms and kinetic studies*, Environmental Science and Pollution Research (Springer), 2020, 27, 26681-26693;
   https://doi.org/10.1007/s11356-020-09043-1,
   ilość punktów MNiSW: 100, Impact Factor 5.8

   Wykonane zadania przez Doktoranta w ramach artykułu:
   a) opracowanie metodyki ekstrakcji i oznaczenia zawartości kwasu salicylowego
   b) wykonanie ekstrakcji i oznaczenia zawartości kwasu salicylowego
   c) opis przebiegu ekstrakcji i oznaczenia zawartości kwasu salicylowego

3. **Piotr Ścigalski**, Przemysław Kosobucki, *Recent Materials Developed for Dispersive Solid-Phase Extraction*", Molecules (MDPI), 2020, 25, 4869;
   https://doi.org/10.3390/molecules25214869,
   ilość punktów MNiSW: 140, Impact Factor 4.2

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* *W przypadku prac dwu- lub wieloautorskich wymagane są oświadczenia kandydata do stopnia doktora oraz współautorów, wskazujące na ich merytoryczny wkład w powstanie każdej pracy (np. twórca hipotezy badawczej, pomysłodawca badań, wykonanie specyficznych badań – np. przeprowadzenie konkretnych doświadczeń, opracowanie i zebranie ankiet itp., wykonanie analizy wyników, przygotowanie manuskryptu artykułu i inne). Określenie wkładu danego autora, w tym kandydata do stopnia doktora, powinno być na tyle precyzyjne, aby umożliwić dokładną ocenę jego udziału i roli w powstaniu każdej pracy.*

Wykonane zadania przez Doktoranta w ramach artykułu:
a) opracowanie koncepcji artykułu
b) przeprowadzenie przeglądu literatury naukowej
c) weryfikacja i zawężenie zbioru zgromadzonej literatury naukowej
d) redakcja i edycja manuskryptu

4. **Piotr Ścigalski**, Przemysław Kosobucki, *Dendrimer Coated Silica as a Sorbent for Dispersive Solid-Phase Extraction of Select Non-Steroidal Anti-Inflammatory Drugs from Water,* Molecules (MDPI), 2024, 29, 380,
https://doi.org/10.3390/molecules29020380,
ilość punktów MNiSW: 140, Impact Factor 4.2

Wykonane zadania przez Doktoranta w ramach artykułu:
a) opracowanie planu i metodologii badań
b) przeprowadzenie prac badawczych
c) analiza i opracowanie wyników
d) redakcja i edycja manuskryptu

Bydgoszcz, 24.09.2024
miejscowość, data

Ścigalski
Podpis Autora rozprawy doktorskiej

P. Kosobucki
Podpis promotora

12.3. Oświadczenia Współautorów artykułów naukowych

Z.16.2021.2022

Załącznik nr 3 do
Instrukcji drukowania, gromadzenia, rejestrowania i udostępniania rozpraw doktorskich przez rady naukowe dyscyplin (dyscyplin artystycznych) prowadzących postępowanie w sprawie nadania stopnia naukowego doktora

Co-author's Declaration

dr hab. Przemysław Kosobucki, prof. PBŚ
(Professional title, name(s) and surname of the Co-author)

Bydgoszcz University of Science and Technology
Faculty of Chemical Technology and Engineering
Department of Food Analysis and Environmental Protection
(Workplace/affiliation)

DECLARATION

I declare that my author's contribution to the journal article/articles mentioned below was as follows*:

Ścigalski Piotr, Kosobucki Przemysław, Dendrimer Coated Silica as a Sorbent for Dispersive Solid-Phase Extraction of Select Non-Steroidal Anti-Inflammatory Drugs from Water, Molecules, 2024, 29, 380, 1-12, https://doi.org/10.3390/molecules29020380, MNiSW 140 points, IF 4.6.

Tasks completed as part of the article:

a) the originator of the work concept,
b) planning all experiments,
c) analysis and development of the results,
d) participation in the preparation of the original shape of the publication,
e) participation in editing the work and writing responses to the reviewers' comments,
f) participation in the preparation of the final version of the publication.

