Piperazine-modified magnetic graphene oxide (Pip@MGO) as a novel nanocomposite for the effective removal of lead ions; using RSM optimization

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Research Article

Keywords: Removal of Pb(II), Nanocomposite, Response surface method, Isotherms, Water treatment

Posted Date: March 7th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1388276/v1>

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Piperazine-modified magnetic graphene oxide (Pip@MGO) as a novel nanocomposite for the effective removal of lead ions; using RSM optimization

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Abstract

In this research, the piperazine-modified magnetic graphene oxide (Pip@MGO) nanocomposite was synthesized and utilized as a nano-adsorbent for the removal of Pb(II) ions from environmental water and wastewater samples. The physicochemical properties of Pip@MGO nanocomposite was characterized by XRD, FESEM, TEM, EDX, TGA, VSM and FT-IR analysis. In this method, the batch removal process were designed by response surface methodology (RSM) based on a central composite design (CCD) model. The results indicated that the highest efficiency of Pb(II) removal was obtained from the quadratic model under optimum conditions of prominent parameters (initial pH: 6.0, adsorbent dosage: 7 mg, initial concentration of lead: 15 mg L⁻¹ and contact time: 27.5 min). Adsorption data showed that lead ions uptake on Pip@MGO nanocomposite followed the Langmuir isotherm model equation and pseudo-second order kinetic model. High adsorption capacity (558.2 mg g⁻¹) and easy magnetic separation capability showed that the synthesized Pip@MGO nanocomposite has great potential in removal of Pb(II) ions from contaminated wastewaters.

Keywords: Removal of Pb(II); Nanocomposite; Response surface method; Isotherms; Water treatment

1. Introduction

Disposal of industrial effluents and wastewaters is considered as one of the most important challenges in the industrial world today. Due to the toxic ingredients of these effluents such as, heavy metal ions and dyes, they are the main cause of pollution of rivers, lakes and underground waters ^{1,2}. Unlike organic pollutants, heavy metal ions are not only degradable or decomposable but also can accumulate in biotic and abiotic systems through the food chain, drinking water and air, resulting in serious damage to the environment and human safety ³. The most notorious heavy metals that cause significant environmental pollution are lead, chromium, mercury, cadmium, arsenic, zinc, copper, and nickel. The concentration of some of them have reached dangerous levels both for the environment and humans. Accordingly, reduction of such pollutants is one of the most significant step in wastewater treatment ⁴. Among the various toxic metal ions, lead is a highly toxic pollutant that is released into the environment due to industrial activities, including mining, plating, battery production, metal smelting, oil refining, printing, and so on. Accumulation of Pb(II) ions in the human body lead to various health consequences, such as: anorexia, gastrointestinal colic, anemia, neurasthenia, kidney and liver damage, and even cancer ⁵. Therefore, in order to environmental clean-up, it is absolutely essential to design appropriate technologies and prepare effective materials for complete removal or reduction of Pb^{2+} ions to an acceptable level, before discharge ⁶.

There are many traditional methods for removing lead, including ions exchange, chemical precipitation, electrodeposition, membrane filtration and reverse osmosis ⁷. However, these techniques usually suffer from some limitations including complexity and high cost of their operation, potential secondary pollution, difficulty in recycling and poor efficiency in low concentration of lead ^{8,9}. Among the various treatment technologies, adsorption is currently preferred as a non-hazardous method for the removal of heavy metal due to its cheapness, selectivity, high efficiency, simple processes, reusability, flexibility in design and availability

of different adsorbents ¹⁰. Generally, an ideal adsorbent should have a high surface area and also adsorption sites, so that the adsorption process takes place in a short equilibrium time ^{10,11}.

In the last two decades, by the development of novel nanotechnologies and the advent of nanomaterials, scientists have been attracted to this field and various novel adsorbents have been emerged ¹². Due to various advantageous in which appears by reducing the size of the adsorbent to nanometers and increasing the surface area and thus increasing the activities sites, the adsorption capacity of these materials increases significantly ^{13,14}.

