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RESEARCH PAPER

Synthesis and Application of Magnetic Fe_3O_4@GO-3,5-Diaminopyrazole Nanocomposite for Pb(II) Adsorption: Optimization and Mechanism

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ABSTRACT

A novel magnetic nanocomposite, Fe_3O_4@GO functionalized with 3,5-diamino-1H-pyrazole (Fe_3O_4GO-PYR), was synthesized through modified Hummers' and hydrothermal methods for efficient Pb(II) removal from aqueous solutions. Graphene oxide (GO) was prepared via oxidation of graphite, followed by deposition of Fe_3O_4 nanoparticles and anchoring of the pyrazole ligand under reflux conditions. Characterization by XRD confirmed crystalline Fe_3O_4 phases on GO sheets, FT-IR revealed functional groups (Fe-O at 566 cm^{-1}, C=O, N-H stretches), SEM showed uniform nanoparticle distribution with altered morphology post-functionalization, and EDX verified elemental composition (C, O, N, Fe). Central composite design (CCD) optimized parameters: pH (2.4-9.6), Pb(II) concentration (3-27 mg/L), adsorbent dose (3-27 mg), and contact time (1-49 min), achieving >95% efficiency at pH ~8-9, 15 mg dose, and 25 min. The point of zero charge ($pH_{pzc} \approx 8$) favored negative surface charge under basic conditions, enhancing electrostatic attraction with Pb^{2+}. Langmuir isotherm and pseudo-second-order kinetics described monolayer adsorption, with favorable thermodynamics indicating spontaneity. This magnetically separable adsorbent addresses nanomaterial recovery challenges, offering scalable wastewater treatment for heavy metal pollution.

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INTRODUCTION

In recent decades, heavy metal pollution was expressed as a global environment issue. High toxicity, carcinogenicity, and biological accumulation have had profound effect on the way what scientists. Therefore, scientists pay special attention to remove heave metal ions from environment and wastewater [1, 2]. To respond to this issue, several protocols were studied by specialists, such as ion exchange,

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membrane separation, chemical precipitation, ultrafiltration, and adsorption [3-5]. Among them, adsorption method is a favorable strategy because it reduces prices and improves designability and selectivity [6, 7]. The mild conditions and simple operation are among the favorable feature in these researches. Absorbent play an important role in the adsorption process. Thus, design and preparation of adsorbents with great efficiency is a kay subject in adsorption filed [8-10].

Different organic and inorganic adsorbents are used for eliminating the pollutant, such as silica gel, zeolite, activated alumina, carbon nanotube, and graphene oxide. These materials afford some advantages: high specific adsorption surface, selectivity, high adsorption capacities, and porous/amorphous structures [11-13]. Graphene oxide (GO) structures were produced from the oxidation of graphite. GO is used in ionic conductors, hydrogen storage, and nanofiltration membrane [14]. One of an important application of these structures is removal of heavy metals and ions. The biocompatibility, attributed exceptional dispersion, and cost effective fabrication are the unique advantages of GO structures [15].

One disadvantage of nanostructures is that difficult to separate them from the environmental medium. Also, the small particle size of nanostructures would aggravate this issue [16]. Fe_3O_4 nanostructures, as a magnetic nanoparticles, are used in various fields and technological application [17, 18]. Given the magnetic property of Fe_3O_4 nanoparticles, the composite adsorbents contain Fe_3O_4 nanoparticles, could achieve the solid-liquid separation facility under an external magnetic field, without filtration and centrifugation [1, 19]. Therefore, magnetic adsorbent nanocomposite could prevent nano-adsorbent flowing into the environmental system and avoid unknown damage to nature.

In this work, we proposed new magnetic composite adsorbent, Fe_3O_4/GO/3,5-diamino-1*H*-pyrazole composite and investigated for Pb^{2+} removal heavy cations from wastewater. The preparation of GO and Fe_3O_4/GO/3,5-diamino-1*H*-pyrazole composite were done via improved hummers and hydrothermal methods. The XRD, FT-IR, SEM, and EDX are used to study the properties of as-prepared nanocomposites. The effect of parameters: pH, time, adsorbent weight, and Pb^{2+} initial concentration on the process were investigated via experimental design. The isoelectric pH, isotherm, kinetics and thermodynamics of the synthesized adsorbent were investigated.

