

RESEARCH PAPER

Modified Iron Oxide Magnetic Nanosheets With Nitrogen-Containing Functional Groups as Chloridazon Adsorbent

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ABSTRACT

Mesostructured iron oxide/ethylene glycol (FeOx/EG) nanosheets with an oval shape were created and employed as a magnetic solid-phase extraction (MSPE) sorbent to extract herbicide chloridazon. Iron oxide layers are intercalated with deprotonated ethylene glycol molecules to provide an interlayer gap of 10.6 Å. Using scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), thermal gravimetric analysis (TGA), and a vibrating sample magnetometer (VSM), the size, shape, content, and characteristics of the produced nanocomposite were determined. The key influencing factors for extracting chloridazon, such as the volume of the sample, the amount of sorbent, and the desorption solvent, were optimized. High-performance liquid chromatography with UV detection was the subject of analyses. The approach demonstrated strong linearity in the range of 0.01–100 µg.mL⁻¹, reasonable repeatability (RSD 3.017%, n = 3), and limits of detection (0.001 µg.mL⁻¹) under the ideal extraction conditions.

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INTRODUCTION

Metal nanoparticles have a high magnetic resistance to their oxide counterparts. However, their high reactivity and toxicity make them unsuitable for direct applications in biotechnology and separation of environmental pollutants. Therefore, metal nanoparticles usually need to be protected with an insulating shell against the surrounding environment [1-4]. For this purpose, they are often used with polymer or silica coating. In the case of silica-coated magnetic nanoparticles, it is impossible to achieve a porous and completely dense silica coating, making it difficult to keep the top of these nanoparticles stable under adverse conditions, especially in play environments. Therefore, modern synthesis methods are still needed to ensure the stability of magnetic nanoparticles at high temperatures and under acidic and alkaline conditions. Carbon-

coated magnetic nanoparticles are remarkably stable under adverse conditions; however, it is very difficult to keep carbon-coated particles in an isolated and scattered state. The protective shell not only prevents magnetic nanoparticles from being damaged but can also be used to further agents with specific components such as active catalytic samples, various compounds, special bonding parts, or other functional groups. Easy separation and controlled replacement of these magnetic nanoparticles operated by an external magnetic field make possible their use as a catalyst base in enzyme stabilization processes and separation of environmental pollutants. Coating thickness can be adjusted by changing the ratio of tetraethyl orthosilicate (TEOS) in water. The surface of magnetic nanoparticles coated with silica is hydrophilic and easily modified with other functional groups. The advantage of this method

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is that the silica coating is oxidized at the surface, which is easily attached to the silica by OH surface groups [5-8].

Chloridazon or pyramin herbicide is a selective and systemic herbicide of the pyridazone group which is specifically used to control broadleaf weeds, especially in beet and lip crops. This herbicide acts as a barrier to plant photosynthesis and disrupts animal metabolism. These toxins and other intermediates used to produce them cannot be broken down by microorganisms. The chemical formula of this herbicide is $C_{10}H_8ClN_3O$, and its IUPAC name is 5-amino- 4- chloro- 2- phenylpyridazin- 3- one [9-16].

In this work, FeO_x/EG (Ethylene glycol) magnetic nanosheets were synthesized with a bottom-up protocol. The surface of these nanosheets was then coated with a cell-gel method with tetracycline orthosilicate (TEOS) and reacted with (amino-propyl) triethoxysilane (APTES) to modify the surface of this nanocomposite with amine-acting groups. Finally, nanocomposite/ SiO_2/NH_2 FeO_x/EG prepared by magnetic solid-phase extraction method (MSPE) was employed to separate chloridazon herbicide. Factors affecting separation efficiency such as adsorption value, sample solution volume, solvent type and volume, extraction and adsorption time, ionic strength, and pH of the solution were investigated.

EXPERIMENTAL

Materials and methods

Materials used

Ammonium bicarbonate, Iron(III) Chloride-6-Water, ethylene glycol, TEOS, APTES, chloridazon toxin, methanol, ammonia 25%, and toluene produces by Sigma Aldrich and Merck.