Recently, graphene oxide (GO) as a single-layered two-dimensional (2D) nanomaterial has aroused great interest between analytical chemists due to large surface area, high mobility and good conductivity. GO has been extensively used as an adsorbent in solid phase extraction of various organic and inorganic contaminants ¹⁵. However, the dispersion of GO nanosheets is very high and their separation from the solution medium is very difficult and also time consuming. In order to facilitate separation after the adsorption process, the creation of magnetic properties through the fabrication of magnetic graphene nanocomposites is recommended ¹⁵⁻¹⁹. Generally, Fe₃O₄ magnetic nanoparticles have been widely used in the construction of nanocomposite adsorbents in magnetic SPE techniques due to their simplicity in synthesis and ease of application ²⁰⁻²³, but pure Fe₃O₄ nanoparticles are rapidly oxidized in the atmosphere and are not suitable for efficient adsorption in complicated matrices. In order to overcome these limitations and enhance the applicability of these types of adsorbents in real wastewater, the Fe₃O₄ surface must be functionalized by a modifier with appropriate functional groups ^{7,24}. Hence, by designing a solid hybrid of magnetic graphene oxide (MGO) with suitable modifier, a good adsorbent can be prepared to remove pollutants.

The main objective of this work is the evaluation of piperazine-functionalized magnetic graphene oxide (Pip@MGO) nanocomposite for the removal of Pb(II) from the aqueous environment. The fabricated Pip@MGO nanocomposite was characterized by XRD, FESEM,

TEM, EDX, TGA, VSM and FT-IR analysis. The most significant parameters in the removal efficiency, including solution pH, initial lead concentration, adsorbent dosage, and contact time, were considered and the optimal values of these variables were evaluated by a statistical approach using response surface methodology (RSM) based on a central composite design (CCD) model. In addition, the isotherm modelling and kinetics parameters were studied to understand the mechanism of adsorption of Pb^{2+} ions on Pip@MGO adsorbent.

2. Experimental

2.1. Reagents

All reagents and chemicals used in this work were of analytical grade, without further purification, and ultrapure distilled water was used in the experiments. The chemicals including, graphite powder, iron(III) chloride hexahydrate, iron(II) chloride tetrahydrate, 3-chloropropyltriethoxysilane, piperazine anhydrous, potassium permanganate, hydrogen peroxide (30 %), sulfuric acid (98 %), hydrochloric acid (37 %), sodium hydroxide, toluene and ethanol were purchased (Merck, Darmstadt, Germany). A stock solution of 1000 mg L^{-1} of Pb^{2+} was prepared by dissolving 0.159 g of $\text{Pb}(\text{NO}_3)_2$ (Merck, Darmstadt, Germany) in 10 mL of concentrated HNO_3 and diluted to 100 mL in a volumetric flask. The working solutions were prepared daily with suitable dilution of this stock solution. The solutions of nitric acid and sodium hydroxide (in the concentration range of 0.01-1.0 M) were used to adjust the pH.

2.2. Apparatus and instruments

A flame atomic absorption spectrometer from GBC Company (Sidney, Australia), Model Savanta, equipped with a deuterium lamp and hollow-cathode lamp was used for determination of lead. Morphology of the synthesized nanocomposite adsorbent was characterized with a by field emission scanning electron microscopy (FESEM, TESCAN, MIRA III, Czech Republic)

instrument. In addition, EDX (energy dispersive spectrometer) and (EMA) element mapping analysis for the surface components of the samples were analysed using EDX-MAP (FESEM, TESCAN, MIRA III, Czech Republic). The structure and size of prepared Pip@MGO was investigated by a transmission electron microscope (JEM-1011, Japan TEM, Zeiss-EM10C-80 KV). FT-IR spectra was recorded with a Fourier Transform Infrared spectrometer (Thermo Nicolet, AVATAR, USA) at room temperature in KBr pellets. Magnetic properties of produced nanocomposite were obtained by a vibrating sample magnetometer (VSM, Meghnatis Daghigh Kavir Co., Kashan, Iran). Thermogravimetric Analysis (TGA) was done using a TA Instruments analyzer (Q600, USA) by scanning to 800 °C with a heating rate of 10 °C min⁻¹. An ultrasonic water bath (ALEX, power 170 W and frequency 32 kHz) was applied to disperse the of Pip@MGO nanocomposite adsorbent in the aqueous solutions. The pH adjustment of sample solutions were done with a Metrohm digital pH meter (632 moled, Switzerland, Swiss) with a combined glass electrode.