MATERIALS AND METHODS

Preparation of GO

Based on modified Hummers procedure [20], sulfuric acid (120 ml) and nitric acid (20 ml) were mixed in ice-bath and then, 1 g of graphene powder was added. 6 g of potassium permanganate (as an oxidant agent) was added to above mixture in stirring conditions. The whole mixture was stirring at 50 °C for 18 h. To remove excess of potassium permanganate, 1 ml of hydrogen peroxide was dropped slowly in ice-bath medium. The black-brown mixture after the completion of exothermic reaction was seen and then, the obtained solid was centrifuged and washed by HCl (10 ml) and DI water (50 ml) to reached pH 7. The washed solid was dried at 50 °C under oven conditions.

Preparation of Fe_3O_4@GO nanostructures

For the synthesis of Fe_3O_4@GO nanostructures, the methods reported in pervious literatures were used [21, 22]. According to this, 180 mg of GO was dispersed in water medium (120 ml) under ultrasound bath conditions. Next, the chloride salts of Fe^{2+} (41.29 mg) and Fe^{3+} (70.77 mg) were added and stirred for 30 min. Afterwards, ammonia solution was added slowly to form the black solid. The whole mixture was kept at 190 °C. Finally, the solid was filtered, washed with DI water, and dried in an oven.

Preparation of 3,5-diamino-1H-pyrazole compound

The mixture of malononitrile (2 g, 0.03 mol), hydrazine hydrate (1 ml, 0.03 mol), and ethanol (20 ml) were mixed and refluxed at 90 °C for 4 h. Then, the whole mixture was kept in ice-bath for 2 h and added 0.5 g of carbon active to the medium. Next, the whole mixture refluxed again at 90 °C for 4 h. At completion, the obtained solid was filtered and washed with DI water. To give pure product, the collected solid was recrystallized in ethanol.

Preparation of isoxazole-3,5-diamine compound

The mixture of malononitrile (2 g, 0.03 mol), hydroxylamine hydrochloride (2 g, 0.028 mol), sodium hydroxide (0.25 g, 0.006 mol), and ethanol (20 ml) were mixed and refluxed at 90 °C for 4 h. Then, the whole mixture was kept in ice-bath for 2

h and added 0.5 g of carbon active to the medium. Next, the whole mixture refluxed again at 90 °C for 4 h. At completion, the obtained solid was filtered and washed with DI water. To give pure product, the collected solid was recrystallized in ethanol.

Preparation of Fe_3O_4@GO@3,5-diamino-1H-pyrazole (Fe_3O_4@GO@PYR NCs)

0.2 g of Fe_3O_4@GO nanocomposite was dispersed in water (25 ml). Then, the solution of 2.25 g of 3,5-diamino-1H-pyrazole in water (25 ml) was added to above mixture. Next, sodium hydroxide (0.1 g) was added. The whole mixture was refluxed at 60 °C for 24 h. At completion, the solid was collected with external magnet, washed with DI water, and dried in oven.

Preparation of Fe_3O_4@GO@isoxazole-3,5-diamine nanocomposite

0.2 g of Fe_3O_4@GO nanocomposite was dispersed in water (25 ml). Then, the solution of 3 g of osoxazole-3,5-diamine in water (25 ml) was added to above mixture. Next, sodium hydroxide (0.1 g) was added. The whole mixture was refluxed at 60 °C for 24 h. At completion, the solid was collected with external magnet, washed with DI water, and dried in oven.

Measuring adsorption efficiency

In this paper, adsorption efficiency (AE) was used to analyze the results. AE shows the value od adsorbed Pb^{2+}, according to following equation (Eq.1):

$$AE\% = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

Where AE shows the adsorption efficiency during specific adsorption times, C_0 shows the primary Pb^{2+} concentration of solution, and C shows the concentration of Pb^{2+} solution after adsorption based on the atomic absorption results.