Apparatus

In this study, data from a high-performance liquid chromatographic instrument of the German KNAUER Smartline model, fitted with a four-solvent pump, manual injection with a loop volume of 20 μ L, and a column filled with polymer C18 (240 x 0.6 mm), were analyzed. Additionally, a UV-Vis detector with an adjustable wavelength range of 200 to 400 nm was utilized, namely the SV-2600UV. Starting at 0.2 mL/min to wash the column, the flow rate increased steadily to 0.5 mL/min, then to 0.7 mL/min, and finally was set at 1 mL/min.

A mixed mobile water phase (0.05% by volume of acetic acid)/acetonitrile with a volume ratio of 50:50 V/V and a flow rate of 1 mL per minute was

used to run samples extracted in the same volume through the C18 column. The UV-Vis detector detected them at 240 nm at a temperature of 20 °C. The injection volume was 20 μ L, and the peak appearance time was 5 minutes. The chromatogram and the region beneath the peak were both measured using the Cromgate software. Using a LEO 1430 VP scanning electron microscope, material morphology was documented. German-made Bruker Tensor model 27 infrared spectroscopy was utilized to further demonstrate the production and analysis of the chemical structure of the drug.

Synthesis of FeO_x/EG nanosheets

The composition of FeO_x/EG was synthesized according to the method reported by Zhao et al [17]. In this way, we added 1 g of six-water chloride iron salt and 4 g of ammonium bicarbonate to 60 mL of ethylene glycol, then stirred it for half an hour. The mixture was then transferred to a Teflon autoclave and placed at 185 ° C for 40 hours. After the reaction was complete, the resulting product was filtered, distilled twice with water and washed with methanol, and finally dried at 60 ° C.

Covering FeO_x/EG nanosheets with silica (Nanocomposite/ SiO_2 FeO_x/EG)

The coating of FeO_x/EG nanosheets with silica was performed with a solvothermal reaction. Nanosheets (0.15 g) were dispersed in a solution of ethanol (80 mL), deionized water (20 mL) and aqueous ammonia solution (25%). The mixture was subjected to ultrasonic for 15 minutes, followed by 0.35 mL of TEOS and dried under vacuum.

Surface modification (nanocomposite/ SiO_2 FeO_x/EG) with nitrogenous functional groups

About 0.1 g of nanocomposite/ SiO_2 FeO_x/EG was poured into 15 mL of dry toluene, the resulting suspension was subjected to ultrasonic for 30 min. After adding APTES (1 mL), the mixture was subjected to a nitrogen gas atmosphere at 120 ° C for 24 hours. The resulting product was washed with dry toluene and acetone and dried under vacuum, respectively, and the resulting nanocomposite was named NH_2/SiO_2 FeO_x/EG .

Preparation of standard solutions

The mother solution was created by dissolving 0.01 g of chloridazon toxin in 10 mL of methanol to create a solution with a concentration of 1000 μ g.mL⁻¹. The working solutions were created