Tetiana Tatarchuk, Mariana Myslin, Ivan Mironyuk, Przemysław Kosobucki, Piotr Ścigalski, Volodymyr Kotsyubynsky, Removal of Congo Red dye, polar and non-polar compounds from aqueous solution using magnesium aluminate nanoparticles, Materials Today: Proceedings (Elsevier), 2021, 35, 4, 518-522, https://doi.org/10.1016/j.matpr.2019.10.012, MNiSW 5 points.

Tasks completed as part of the article:

a) planning sorption experiments,
b) analysis and development of the results,
c) participation in the preparation of the original shape of the publication,
d) participation in editing the work and writing responses to the reviewers' comments,
e) participation in the preparation of the final version of the publication.

Tetiana Tatarchuk, Mu. Naushad, Jolanta Tomaszewska, Przemysław Kosobucki, Mariana Myslin, Hanna Vasylyeva, Piotr Ścigalski, Adsorption of Sr(II) ions and salicylic acid onto magnetic magnesium-zinc ferrites: isotherms and kinetic studies, Environmental Science and Pollution Research (Springer), 2020, 27, 26681-26693, https://doi.org/10.1007/s11356-020-09043-1, MNiSW 100 points, Impact Factor 5.8.

Tasks completed as part of the article:

a) planning sorption experiments,
b) analysis and development of the results,
c) participation in the preparation of the original shape of the publication,
d) participation in editing the work and writing responses to the reviewers' comments,
e) participation in the preparation of the final version of the publication.

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[*] *In the case of two- or multi-author papers, declarations of a candidate for the doctoral degree and co-authors are required, indicating their substantive contribution to the creation of each paper (e.g. the creator of the research hypothesis, the originator of the research, performance of specific research – e.g. carrying out particular experiments, developing and collecting questionnaires, etc., analysis of the results, preparation of the article manuscript and others). Identification of the contribution of a given author, including a candidate for the doctoral degree, should be precise enough to allow for an accurate assessment of his/her participation and role in the creation of each paper.*

Z.16.2021.2022

Załącznik nr 3 do
Instrukcji drukowania, gromadzenia, rejestrowania i udostępniania rozpraw doktorskich przez rady naukowe dyscyplin (dyscyplin artystycznych) prowadzących postępowanie w sprawie nadania stopnia naukowego doktora

Ścigalski Piotr, Kosobucki Przemysław, Recent Materials Developed for Dispersive Solid Phase Extraction, Molecules, 2020, 25, 21, 1-26, https://www.mdpi.com/1420-3049/25/21/4869, MNiSW 140 points, IF 4.6.

Tasks completed as part of the article:

a) the originator of the work concept,
b) participation in the preparation of the original shape of the publication, including literature analysis,
c) participation in editing the work and writing responses to the reviewers' comments,
d) participation in the preparation of the final version of the publication.

At the same time, I hereby agree to the submission of the above-mentioned paper(s) by M. Sc. Piotr Ścigalski as part of the doctoral dissertation based on a collection of published and thematically related scientific papers.

Bydgoszcz 26.09.2024
Place, date

P. Kosobucki
dr hab. Przemysław Kosobucki
prof. PBŚ
Co-author's signature

Z.16.2021.2022

Załącznik nr 3 do
Instrukcji drukowania, gromadzenia, rejestrowania i udostępniania rozpraw doktorskich przez rady naukowe dyscyplin (dyscyplin artystycznych) prowadzących postępowanie w sprawie nadania stopnia naukowego doktora

Co-author's Declaration

dr hab. inż. Jolanta Tomaszewska, prof. PBŚ
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Bydgoszcz University of Science and Technology
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(Workplace/affiliation)

DECLARATION

I declare that my author's contribution to the journal article/articles mentioned below was as follows*:

Tetiana Tatarchuk, Mu. Naushad, Jolanta Tomaszewska, Przemysław Kosobucki, Mariana Myslin, Hanna Vasylyeva, Piotr Ścigalski, Adsorption of Sr(II) ions and salicylic acid onto magnetic magnesium-zinc ferrites: isotherms and kinetic studies, Environmental Science and Pollution Research (Springer), 2020, 27, 26681-26693, https://doi.org/10.1007/s11356-020-09043-1, MNiSW 100 points, Impact Factor 5.8.

Tasks completed as part of the article:

a) analysis of results,
b) participation in the preparation of the original shape of the publication, including literature analysis.