Optimization of the adsorption process via response surface method

In this paper, the central composite design (CCD) method was applied to optimize the adsorption process to eliminate Pb^{2+}. The number of experiments will vary based on the number of factors in this method. To investigate the effect of operating factors on the Pb^{2+} removal process and modeling, four main parameters include primary Pb^{2+} concentration (mg/L), pH of primary solution, reaction time (min), and adsorbent weight (mg) were shown in Table 1. Then, Design Expert 1 software proposed the experiment based on these five factors and 50 experiments were recommended by the software. The following polynomial second-order equation was applied to correlate between dependent and non-dependent

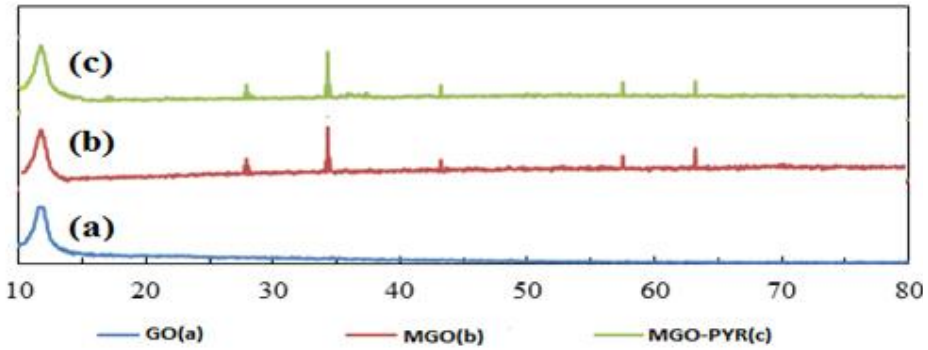

Fig. 1. XRD patterns of GO (a), Fe_3O_4@GO (b), and Fe_3O_4@GO@PYR nanostructures (c).

Table 1. Variables levels for elimination of Pb^{2+}.

No.	Variables	Parameters and levels				
		-2	-1	0	1	2
1	$[Pb^{2+}]_0$ (mg/L) (X_1)	3	5	15	25	27
2	Temperature (°C) (X_2)	23	25	35	45	47
3	pH (X_3)	2.4	3	6	9	9.6
4	Adsorbent Weight (mg) (X_4)	3	5	15	25	27
5	Time (min) (X_5)	1	5	25	45	49

variables (Eq. 2).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{1 \le i \le j}^{k} \beta_{ij} X_i X_j \qquad (2)$$

where Y is the response variable (adsorption efficiency), Xi and Xj are the experimental levels of variables, βi is the linear correlation coefficient, βii is the second-order correlation coefficient, bij is the cross-correlation coefficient and i, j and k are the number of variables [8].

RESULTS AND DISCUSSION

Fig. 1 shown the XRD patterns of GO, Fe_3O_4@GO, and Fe_3O_4@GO@PYR nanostructures, respectively. As shown in Fig. 1a, the observed peak at $2\vartheta \sim 10°$ is related to GO [23]. Also, the characteristic peaks of Fe_3O_4 were shown in Fig. 1b [24]. It is clear that the synthesis of Fe_3O_4@GO nanostructures were done successfully. According to Fig. 1c, due to the non-crystalline structure of PYR compound and its location between Fe_3O_4@GO nanostructures [25], there is no much change in the final pattern.

Fig. 2 shows the FT-IR spectrum of Fe_3O_4@GO@PYR nanostructures. The study of functional groups shows that the band located at 566 cm^{-1} is related to Fe-O vibration [26]. Two bands at 1627 and 1573-1410 cm^{-1} were caused by stretching vibrations of C=O and C=C functional groups, respectively [27]. The observed broad peak around 3420 cm^{-1} is also ascribed to the OH/NH/COOH stretching vibrations.

Characterization and investigation of surface morphology were conducted by SEM technique (Fig. 3). Fig. 3a shows the two-dimensional sheets of GO structures. As can be seen in Fig. 3b, the spherical Fe_3O_4 nanoparticles are uniformly presented on the surface of GO, which means the formation of Fe_3O_4@GO nanostructure was