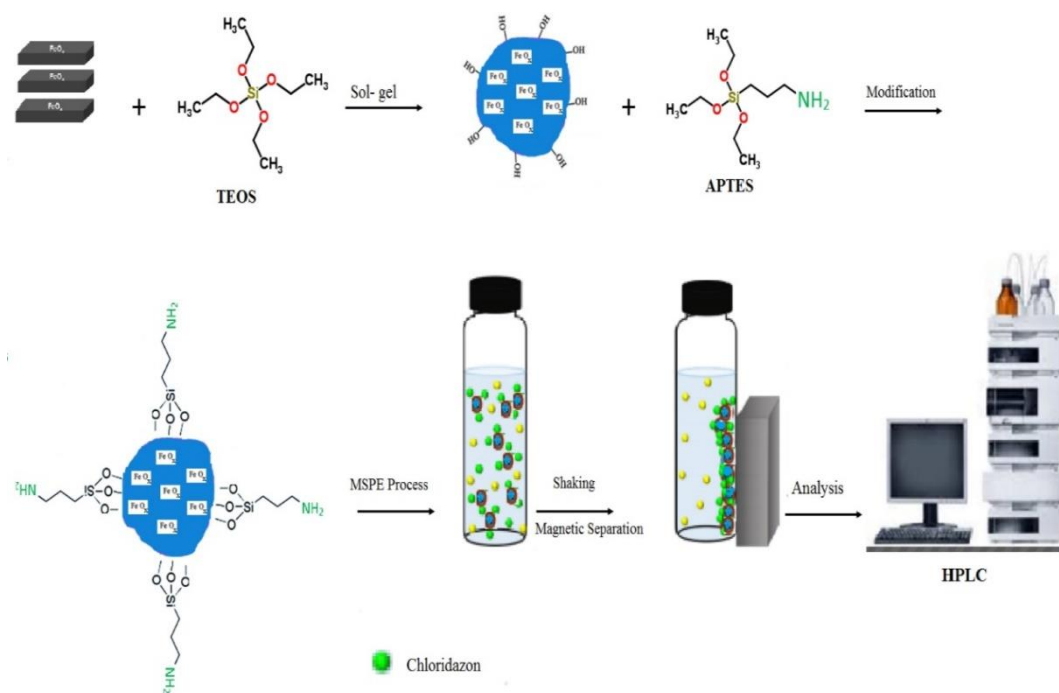


Fig. 1. Schematic representation of synthesis FeO_x/EG/SiO₂/NH₂ nanocomposite for extraction of Chloridazon.

by daily adding the required amounts of water. Analyses were performed on the prepared mother solution with a final concentration of 1 µg.mL⁻¹ in the solution (water). To keep the chloridazon from degrading, it was stored in a dark area at 4 °C.

Magnetic solid-phase extraction process (MSPE)

In this method, 2 mg of the adsorbent was poured into a 15 mL laboratory tube, and then the adsorbent was activated by 0.3 mL of methanol and 2 mL of deionized distilled water, respectively. The activated adsorbent was transferred to a 250 mL beaker and 50 mL of the sample solution was added to it. After shaking for 5 minutes, the adsorbent was collected by a magnet at the bottom of the beaker and the upper solution was discarded. Finally, by collecting the adsorbent at the bottom of the container by a magnet, the analyte washing solution was separated from the container and injected into the HPLC-UV device and the analysis data were obtained.

The schematic representation of the synthesis of FeO_x/EG/SiO₂/NH₂ nanocomposite for extraction of Chloridazon is shown in Fig. 1.

RESULT AND DISCUSSION

The identification of the synthesized sample

was performed by FT-IR, SEM, XRD, TGA, and VSM techniques.

Study of the structure and morphology of nanocomposite NH₂/SiO₂/FeO_x/EG using SEM images

Figs. 2a and 2b show the scanning electron microscopy images of FeO_x/EG and nanocomposite FeO_x/EG/SiO₂/NH₂, respectively.

Investigation of FT-IR spectrum related to FeO_x/EG and FeO_x/EG/SiO₂/NH₂ nanocomposite

Fig. 3 illustrates the FT-IR peaks associated with the FeO_x/EG pure nanocomposite observed in the 1629 cm⁻¹ peak associated with the vibration of water-absorbing mesoporous-OH groups and hydroxyl groups of the synthesized material structure. In addition, the peaks of 1094 cm⁻¹ are related to the asymmetric tensile vibrations of Si-O-Si and the peaks of 806 cm⁻¹ are attributed to the symmetrical stretching of Si-O-Si. Si-O-Si bending vibrations are also observed in 461 cm⁻¹ area [18].

Investigation of VSM spectrum of nanocomposite FeO_x/EG and FeO_x/EG/SiO₂/NH₂

Fig. 4 shows the magnetic properties of the nanocomposite. As can be seen from this figure, the S-shaped magnetic waste ring indicates the