2.3. Synthesis of Pip@MGO nanocomposite

2.3.1 Preparation of Graphene Oxide (GO)

Graphene Oxide (GO) was prepared according to Hummers' method with some modifications. Accordingly, 1.0 g of graphite powder was added to 50 mL of H₂SO₄ (98%) in an ice bath. Afterwards, KMnO₄ (2 g) was added slowly. The addition should be in a way that the temperature does not exceed abruptly. After 2 hours of stirring below 10 °C, and 1 hour at 35 °C; 50 mL of deionized water was added. The mixture is heated at 85 °C for 1 hour. Then 10 mL of H₂O₂ (30%) was added in which the solution turned bright yellow. The mixture was filtered and was washed with HCl (5%) and deionized water for several times. Finally the obtained GO was dried at 60 °C in oven for 24 hours ²⁵.

2.3.2 Preparation of Magnetic Graphene Oxide (MGO)

In a 250 mL round-bottom flask, 0.5 g of GO was added to deionized water (100 mL) and it was sonicated for 15 minutes. Subsequently, in another flask, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1 g) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.4 g) were mixed totally in deionized water (50 mL), for 1 hour at 80 °C. The flask containing GO was added to the solution of Fe(III)/Fe(II) and then sonicated for 30 minutes in sonication bath. The mixture was heated to 80 °C and after 30 minutes, 15 mL of ammonia (30%) was added to it, resulted in MGO. The mixture was stirred for another 30 minutes and MGO was separated with an external magnet. The MGO was washed several times with deionized water and finally the obtained MGO was dried at 60 °C in oven for 24 hours.

2.3.3 Preparation of piperazine modified Magnetic Graphene Oxide (Pip@MGO)

In a 100 mL round bottom flask, 0.5 g of MGO was added to 50 ml of toluene and the mixture was sonicated for 15 minutes. In another flask, 3-chloropropyltriethoxysilane (1 mmol, 0.24 g) and piperazine (1 mmol, 0.09 g) was premixed in 20 mL of toluene for 1 hour at room-temperature. The latter flask was added to MGO containing flask and the mixture was refluxed for 24 hours. Afterwards, Pip@MGO was separated with an external magnet and it was washed several times with ethanol. Finally, the collected Pip@MGO nanocomposite was dried at 60 °C in oven for 24 hours and stored.

2.4. Collection of real samples

Four water samples including river water of Arvand Rud and Bahmanshir (Khuzestan Province, southwest of Iran), Persian Gulf seawater (Mahshahr, Khuzestan Province, Iran) and petrochemical wastewater sample (Abadan Petrochemical Company, Khuzestan Province, Iran) were collected in amber glass containers, which were previously pre-cleaned and acid-

washed, and filtered through filter paper (Whatman, No. 1 Quantitative Filter Papers, 110 mm). Then, the treated samples were stored at 4°C in the dark until analysis.

2.5. General procedures

In order to adsorb of Pb(II) ions on the Pip@MGO nanocomposite, a batch method was used. According to response surface methodology, 30 experiments were done and the influence of effective parameters, including solution pH, initial concentration of Pb(II), adsorbent dosage and contact time were investigated on the lead removal efficiency. Briefly, 10 mL of solution containing different concentrations of lead at a given pH (in the range of 5-7) was transferred to the test tubes and the known weight of adsorbent was added and sonicated in an ultrasonic bath for 2 min, then shaken (at 200 rpm) for a certain period of time, using an incubator shaker. After contact time, the liquid and solid phases were separated by an external magnet and the residual Pb²⁺ concentration was measured by FAAS. The removal percentage (% R) and adsorption capacity of Pb(II) ions (q_e ; mg g⁻¹) were determined by the Eqs. (1) & (2):

$$\% R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e) V}{M} \quad (2)$$

where C_0 is initial and C_e is the final concentration of Pb(II) ions (mg L⁻¹), V (L) is the volume of solution and M (mg) is the mass of adsorbent.