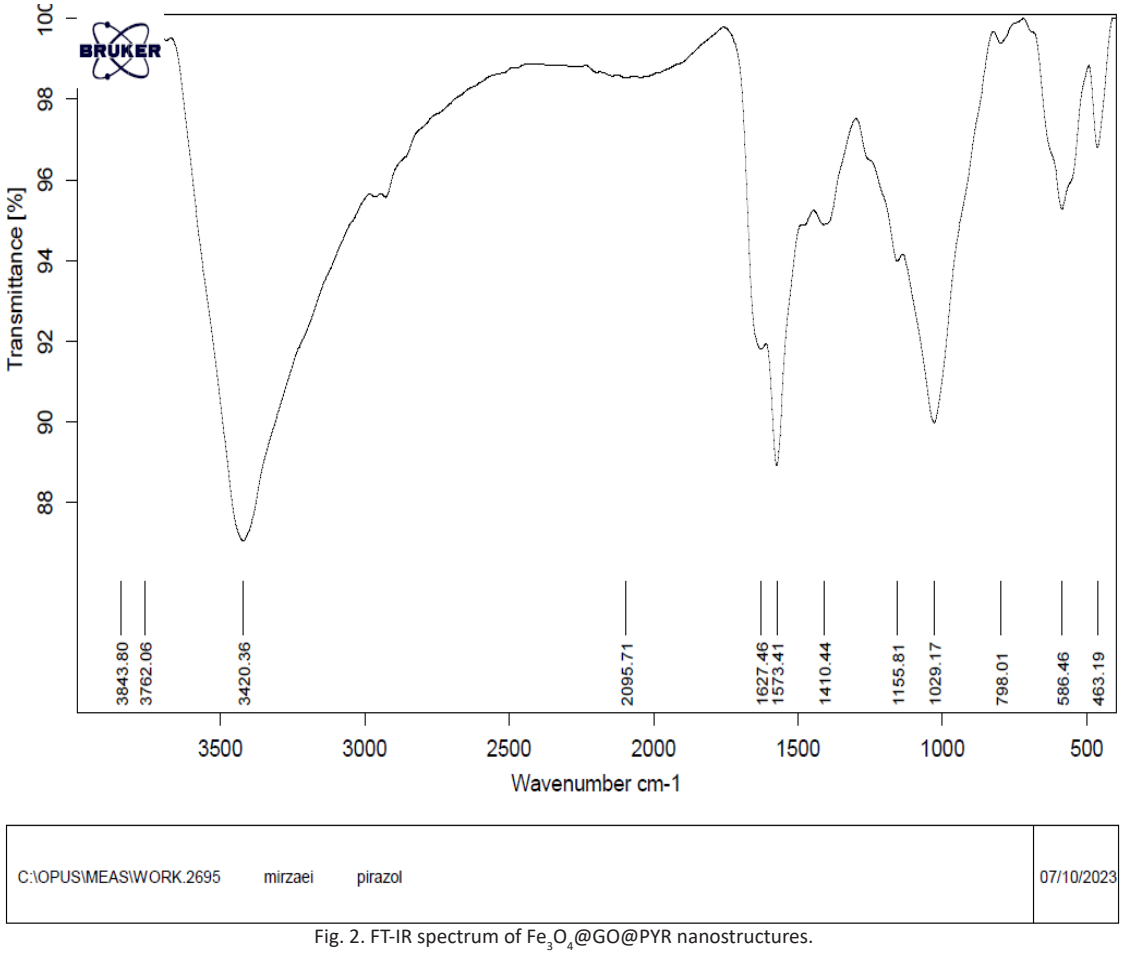

Fig. 2. FT-IR spectrum of Fe_3O_4@GO@PYR nanostructures.

successfully synthesized. From Fig. 3c, PYA was successfully anchored o the surface of Fe_3O_4@GO nanostructures and also influenced on the particle size and morphology of Fe_3O_4@GO nanostructure. The SEM image indicated that PYR was loaded non-uniformly. In addition to SEM study, EDS analysis was done and confirms the presence of C, N, O, and Fe elements in Fe_3O_4@GO@PYR nanocomposites. The results of EDS were displayed in Fig. 4.