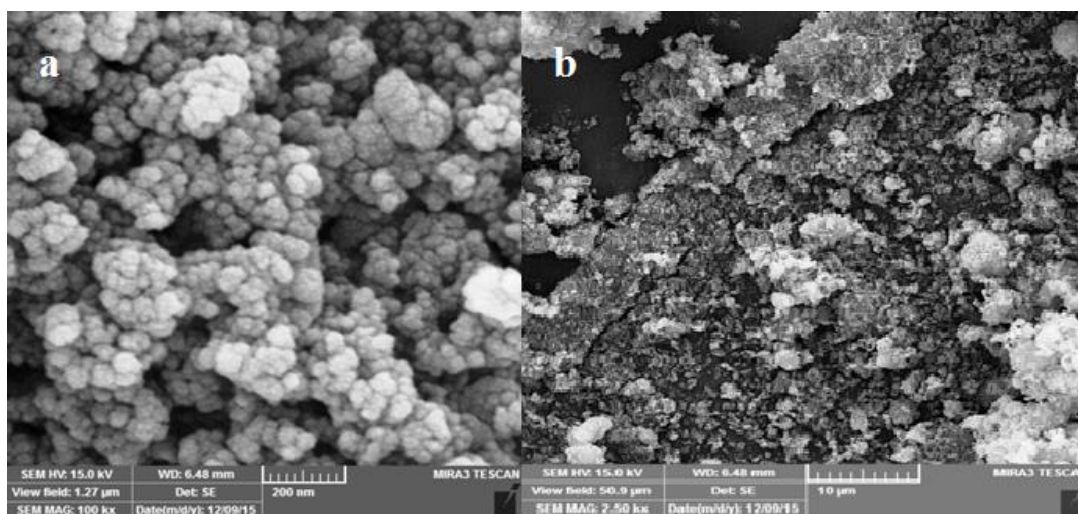


Fig. 2. SEM image of FeO_x\EG and FeO_x\EG\SiO₂\NH₂ nanocomposite.

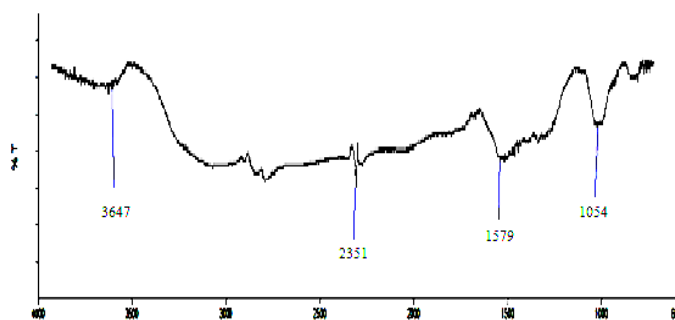


Fig. 3. FT-IR spectrum of the synthesized FeO_x\EG\SiO₂\NH₂ nanocomposite.

magnetic property of the composition, which is equal to $M_s = 20$ emu/g. The residual or residual magnetism in the absence of an external magnetic field is close to zero, so the composite exhibits the behavior of a super-para-magnet [18,19].

Optimization of MSPE solid phase extraction method

To evaluate the ability and efficiency of FeO_x\EG\SiO₂\NH₂ nanocomposite, it was used as a test solution in the process of extraction with a solid magnetic phase of chloridazon toxin. In this work, several parameters such as adsorbent value, sample solution volume, solvent, and adsorbent volume, solvent type adsorbent, ionic strength, extraction time, adsorbent time, and pH of the solution for synthesized adsorbent were investigated and optimized. The parameters were analyzed in each experiment with 100 mg / L of chloridazon toxin solution in twice distilled water. The subunit of chromatograms was measured to assess the factors affecting the efficiency of analyte extraction.

The amount of adsorbent

To study the effect of the adsorbent on chloridazon herbicide extraction, different values of the adsorbent (10, 20, 30, 40, and 50 mg) were investigated. First, 50 mL of the sample solution was transferred to the beaker and 10 mg of the adsorbent was added to the sample solution after activation, and the mixture was shaken for 5 min. After completing the extraction process, by placing the beaker on the magnet, the adsorbent was separated from the sample solution in less than one minute. After separating the topical solution, chloridazon was dissolved with 1 mL of methanol solvent and adsorbent from the adsorbent surface, and 20 μL of the final solution was injected into the high-performance liquid chromatography machine for analysis. Higher adsorbent values were similarly investigated. As can be seen from Fig. 5, as the adsorbent value increases, more adsorption, and pre-condensation absorption is evident. However, beyond 30 mg, a small increase in the area under

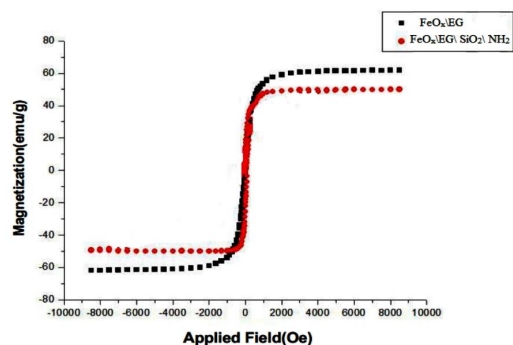


Fig. 4. Magnetic curve FeO_x/EG and FeO_x/EG/SiO₂/NH₂ nanocomposite.