2.6. Experimental design

Response surface methodology (RSM) is a well-known and useful method that is widely used to optimize adsorption techniques and experimental design, modeling in chemical reactions and industrial processes²⁶. In this work, the central composite design (CCD) under RSM was applied for designing the experiments. Therefore, the effect of four independent variables,

including pH (in the range of 5-7), initial concentration of lead (in the range of 5-25 mg L⁻¹), adsorbent dosage (in the range of 1-13 mg) and contact time (in the range of 2.5-52.5 min) on the Pb(II) removal efficiency (% R) were investigated. The statistical software Design Expert (Version 11.0.3.0), Stat-Ease, Inc. was applied to analyze the experimental data. As shown in Table 1, for four independent factors at 5 levels ($-\alpha$, -1, 0, 1, $+\alpha$) thirty runs were designed, including six repeated runs for a central point, eight axial runs and 16 full factorial runs.

In this study, the proposed model was determined and confirmed by analysis of variance (ANOVA). In addition, R^2 , predicted R^2 , adjusted R^2 and F-test values were performed to evaluate and express the quality of the produced models.

3. Results and discussion

3.1. Characterization studies

In the FT-IR spectrum of the Pip@MGO (Fig. 1(a)), the stretching vibration of C-H bonds of the graphene oxide (GO) is apparent in the 2928 cm⁻¹. The hydroxyl groups and also carboxylic groups on the surface of the GO is obvious at 3443 cm⁻¹. It should be mentioned that the F-O vibration is also seen at 580 cm⁻¹. The stretching vibration of C=C bonds of GO is apparent at 1635 cm⁻¹. The CH₂ bending vibration is located at 1456 cm⁻¹ which can be attributed to the methylene groups of piperazine and also the propyl silane linker. The Si-O vibration of the silane linker appear about 462, 1040 and 1117 cm⁻¹.

Thermogravimetric analysis (TGA) diagram of Pip@MGO is presented in Fig. 1(b). The first weight loss from room-temperature to 250 °C is due to the removal of adsorbed moisture entrapped physically in the nanocomposite. The second weight loss occurs from 250-800°C which can be attributed to the breakdown of organic moieties from the nanocomposite. According to Fig. 1(c), the XRD pattern of the nanocomposite clearly shows the characteristic

2 θ peaks of Fe₃O₄ at 30.2°, 35.52°, 43.5°, 54, 57° and 63° are attributed to the crystal planes of magnetite at 220, 311, 400, 422, 511 and 440, respectively ²⁷.

The VSM curve of produced adsorbent is presented in Fig. 1(d). The results demonstrate that the nanocomposite contains magnetite nanoparticles which are super paramagnetic and the highest saturation magnetization is at 27.9 emu/g. It is apparent from the magnetization that the nanocomposite is sufficiently magnetic to be easily separable via an external magnet.

The SEM images of the nanocomposite at two different magnifications has been recorded. According to the Fig. 2, the layered character of the graphene oxide and also the magnetite nanoparticles are easily observed. The nanoparticles are agglomerated to some extent, but they have been distributed on the whole surface of the graphene oxide. In addition, Fig. 3(a) shows the distribution of elements in the specified area by EDX mapping. It can be seen that nitrogen as a constituent of the piperazine group has been distributed uniformly all over the specific area which is an indication of the even functionalization of the whole surface without any accumulation. Fig. 3(b) illustrates the results of energy-dispersive X-ray spectrum (EDX) analysis of Pip@MGO. This data indicates the approximate chemical composition and confirms successful immobilization of piperazine which contains nitrogen. The iron is also present in the analysis due to the presence of Fe₃O₄ nanoparticles in the nanocomposite.

TEM images of the Pip@MGO nanocomposite is illustrated in Fig. 4. The layered 2D character of the graphene oxide is beautifully viewed in the TEM image which contains the magnetite nanoparticles located on its surface.