Investigation of the adsorption process by 3,5-diaminopyrazole functionalized magnetic graphene oxide for the removal of lead heavy metal

Figs. 5 and 6 present the two-dimensional and three-dimensional plots illustrating the effects

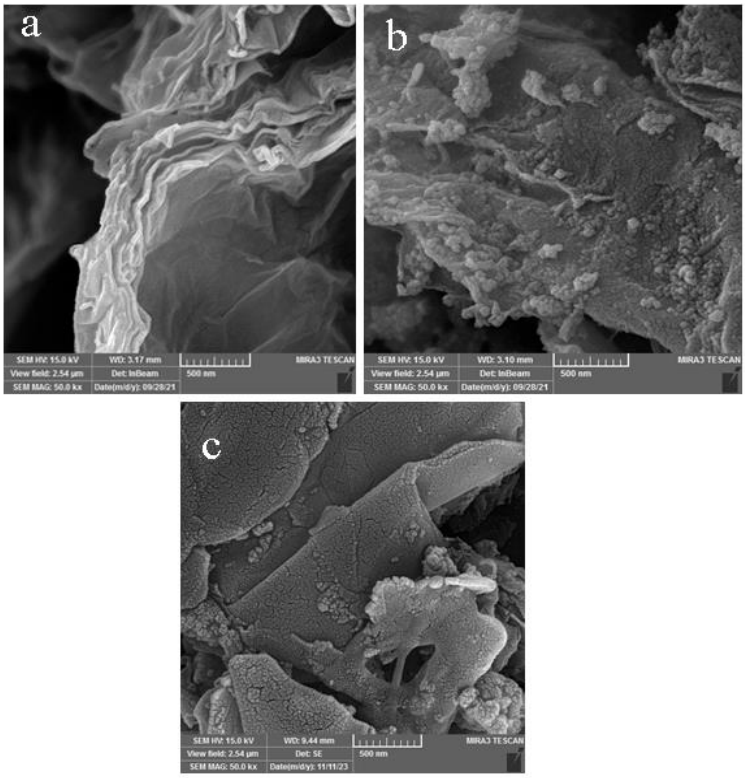

Fig. 3. SEM images of GO (a), Fe_3O_4@GO (b), and Fe_3O_4@GO@PYR nanostructures (c).

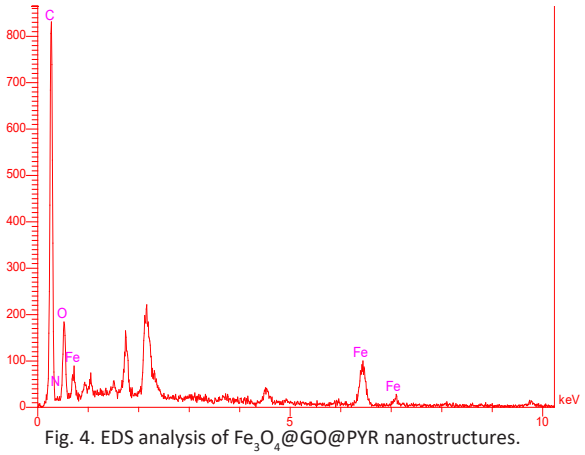

Fig. 4. EDS analysis of Fe_3O_4@GO@PYR nanostructures.

of pH and lead concentration on the adsorption efficiency for a solution containing 15 mg of adsorbent and a contact time of 25 minutes. As observed, the adsorption efficiency increases with both the rise in pH and the increase in lead concentration. The pH of the solution plays a crucial role in the overall adsorption process and capacity, as it affects not only the surface charge of the adsorbent but also the degree of ionization of the species in the solution and the dissociation of functional groups at the active sites of both the adsorbent and the solution.