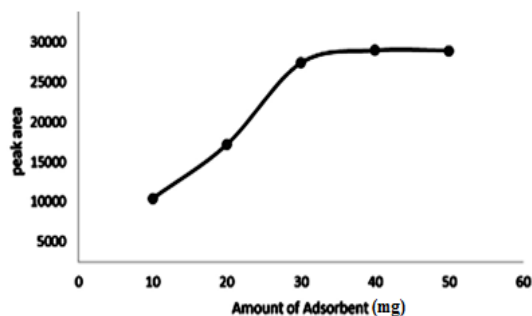


Fig. 5. Curve of changes in the area of the analysis peak based on changes in the amount of adsorbent.

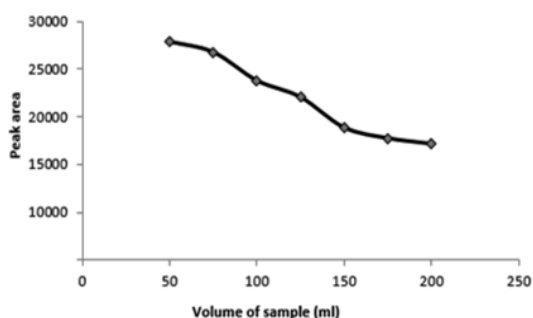


Fig. 6. Diagram of changes in analyte peak area in terms of sample solution volume changes.

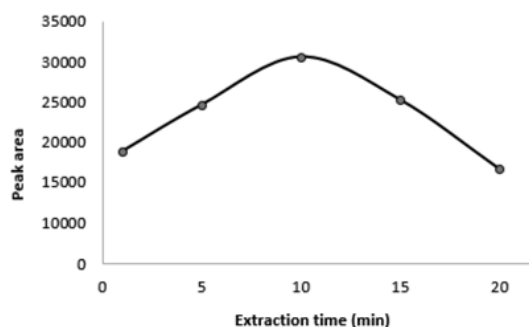


Fig. 7. Analyte peak area of the curve in terms of changes in extraction time.

the peak is not observed. Thus, 30 mg was chosen as the optimal amount.

Sample volume solution

To achieve more reliable and effective pre-concentration extraction with low operating time, the effect of sample solution volume with a series of different water volumes (50, 75, 100, 125, 150, 175, and 200 mL) was examined. As can be seen from Fig. 6, the extraction efficiency is observed by decreasing the area under the peak at higher values. Therefore, the volume of 50 mL was selected as the optimal volume.

Extraction time

To study the effect of extraction time on the yield of chloridazon toxin extraction, the extraction time was changed within the range of 1 to 20 min. Between the 1st to 10th minute, the curve is almost upward, indicating that the absorption of the analyte was high during these times. However, after 10 minutes, the extraction efficiency began to decrease. Thus, a 5-minute duration was chosen as the optimal time (Fig. 7).

Elution time

The time-absorbing time graph was obtained by increasing the time period from 1 to 5 minutes. The results demonstrated that time has no significant effect on the yield of poison extraction, and the amount of extracted toxin remained almost constant with increasing the absorption time. Fig. 8 illustrates that 1 minute is sufficient for adsorption to remove chloridazon toxin from the adsorbent.

Type of solvent and adsorbent

Choosing the right type of solvent and adsorbent is one of the most important factors in the mineral analysis. An appropriate solvent can effectively and adsorb the adsorbed analyte. Therefore, for this purpose, five solvents of strontium, methanol, chloroform, and acetone were used in this experiment. Among these solvents, methanol was utilized as the optimal solvent for subsequent experiments (Fig. 9).

Soluble and absorbable volume

To achieve high concentration factors, it is important to find the minimum required volume of solvent and adsorbent from the surface of

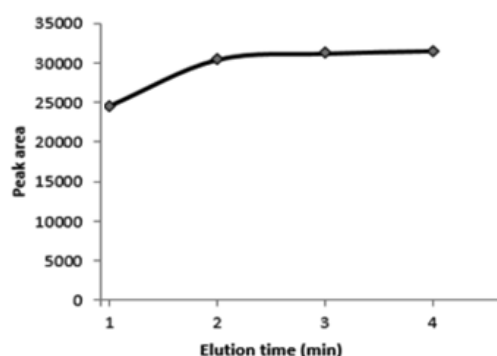


Fig. 8. Curve changes the area of the peak analysis in terms of absorption time changes.