At the same time, I hereby agree to the submission of the above-mentioned paper(s) by M. Sc. Piotr Ścigalski as part of the doctoral dissertation based on a collection of published and thematically related scientific papers.

Bydgoszcz, 17.05.2021
Place, date

Co-author's signature

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* *In the case of two- or multi-author papers, declarations of a candidate for the doctoral degree and co-authors are required, indicating their substantive contribution to the creation of each paper (e.g. the creator of the research hypothesis, the originator of the research, performance of specific research – e.g. carrying out particular experiments, developing and collecting questionnaires, etc., analysis of the results, preparation of the article manuscript and others). Identification of the contribution of a given author, including a candidate for the doctoral degree, should be precise enough to allow for an accurate assessment of his/her participation and role in the creation of each paper.*

Z.16.2021.2022

Załącznik nr 3 do
Instrukcji drukowania, gromadzenia, rejestrowania i udostępniania rozpraw doktorskich przez rady naukowe dyscyplin (dyscyplin artystycznych) prowadzących postępowanie w sprawie nadania stopnia naukowego doktora

Co-author's Declaration

Assistant Professor, Tetiana Tatarchuk
(Professional title, name(s) and surname of the Co-author)

Chemistry Department, Jagiellonian University, Kraków, PL
(Workplace/affiliation)

DECLARATION

I declare that my author's contribution to the journal article/articles mentioned below was as follows*:

1. Tetiana Tatarchuk, Mu. Naushad, Jolanta Tomaszewska, Przemysław Kosobucki, Mariana Myslin, Hanna Vasylyeva, Piotr Ścigalski, Adsorption of Sr(II) ions and salicylic acid onto magnetic magnesium-zinc ferrites: isotherms and kinetic studies, Environmental Science and Pollution Research (Springer), 2020, 27, 26681-26693, https://doi.org/10.1007/s11356-020-09043-1, 100 MNiSW points, Impact Factor 5.8.
   Tasks completed as part of the article:
   a) the creator of the research hypothesis, conceptualization;
   b) the originator of the research (methodology, supervision);
   c) project administration;
   d) analysis of all results: analysis of structure and morphology of the magnesium-zinc ferrites adsorbents and their adsorption properties;
   e) preparation of the article manuscript, review, and editing;
   f) corresponding author of the manuscript.

2. Tetiana Tatarchuk, Mariana Myslin, Ivan Mironyuk, Przemysław Kosobucki, Piotr Ścigalski, Volodymyr Kotsyubynsky, Removal of Congo Red dye, polar and non-polar compounds from aqueous solution using magnesium aluminate nanoparticles, Materials Today: Proceedings (Elsevier), 2021, 35, 4, 518-522, https://doi.org/10.1016/j.matpr.2019.10.012, 5 MNiSW points, Impact Factor –.
   Tasks completed as part of the article:
   a) the creator of the research hypothesis, conceptualization;
   b) the originator of the research (methodology, supervision);
   c) project administration;
   d) analysis of all results: analysis of structure and morphology of the sample and its adsorption properties;
   e) preparation of the article manuscript, review, and editing;
   f) corresponding author of the manuscript.

At the same time, I hereby agree to the submission of the above-mentioned paper(s) by M. Sc. Piotr Ścigalski as part of the doctoral dissertation based on a collection of published and thematically related scientific papers.

Kraków, 20-05-2024
Place, date

....
Co-author's signature

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* *In the case of two- or multi-author papers, declarations of a candidate for the doctoral degree and co-authors are required, indicating their substantive contribution to the creation of each paper (e.g. the creator of the research hypothesis, the originator of the research, performance of specific research – e.g. carrying out particular experiments, developing and collecting questionnaires, etc., analysis of the results, preparation of the article manuscript and others). Identification of the contribution of a given author, including a candidate for the doctoral degree, should be precise enough to allow for an accurate assessment of his/her participation and role in the creation of each paper.*

Co-author's Declaration

Associated Professor Hanna Vasylyeva

Department of Theoretical Physics, Faculty of Physics, Uzhhorod National University,
Uzhhorod, Ukraine

DECLARATION

I declare that my author's contribution to the journal article mentioned below was as follows*:

1. Tetiana Tatarchuk, Mu. Naushad, Jolanta Tomaszewska, Przemysław Kosobucki, Mariana Myslin, Hanna Vasylyeva, Piotr Ścigalski, Adsorption of Sr (II) ions and salicylic acid onto magnetic magnesium-zinc ferrites: isotherms and kinetic studies, Environmental Science and Pollution Research (Springer), 2020, 27, 26681-26693, https://doi.org/10.1007/s11356-020-09043-1, 100 MNiSW points, Impact Factor 5.8.
   Tasks completed as part of the article:
   a) adsorption of the strontium cations by magnetic magnesium-zinc ferrite nanoparticles from aqueous solutions

At the same time, I hereby agree to the submission of the above-mentioned paper by M. Sc. Piotr Ścigalski as part of the doctoral dissertation based on a collection of published and thematically related scientific papers.

30.07.2024
....
Place, date Co-author's signature

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* *In the case of two- or multi-author papers, declarations of a candidate for the doctoral degree and co-authors are required, indicating their substantive contribution to the creation of each paper (e.g. the creator of the research hypothesis, the originator of the research, performance of specific research – e.g. carrying out particular experiments, developing and collecting questionnaires, etc., analysis of the results, preparation of the article manuscript and others). Identification of the contribution of a given author, including a candidate for the doctoral degree, should be precise enough to allow for an accurate assessment of his/her participation and role in the creation of each paper.*

Онлайн сервіс створення та перевірки кваліфікованого та удосконаленого електронного підпису

ПРОТОКОЛ

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П.І.Б.: Васильєва Ганна Володимирівна
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Załącznik nr 3 do
Instrukcji drukowania, gromadzenia, rejestrowania i udostępniania rozpraw doktorskich przez rady naukowe dyscyplin (dyscyplin artystycznych) prowadzących postępowanie w sprawie nadania stopnia naukowego doktora

Co-author's Declaration

Mgr. Mariana Myslin
(Professional title, name(s) and surname of the Co-author)

Chemistry Department, Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, UA
(Workplace/affiliation)

DECLARATION

I declare that my author's contribution to the journal article/articles mentioned below was as follows1 *:

1. Tetiana Tatarchuk, Mu. Naushad, Jolanta Tomaszewska, Przemysław Kosobucki, Mariana Myslin, Hanna Vasylyeva, Piotr Ścigalski, Adsorption of Sr(II) ions and salicylic acid onto magnetic magnesium-zinc ferrites: isotherms and kinetic studies, Environmental Science and Pollution Research (Springer), 2020, 27, 26681-26693, https://doi.org/10.1007/s11356-020-09043-1, 100 MNiSW points, Impact Factor 5.8.
   Tasks completed as part of the article:
   a) the synthesis of Mg-Zn ferrites adsorbents by auto-combustion sol-gel method;
   b) analysis of structure, morphology, and magnetic properties of the magnesium-zinc ferrites adsorbents (XRD, SEM, BET, VSM);
   c) performance of specific research: determination of the point of zero charge of the magnesium-zinc ferrites adsorbents;
   d) analysis of the results: applying of adsorption isotherm models (Langmuir, Freundlich, Dubinin-Radushkevich, and Sips models) to analyze the mechanism of Sr(II) ions adsorption;
   e) analysis of the results: applying of kinetics models (pseudo-first-order, pseudo-second-order, intra-particle diffusion, and Elovich models) to analyze the mechanism of Sr(II) ions adsorption;
   f) analysis of the results: applying kinetics models (pseudo-first-order, pseudo-second-order, intra-particle diffusion, and Elovich models) to analyze the mechanism of salicylic acid adsorption;
   g) preparation of the article manuscript.

2. Tetiana Tatarchuk, Mariana Myslin, Ivan Mironyuk, Przemysław Kosobucki, Piotr Ścigalski, Volodymyr Kotsyubynsky, Removal of Congo Red dye, polar and non-polar compounds from aqueous solution using magnesium aluminate nanoparticles, Materials Today: Proceedings (Elsevier), 2021, 35, 4, 518-522, https://doi.org/10.1016/j.matpr.2019.10.012, 0 MNiSW points, Impact Factor 24.2.
   Tasks completed as part of the article:
   a) the synthesis of magnesium aluminate nanoparticles by auto-combustion sol-gel method;
   b) analysis of the structure and morphology of the sample using XRD, FE-SEM, EDS, and IR spectroscopy methods;
   c) the calculation of crystallite size using the modified Scherer, Williamson-Hall, and SSP methods;