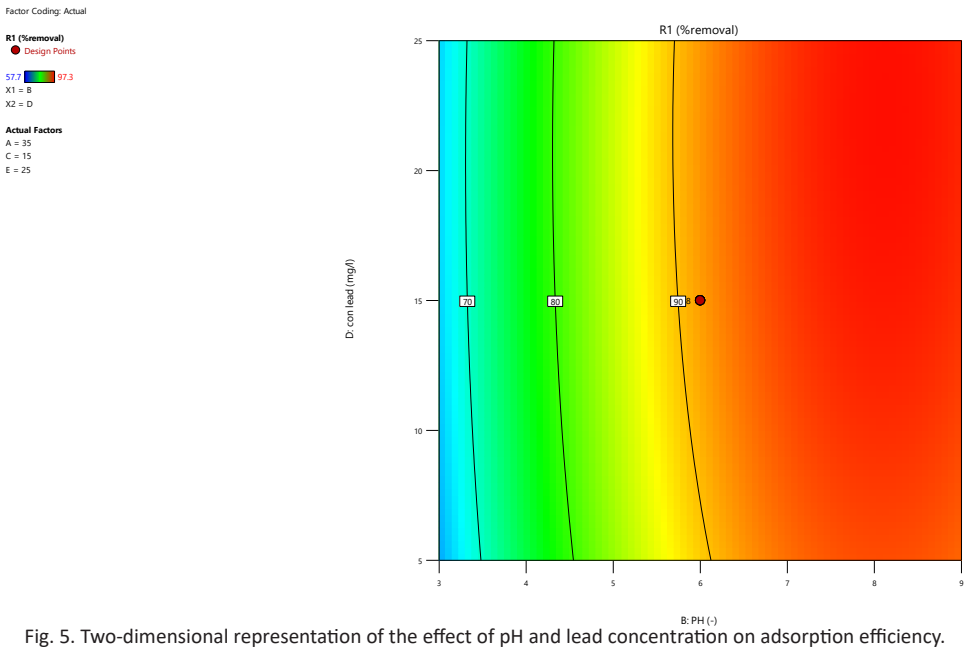

Fig. 5. Two-dimensional representation of the effect of pH and lead concentration on adsorption efficiency.

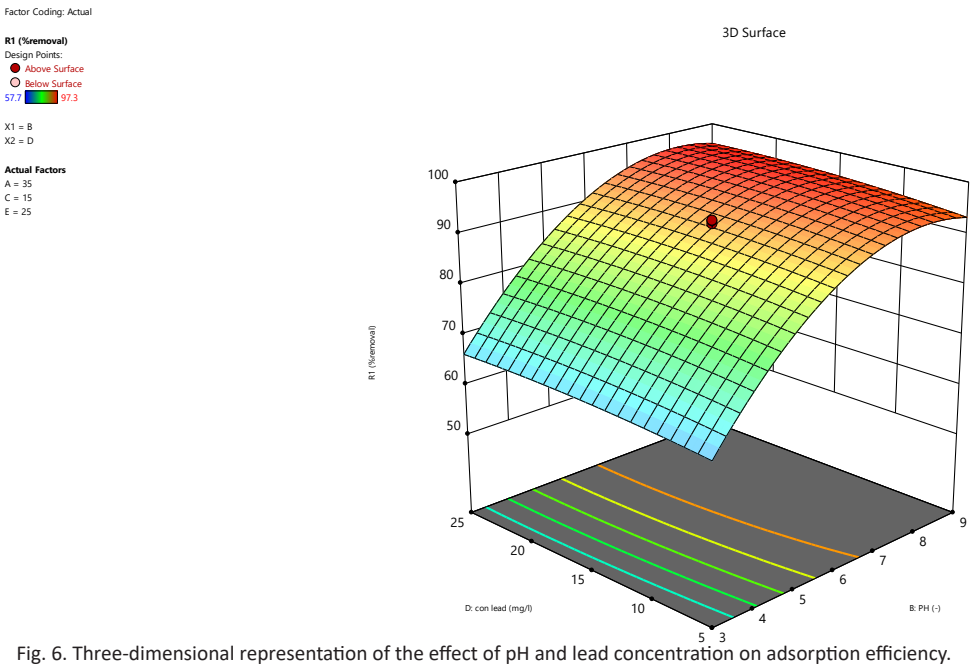

Fig. 6. Three-dimensional representation of the effect of pH and lead concentration on adsorption efficiency.