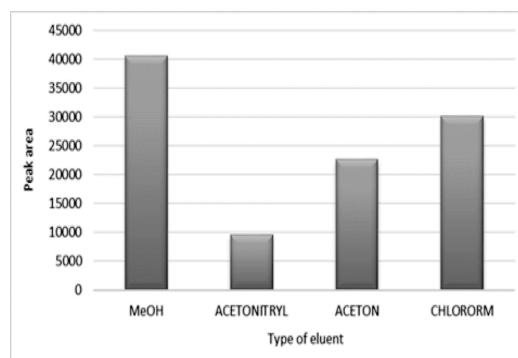


Fig. 9. Analyte peak area of the curve in terms of changes desorption solvent.

Table 1: Data from extraction Chloridazon with $\text{FeO}_x/\text{EG}/\text{SiO}_2/\text{NH}_2$ in optimum condition.

Compound	Current method			
	DLR ^a	(R ²) ^b	LOD ^c	%RSD ^d
Chloridazon	0.01-100	0.998	0.001	3.017

^aDynamic Linear Rang (μgml^{-1}).

^bRegression coefficient

^cLimit of detection calculated as three times the baseline noise (μgml^{-1}).

^dRelative Standard Deviation

magnetic nanoparticles. For this purpose, the volume of methanol was investigated as soluble and absorbable with the volumes of 1, 1.5, 2, and 2.5 mL. According to the results shown in Fig. 10, the volume of solvent and adsorbent volume does not have a significant effect on analytical extraction; therefore, the amount of volume of 1 mL was selected as the optimal solvent and adsorbent.

Ionic power

To investigate the effect of salt effect on extraction efficiency, chloridazon solutions containing NaCl salt with a concentration of 0-0.5% by weight-volume were prepared. Fig. 11 shows that the extraction efficiency increases with increasing NaCl concentration to 1% but then decreases to 5% salt concentration in the sub-peak surface curve. The best extraction was obtained when the sample solution containing 1% salt. Therefore, further studies were performed with 1% NaCl concentration.

pH

The pH of the sample solution is one of the important factors in the transfer of analytes from the sample solution to the adsorbent and plays an important role in the pre-concentration of chloridazon herbicide. By examining the pH

of the solution, Therefore, the effect of pH was investigated by adding HCl or NaOH in the range of 2-8. As can be seen, the area under the peak has the highest value at pH = 5, and as the pH increases, the area under the peak declines. Therefore, pH = 5 was considered the optimal pH in subsequent experiments (Fig. 12).

Quantitative studies and analysis of real samples

Under optimal conditions, the magnetic phase extraction method was evaluated by testing the analytical parameters of chloridazon toxin in the sample. The results of the study are given in Table 1. For the toxin in question, by absorbing the nanocomposite $\text{FeO}_x/\text{EG}/\text{SiO}_2/\text{NH}_2$, the detection limit was calculated based on the signal-to-noise ratio = 3, which was $0.001 \mu\text{gml}^{-1}$ (Table 1). The linear range of this method was tested by extracting different water standards by increasing the concentration. With the desired adsorbent, this method obtained a good linear range with a correlation coefficient of 0.998. The accuracy of the method was determined by repeating the extraction to 3 times of aqueous solutions with a concentration of $1 \mu\text{gml}^{-1}$ under optimal conditions which illustrates its valid repeatability. Relative standard deviation using $\text{FeO}_x/\text{EG}/\text{SiO}_2/\text{NH}_2$ nanocomposite adsorbent (RSD%) 3.017% obtained shows that the

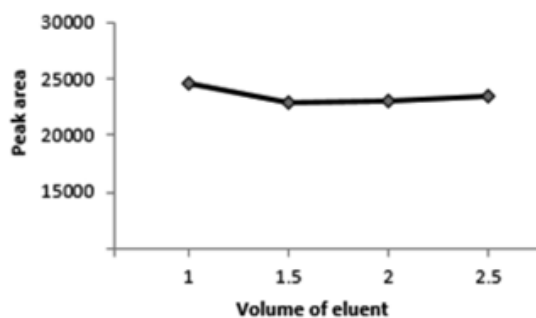


Fig. 10. Changes in the analyte peak area in terms of adsorbent volume changes.