3.2. Optimization by RSM

To achieve maximum lead removal efficiency, the effect of four independent parameters including solution pH (A), Pb²⁺ concentration (B), adsorption dosage (C) and shaking time (D) was performed via RSM design based CCD experiments. According to the obtained data, the

quadratic model equation was used to describe the relationship between the removal efficiency (% R) and the effective parameters as well as the interaction of operating parameters. This model is expressed in according with equation 1 as follows, in terms of coded factors:

$$\begin{aligned} \% R = & +96.28 - 4.08 A - 4.037 B + 6.48 C + 12.99 D + 6.29 AC - 6.86 AD - 1.94 BD + 8.12 CD \\ & - 20.30 A^2 - 6.41 B^2 - 13.99 C^2 - 9.33 D^2 \end{aligned} \quad (1)$$

The ANOVA results for the removal efficiency of Pb(II) is summarized in Table 2. As shown, the F-value was 228.36 and p-value was less than 0.05 ($p < 0.0001$), therefore implies that the quadratic model was statistically significant. Based on this concept ($p < 0.05$) factors of A, B, C, D, AC, AD, BD, CD, A^2 , B^2 , C^2 and D^2 are significant model terms on removal efficiency of Pb(II) ions. In addition, the Lack of fit P-value (0.2516) represented the LOF is not significantly relative to the pure error. The fit of proposed model was evaluated using coefficient of determination R^2 (0.9938) and adjusted R^2 (0.9895), which indicate a good relationship between the actual (experimentally observed) values and values predicted by the model, and the predicted- R^2 (0.9777) showed that the model had a high potential to predict the response.

Three-dimensional (3D) surface plots, which obtained using the CCD design, are given in Fig. 2. By applying these 3D diagrams, the simultaneous effects of independent parameters and their interaction on the removal efficiency can be investigated.

The initial pH of lead ion solution is one of the significant factor affecting the removal efficiency. As can be seen from Fig. 5(a and b), the maximum removal efficiency of Pb(II) was achieved at pH 6.0. It can be explained that; at low pH values, due to presence of excessive amounts of H^+ ions in the lead solution, competition occurs in the active sites on the adsorbent surface and thus the removal efficiency decreased. However, at high pH values, despite the increase in de-protonation of adsorbent surface, Pb(II) ions are converted to hydroxide form and affect the absorption process, eventually reducing the removal efficiency. Fig. 5(a and d)

shows that increasing the adsorbent dose increases the removal of ions, because it increases the number of adsorbent active sites and enhances the distribution coefficient of Pb(II) solution ⁴. It is clear that, the optimum adsorbent dose for Pb²⁺ removal is in the range of 6-8 mg of Pip@MGO nanocomposite.

The results of Fig. 5(b and d) indicate that the removal efficiency increases with increasing contact time between lead ion and adsorbent, and after 25 minutes the removal percentage reaches more than 90 %. As it is observed in Fig. 5(c), the removal efficiency decreased on increasing lead (II) concentration. It can be said that at higher concentration levels, because the adsorbent active sites are saturated with lead ions, the adsorption did not changed and the adsorption performance is decreased. As a result of experimental investigations, in the concentration range of 14-16 mg L⁻¹ of Pb²⁺ and in the constant amount of adsorbent dosage, the removal process was reached to equilibrium.

The maximum removal efficiency of lead was obtained at the optimum value of each independent parameter determined by RSM. The optimal experimental conditions were pH, 6; initial concentration of Pb(II), 15 mg L⁻¹; adsorbent dosage, 7 mg; and contact time, 27.5 min. The desirability function value under the optimum conditions was found to be 1, which indicate the accuracy of the RSM divination.

3.3. Adsorption experiments study

In order to find the adsorption mechanism of lead ions on the Pip@MGO nanocomposite, the experimental data and homogeneity or heterogeneity of adsorbent were analysed by adsorption isothermal models. There are many isotherm models in the literature to describe the analyte adsorption on the adsorbents, however, in the present study, three conventional models including Freundlich, Langmuir and Temikin isotherm equations were used ²⁸. For this purpose, in batch mode; 0.01 g of Pip@MGO nanocomposite was added to 10 mL of

Pb²⁺ solution with initial concentrations range of 50- 600 mg L⁻¹, which was stabilized in pH=6.0, and shaken (200 rpm) for 60 min at 25 °C. Subsequently, the magnetic adsorbent was isolated and the lead equilibrium concentration of each experiment was determined by FAAS, and the experimental data were adjusted with the mentioned isotherm models.