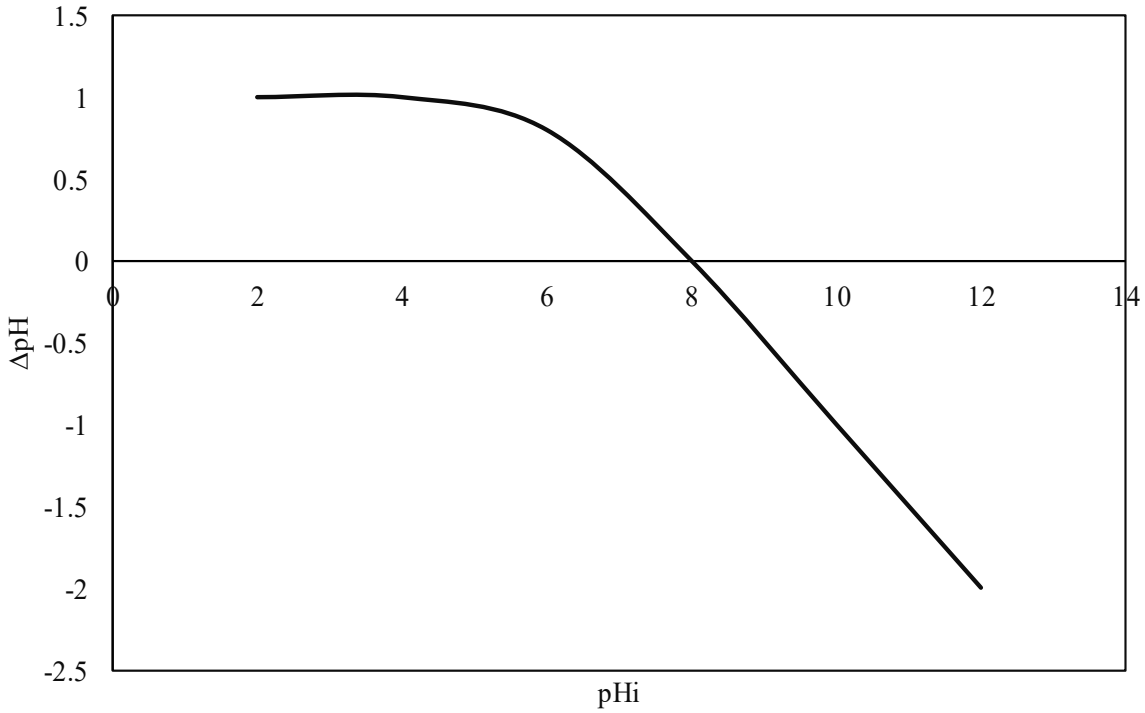

Fig. 7. Plot investigating the isoelectric point for the pyrazole ligand.

To investigate the influence of pH variation on adsorption efficiency, the point of zero charge (pHpzc) was determined. For this purpose, six solutions of 0.1 M sodium nitrate, each with a volume of 15 mL, were prepared. The initial pH values of the solutions were adjusted to 2.4, 3, 6, 9, and 9.6 using nitric acid and sodium hydroxide. Subsequently, 16 mg of the adsorbent was added to each solution, and the mixtures were stirred at a constant rate for two days. After the equilibration period, the final pH values of the solutions were measured again, and the difference (ΔpH) between the initial and final values was plotted against the initial pH (pHi) to determine the point of zero charge (Fig. 7).

The results indicated that the pHpzc value was approximately 8. Analysis of the pHpzc plot revealed that under acidic conditions, the adsorbent surface carries a positive charge, while under basic conditions, it becomes negatively charged. Considering the positive ionic nature of lead, a negatively charged adsorbent surface is favorable for electrostatic attraction between the adsorbent and the metal ions. Therefore, a basic pH condition is desirable for efficient lead adsorption, which is consistent with the trends observed in our experimental design results.

CONCLUSION

In conclusion, the synthesized Fe_3O_4@GO nanocomposite functionalized with 3,5-diamino-1H-pyrazole (Fe_3O_4GO-PYR) demonstrates exceptional efficacy as a magnetically recoverable adsorbent for Pb(II) removal from aqueous solutions, achieving over 95% efficiency under optimized conditions (pH ≈8-9, 15 mg adsorbent, 25 min contact time). Comprehensive characterization via XRD, FT-IR, SEM, and EDX confirmed successful integration of magnetic Fe_3O_4 nanoparticles onto graphene oxide sheets with pyrazole ligand anchoring, enhancing surface functionality, selectivity, and ease of separation. Central composite design optimization revealed pH-dependent adsorption dominated by electrostatic attraction at the point of zero charge (pH_{pzc} ≈8), with Langmuir isotherm and pseudo-second-order kinetics indicating monolayer chemisorption. This nanocomposite overcomes limitations of pristine nanomaterials, such as separation difficulties, offering a cost-effective, scalable solution for heavy metal remediation in wastewater. Future work should explore multi-

metal systems and real effluents to advance industrial applicability.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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