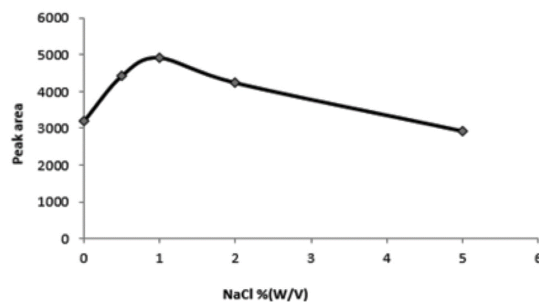


Fig. 11. Changes in the analyte peak area in terms of changes in salt concentration.

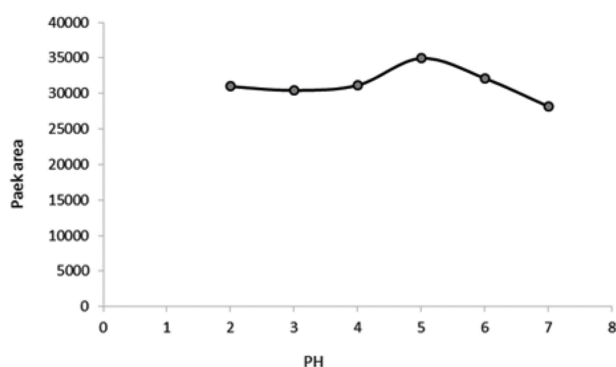


Fig. 12. Changes in the analyte peak area according to the pH of the solution.

absorbent has good reproducibility.

In comparison to other methods in literature data for extraction and determination of chloridazon, the proposed method demonstrates a better limit of detection (Table 1).

CONCLUSION

The prepared nanocomposite was successfully used in the pre-condensation process of chloridazon toxin in water. The method used has a valid linear range, repeatability, and high sensitivity. This proposed method can be applied to other studies of low-concentration water-soil molecular mold polymers. The results indicate that the prepared nanocomposite adsorbent has a high extraction power. Advanced adsorption properties due to its composite properties include high surface area and uniform dispersion of $\text{FeOx}\backslash\text{EG}\backslash\text{SiO}_2\backslash\text{NH}_2$.

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

REFERENCES

1. Abolghasemi MM, Piryaei M. Head space solid phase microextraction of 15 pesticides in water samples using MnO_2 nanowires decorate on graphenized pencil lead fiber.

Separation Science and Technology. 2022;57(3):419-25. <https://doi.org/10.1080/01496395.2021.1901743>

2. Babashpour-Asl M, Piryaei M. Analysis of Grammosciadium platycarpum Boiss. & Hausskn. Essential Oil Using of Three Dimensional Nanocomposite Based on MgAl Layered Double Hydroxide as a Fiber Coating of SPME. Journal of Medicinal plants and By-product. 2021;10(2):161-7.
3. Wang S, Kirillova K, Lehto X. Travelers' food experience sharing on social network sites. Journal of Travel & Tourism Marketing. 2017;34(5):680-93. <https://doi.org/10.1080/10548408.2016.1224751>
4. Piryaei M, Amirifard H. Synthesis Nanostructure $\text{MnMoO}_4/\text{NiCo}_2\text{O}_4$ on Graphenized Pencil Lead as Solid Phase Microextraction Fiber for Measurement of Environmental Pollutants in Surface Waters Samples. Polycyclic Aromatic Compounds.1-17. <https://doi.org/10.1080/10406638.2023.2182797>
5. Kassae MZ, Motamedi E, Majdi M. Magnetic Fe_3O_4 -graphene oxide/polystyrene: Fabrication and characterization of a promising nanocomposite. Chemical Engineering Journal. 2011;172(1):540-9. <https://doi.org/10.1016/j.cej.2011.05.093>
6. Bianchi F, Chiesi V, Casoli F, Luches P, Nasi L, Careri M, et al. Magnetic solid-phase extraction based on diphenyl functionalization of Fe_3O_4 magnetic nanoparticles for the determination of polycyclic aromatic hydrocarbons in urine samples. Journal of Chromatography A. 2012;1231:8-15. <https://doi.org/10.1016/j.chroma.2012.02.015>
7. Zhang S, Niu H, Hu Z, Cai Y, Shi Y. Preparation of carbon coated Fe_3O_4 nanoparticles and their application