In the Langmuir model, it is assumed that the adsorption is monolayer and occurs at a homogeneous surface, without interaction between the adsorbed materials ²⁹. The linearity of the Langmuir model is described by the equation (2) as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (2)$$

where, C_e (mg L⁻¹) and q_e (mg g⁻¹) are Pb(II) ion concentration and quantity of lead ions adsorbed onto the adsorbent surface at equilibrium, q_{max} (mg g⁻¹) is the maximum adsorption capacity and K_L (mL mg⁻¹) is the Langmuir adsorption equilibrium constant. q_{max} and K_L could be calculated with a straight line drawn from C_e/q_e versus C_e .

The Freundlich isotherm is not accept the capacity of one layer and is based on the assumption of adsorption on heterogeneous surfaces, due to the increase in the amount of analyte adsorbed in the solution ³⁰. This model is linear by the equation (3) as follows:

$$\log q_e = \log k_f + \left(\frac{1}{n}\right) \log C_e$$

(3)

where, n and K_F (mg g⁻¹ (L mg⁻¹)^{1/n}) are Freundlich constants, which are related to the heterogeneity factor and adsorption capacity, respectively. These constants can be calculated by plotting of $\log q_e$ versus $\log C_e$. The n value should be in the range 1 to 10 for favorable adsorption process.

The Temkin isotherm model contains a parameter which considers the adsorbent-adsorbate interactions and assumes that the adsorption heat decline linearly with the surface covered

between the adsorbates and adsorbent ³¹. The linearity of Temkin model is given by equation (4):

$$q_e = B \ln K_T + \left(\frac{RT}{b}\right) \ln C_e \quad (4)$$

where, $B=RT/b_T$, b_T (J mol⁻¹) is the constant of Temkin that is related to the heat of adsorption, K_T (L g⁻¹) is the equilibrium binding constant, R and T are the gas constant (8.3145 J mol⁻¹ K⁻¹) and absolute temperature in Kelvin, respectively. The B and K_T values can be calculated from slope and intercept of a graph between q_e and $\ln C_e$.

The Langmuir, Freundlich and Temkin parameters for the lead ions adsorption onto the Pip@MGO nanocomposite were listed in Table 3. As can be seen, the higher value of R^2 (0.996) for Langmuir model, compared to other models, indicates the suitability of the adsorption data and correlation of the Pb(II) monolayer adsorption on homogeneous surface of the nanocomposite adsorbent. The maximum adsorption capacity (q_{max}) of Pip@MGO nanocomposite for Pb(II) is 558.2 mg g⁻¹ and it helps the fact that the proposed adsorbent has a high surface area, especially in the nano proportions.

3.4 Adsorption kinetics study

The kinetic study of the adsorption process provides information on the adsorption mechanism and how the Pb(II) ions are transferred from the liquid phase to the solid phase. Therefore, two kinetic models, including pseudo-first-order and pseudo-second-order equations were applied to fit the experimental data. These experiments were performed by shaking 0.01 g of Pip@MGO nanocomposite in 10 mL solution of 10 mg L⁻¹ Pb(II) at pH 6 for 2, 3, 5, 10, 30 and 90 min. The linearized forms of pseudo-first-order and pseudo-second-order models ³² are as equation (5) and (6), respectively:

$$\ln(q_e - q_t) = \ln q_e - K_1 t$$

(5)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (6)$$

where, q_e and q_t are the adsorbed amount of Pb(II) ions at equilibrium and time t (mg g^{-1}), respectively. k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the rate constant of pseudo-1st and 2nd order, respectively. The constants of k_1 and k_2 can be calculated by plotting of equation (5) and (6). The data obtained from the two kinetic models are shown in Table 4. According to these data, a comparison of the correlation coefficient values for both models shows that R^2 (0.994) for the pseudo-second-order is greater than R^2 (0.724) for the pseudo-first-order, therefore it expresses the good fitting of the experimental data with this model.