---

* *In the case of two- or multi-author papers, declarations of a candidate for the doctoral degree and co-authors are required, indicating their substantive contribution to the creation of each paper (e.g. the creator of the research hypothesis, the originator of the research, performance of specific research – e.g. carrying out particular experiments, developing and collecting questionnaires, etc., analysis of the results, preparation of the article manuscript and others). Identification of the contribution of a given author, including a candidate for the doctoral degree, should be precise enough to allow for an accurate assessment of his/her participation and role in the creation of each paper.*

d) performance of specific research: the adsorption experiments using Congo Red dye as a model pollutant and UV–Vis spectrophotometry analysis;
e) analysis of the results: applying of adsorption isotherm models to analyze the mechanism of Congo Red dye adsorption;
f) preparation of the article manuscript.

At the same time, I hereby agree to the submission of the above-mentioned paper(s) by M. Sc. Piotr Ścigalski as part of the doctoral dissertation based on a collection of published and thematically related scientific papers.

Ivano-Frankivsk, 20-05-2024
Place, date

....
Co-author's signature

Z.16.2021.2022

Załącznik nr 3 do
Instrukcji drukowania, gromadzenia, rejestrowania i udostępniania rozpraw doktorskich przez rady naukowe dyscyplin (dyscyplin artystycznych) prowadzących postępowanie w sprawie nadania stopnia naukowego doktora

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(Workplace/affiliation)

DECLARATION

I declare that my author's contribution to the journal article/articles mentioned below was as follows*:

1. Tetiana Tatarchuk, Mu. Naushad, Jolanta Tomaszewska, Przemysław Kosobucki, Mariana Myslin, Hanna Vasylyeva, Piotr Ścigalski, Adsorption of Sr(II) ions and salicylic acid onto magnetic magnesium-zinc ferrites: isotherms and kinetic studies, Environmental Science and Pollution Research (Springer), 2020, 27, 26681-26693, https://doi.org/10.1007/s11356-020-09043-1, 100 MNiSW points, Impact Factor 5.8.

   Tasks completed as part of the article:
   a) Writing – review & editing.

At the same time, I hereby agree to the submission of the above-mentioned paper(s) by M. Sc. Piotr Ścigalski as part of the doctoral dissertation based on a collection of published and thematically related scientific papers.

Naushad

Riyadh, 23-09-2024
Place, date

Co-author's signature

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[*] *In the case of two- or multi-author papers, declarations of a candidate for the doctoral degree and co-authors are required, indicating their substantive contribution to the creation of each paper (e.g. the creator of the research hypothesis, the originator of the research, performance of specific research – e.g. carrying out particular experiments, developing and collecting questionnaires, etc., analysis of the results, preparation of the article manuscript and others). Identification of the contribution of a given author, including a candidate for the doctoral degree, should be precise enough to allow for an accurate assessment of his/her participation and role in the creation of each paper.*

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DECLARATION

I declare that my author's contribution to the journal article/articles mentioned below was as follows*:

1. Tetiana Tatarchuk, Mariana Myslin, Ivan Mironyuk, PrzemysławKosobucki, Piotr Ścigalski, VolodymyrKotsyubynsky, Removal of Congo Red dye, polar and non-polar compounds from aqueous solution using magnesium aluminate nanoparticles, Materials Today: Proceedings (Elsevier), 2021, 35, 4, 518-522,https://doi.org/10.1016/j.matpr.2019.10.012, 5MNiSW points, Impact Factor–.
   Tasks completed as part of the article:
   a) the participation in the preparation of the article manuscript.

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Ivano-Frankivsk, 21-05-2024
Place, date

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DECLARATION

I declare that my author's contribution to the journal article/articles mentioned below was as follows*:

1. Tetiana Tatarchuk, Mariana Myslin, Ivan Mironyuk, Przemysław Kosobucki, Piotr Ścigalski, Volodymyr Kotsyubynsky, Removal of Congo Red dye, polar and non-polar compounds from aqueous solution using magnesium aluminate nanoparticles, Materials Today: Proceedings (Elsevier), 2021, 35, 4, 518-522, https://doi.org/10.1016/j.matpr.2019.10.012, 5 MNiSW points, Impact Factor –.
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Ivano-Frankivsk, 20-05-2024

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