- for solid-phase extraction of polycyclic aromatic hydrocarbons from environmental water samples. *Journal of Chromatography A*. 2010;1217(29):4757-64. <https://doi.org/10.1016/j.chroma.2010.05.035>
8. Abolghasemi MM, Piryaei M, Amirifard H. Hierarchically Synthesis of Nanoflower Layered Double Hydroxide/ Molybdenum Disulfide on Electrochemically Anodized HB Pencil Lead for Determination Trace Amounts of Polycyclic Aromatic Hydrocarbons. *Polycyclic Aromatic Compounds*. 2022;42(7):4078-85. <https://doi.org/10.1080/10406638.2021.1881571>
 9. Li F, Li X, Cui P. RETRACTED: Adsorption of U(VI) on magnetic iron oxide/Paecilomyces catenannulatus composites. *Journal of Molecular Liquids*. 2018;252:52-7. <https://doi.org/10.1016/j.molliq.2017.12.136>
 10. Liu X, Han Y, Cheng Y, Xu G. Microwave-assisted ammonia modification of activated carbon for effective removal of phenol from wastewater: DFT and experiment study. *Applied Surface Science*. 2020;518:146258. <https://doi.org/10.1016/j.apsusc.2020.146258>
 11. Xiao J, Song W, Hu R, Chen L, Tian X. One-Step Arc-Produced Amino-Functionalized Graphite-Encapsulated Magnetic Nanoparticles for the Efficient Removal of Radionuclides. *ACS Applied Nano Materials*. 2019;2(1):385-94. <https://doi.org/10.1021/acsanm.8b01970>
 12. Ding C, Cheng W, Nie X, Niu Z, Duan T, Zhang Y, et al. Spectroscopic and theoretical investigation on efficient removal of U(VI) by amine-containing polymers. *Chemical Engineering Journal*. 2019;367:94-101. <https://doi.org/10.1016/j.cej.2019.02.142>
 13. Xiong J-Q, Kim S-J, Kurade MB, Govindwar S, Abou-Shanab RAI, Kim J-R, et al. Combined effects of sulfamethazine and sulfamethoxazole on a freshwater microalga, *Scenedesmus obliquus*: toxicity, biodegradation, and metabolic fate. *Journal of Hazardous Materials*. 2019;370:138-46. <https://doi.org/10.1016/j.jhazmat.2018.07.049>
 14. Chen Y, Li J, Yuan Z, Feng J, Chen Z. Metabolic fate and subchronic biological effects of core-shell structured Fe₃O₄@SiO₂-NH₂ nanoparticles. *Nanotoxicology*. 2018;12(6):621-36. <https://doi.org/10.1080/17435390.2018.1471537>
 15. Ghasemzadeh MA, Abdollahi-Basir MH, Babaei M. Fe₃O₄@SiO₂-NH₂ core-shell nanocomposite as an efficient and green catalyst for the multi-component synthesis of highly substituted chromeno[2,3-b]pyridines in aqueous ethanol media. *Green Chemistry Letters and Reviews*. 2015;8(3-4):40-9. <https://doi.org/10.1080/17518253.2015.1107139>
 16. Li J, Yuan Z, Liu H, Feng J, Chen Z. Size-dependent tissue-specific biological effects of core-shell structured Fe₃O₄@SiO₂-NH₂ nanoparticles. *Journal of Nanobiotechnology*. 2019;17(1):124. <https://doi.org/10.1186/s12951-019-0561-4>
 17. Zhao Y, Truhlar DG. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theoretical Chemistry Accounts*. 2008;120(1):215-41. <https://doi.org/10.1007/s00214-007-0310-x>
 18. Zhu L, Zeng X, Li X, Yang B, Yu R. Hydrothermal synthesis of magnetic Fe₃O₄/graphene composites with good electromagnetic microwave absorbing performances. *Journal of Magnetism and Magnetic Materials*. 2017;426:114-20. <https://doi.org/10.1016/j.jmmm.2016.11.063>
 19. Zhang Y, Jiao Z, Hu Y, Lv S, Fan H, Zeng Y, et al. Removal of tetracycline and oxytetracycline from water by magnetic Fe₃O₄@graphene. *Environmental Science and Pollution Research*. 2017;24(3):2987-95. <https://doi.org/10.1007/s11356-016-7964-7>