3.5. Applications and reusability

In order to evaluate the application of the proposed method in the removing lead ions from real samples, three different water and wastewater samples, including Arvand Rud and Bahmanshir rivers, Persian Gulf seawater and petrochemical wastewater samples were investigated. To examine the effect of the sample matrices on the removal process, all samples were spiked by known concentrations of Pb(II) ions at two levels, 5 and 10 mg L^{-1} , subsequently the suggested method was performed under optimum conditions. The analysis results of each sample along with the recoveries are presented in Table 5. As can be seen, the removal efficiency of the lead ions in the studied samples were upper 93% which show well suitability of the developed nanocomposite adsorbent for removing of Pb(II) ions in various real samples.

The regeneration cycles of Pip@MGO nanocomposite were carried out using acidic solution. The adsorption/desorption study proved that the adsorbent with nitric acid (1 M) could be reused for four cycles. The removal efficiency of Pip@MGO nanocomposite for lead decreased to 90 % after mentioned cycles.

3.6. Comparison to methods in literature

A comparative study of the analytical results of Pb(II) adsorption on the Pip@MGO nanocomposite with other adsorbents in the literature is reported in Table 6. From this table, it is obvious that Pip@MGO nanocomposite has a good adsorption capacity (mg g^{-1}) for lead uptake compared to most mentioned adsorbents, while the adsorbent dosage used is less or comparable to other adsorbents.

4. Conclusions

In this present study, we have constructed a new magnetic graphene oxide-functionalized piperazine (Pip@MGO) nanocomposite to remove Pb(II) ions from contaminated waters. The synthesized nanocomposite adsorbent was analyzed by using XRD, FESEM, TEM, EDX, TGA, VSM and FT-IR techniques. The influence of four key parameters consisting initial pH, adsorbent dosage, initial concentration of lead and contact time on the removal efficiency were evaluated by RSM based on the central composite design (CCD) model. As a result of mathematical optimization, the maximum adsorption efficiency was obtained at pH 6.0, adsorbent dose of 7 mg, initial Pb^{2+} concentration of 15 mg L^{-1} and contact time of 10 min.

The isotherm studies indicated that lead adsorption equilibrium data were more appropriate with Langmuir isotherm model. In addition, the obtained equilibrium data were applied to the kinetic equations and found to be consistent with the pseudo-second order model for lead adsorption. The suggested nanocomposite adsorbent represented good adsorption capacity and could be regenerated by nitric acid and reused for up to four adsorption-desorption cycles. According to our findings, the Pip@MGO nanocomposite as an effective adsorbent can be successfully used for the removal of Pb(II) ions from different real samples and changes in the sample matrices do not have a significant effect on the removal efficiency of the proposed methodology.

Acknowledgement

The authors greatly appreciate the financial support of this work by Khorramshahr University of Marine Science and Technology Research Council.

Data Availability

All data generated or analysed during this study are included in this published article.

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Table 1

Levels of the independent variables for CCD experiments.

Variables	Units	Type	Coded levels				
			$-\alpha$	-1	0	+1	$+\alpha$
Initial pH	-	A	5	6	7	8	9
Lead ions conc.	(mg L ⁻¹)	B	5	10	15	20	25
Adsorbent dosage	(mg)	C	1	4	7	10	13
Time	(min)	D	2.5	15	27.5	40	52.5

Table 2

ANOVA results for Pb(II) removal.

Source	Sum of Squares	Df	Mean Square	F-Value	P-Value	
Model	22574.70	12	1881.23	228.36	< 0.0001	significant
A-pH	276.76	1	276.76	33.60	< 0.0001	
B-Conc.	356.51	1	356.51	43.28	< 0.0001	
C-Ads. Do.	1046.76	1	1046.76	127.06	< 0.0001	
D-time	3792.62	1	3792.62	460.38	< 0.0001	
AC	577.20	1	577.20	70.07	< 0.0001	
AD	601.48	1	601.48	73.01	< 0.0001	
BD	42.58	1	42.58	5.17	0.0363	
CD	1038.45	1	1038.45	126.06	< 0.0001	
A ²	10940.59	1	10940.59	1328.05	< 0.0001	
B ²	1126.77	1	1126.77	136.78	< 0.0001	
C ²	5024.35	1	5024.35	609.89	< 0.0001	
D ²	2158.91	1	2158.91	262.06	< 0.0001	
Residual	140.05	17	8.24			
Lack of Fit	114.63	12	9.55	1.88	0.2516	not significant
Pure Error	25.42	5	5.08			
Cor Total	22714.75	29				

Table 3

Isotherm parameters for the adsorption of Pb(II) ions onto Pip@MGO nanocomposite.

Isotherm	Parameters	Values of parameters
Langmuir	R^2	0.996
	K_L (L g ⁻¹)	0.029
	q_m (mg g ⁻¹)	558.2
	R_L	0.06-0.41
Freundlich	R^2	0.899
	K_F (L g ⁻¹)	1.624
	n	0.27
Temkin	R^2	0.729
	A_T (L g ⁻¹)	0.38
	b_T	20.34
	B (J mol ⁻¹)	121.88

Table 4

Kinetic parameters for the adsorption of Pb(II) ions with Pip@MGO nanocomposite.

Models	Parameters	Cd(II)
Pseudo-1 st -order	q_e (mg g ⁻¹)	0.22
	k_1 (min ⁻¹)	- 0.058
	R^2	0.724
Pseudo-2 nd -order	q_e (mg g ⁻¹)	9.51
	K_2 (g mg ⁻¹ min ⁻¹)	0.049
	R^2	0.994

Table 5

Removal of Pb(II) from various water and wastewater samples using proposed method.

Sample	Add concentration (mg L ⁻¹)	Removal (%)
River water (Karun)	5	> 99
	10	> 99
River water (Bahmanshir)	5	> 99
	10	> 99
Wastewater effluent (Abadan Petrochemical Company)	5	> 99
	10	96
Seawater (Persian Gulf)	5	> 99
	10	93

Table 6

Comparative study of adsorption capacity of Pip@MGO nanocomposite with different adsorbents for removal of Pb (II).

Adsorbent	pH	q_m (mg g ⁻¹)	Equilibrium time (min)	Adsorbent Dosage (g/L)	Ref.
Rice husk nanoadsorbent	8	6.1	70	12	3
Bentonite enriched-SH groups	5	12	146	1.5	4
Fe ₃ O ₄ @glycidylmethacrylate- acrylamide	6	158.7	10 s	0.2	7
GO nanocomposite decorated with NiFe ₂ O ₄ nanoparticles	8.5	957	18	-	26
EDTA-magnetic GO	4.2	479	20	-	33
Thiourea modified magnetic ZnO/nano Celloluse	6.5	554.4	14.5	0.2	34
Fe ₃ O ₄ -EDTA	7.9	112	10	1.1	35
Modified red mud	5	551.1	60	1.0	36
Fe ₃ O ₄ /FeMoS ₄ /MgAl-LDH	5	190.7	60	3.0	37
Amino/thiol bifunctionalized magnetic nanoparticle	5	110.1	3	1.0	38
Bifunctionalized GO/MnFe ₂ O ₄ Magnetic Nanohybrids	5.5	366.4	120	-	39
Pip@MGO nanocomposite	6	558.2	27.5	0.7	Present work

a

Figure Captions

Fig. 1. (a) FT-IR spectrum, (b) TGA diagram, (c) XRD pattern and (d) VSM curve of Pip@MGO nanocomposite.

Fig. 2. SEM images of Pip@MGO.

Fig. 3. Elemental mapping of Pip@MGO.

Fig. 4. TEM image of the Pip@MGO.

Fig. 5. 3D response surface plots of Pb(II) adsorption on Pip@MGO nanocomposite.

Fig. 1 (a)

Fig. 1 (b)

Fig. 1 (c)

Fig. 1 (d)

Fig. 2

Fig. 3 (a)

Fig. 3 (b)

Fig. 4

Fig. 5