



Magnetic Removal of Acid Dyes from Wastewater with Ionic Liquid Linked-Nanoparticles

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ABSTRACT

The acid dyes are one of the most widely used commercial dyes used in the textile industries. This work investigates the ability of magnetite nanoparticles functionalized with imidazolium based ionic liquid as an efficient sorbent for removal of the Acid Blue 113 from wastewater. Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) were used to characterize the synthesized nanosorbent. The results showed that under optimal conditions, the dye removal efficiency of the supported ionic liquid is 98.6% after a single run. The isothermal data of AB113 sorption conformed well to the Langmuir model and the maximum sorption capacity of IL@Fe₃O₄ for Ab113 was 92.59 mg g⁻¹. Regeneration of the used sorbent could be possible and the modified magnetic nanoparticles exhibited good reusability. The use of such a system can provide fast and efficient removal of the acid dyes from wastewater by using an external magnetic field. Prog. Color Colorants Coat. 7(2014), 27-38. © Institute for Color Science and Technology.

1. Introduction

Textile industries produce large volume of effluents, which are very toxic, resistant to physicochemical treatments and not easily biodegradable and the resulted water contamination is a major concern. In addition to their unwanted colors, some of these dyes may degrade to produce carcinogens and toxic products. Hence, the treatment of such effluents does not depend on biological degradation alone [1]. The traditional processes (e.g., flocculation, sedimentation, filtration) and biological-based processes (e.g., activated sludge, sequential bed

reactors, anaerobic/ anoxic) prove to be insufficient for purifying a significant quantity of wastewaters [2]. Other methods such as combined coagulation, electrochemical oxidation and oxidative degradation have been investigated [3-5]; but the drawbacks of these methods are mainly due to the creation of a more concentrated pollutant-containing phase and the deactivation of catalysts during the course of the reaction by poisoning and fouling.

Adsorption technology has become known and taken a place as one of the most effective technologies for the

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removal of organic compounds such as dyes [6, 7]. Nowadays, due to their high surface to volume ratio, nanoparticles are widely used [8]. On the other hand, because of the small size of the nanoparticles, separation of the nanosized sorbents from matrices is very complicated in practice. Magnetic nanosized sorbents have overcome this dilemma and appear to be promising especially in the case of environmental samples [9, 10]. Application of an external magnetic field for the recovery of the nanoparticles is a main advantage of these magnetic nanosorbents. In addition, these nanoparticles are capable of being functionalized by an appropriate material to extract the target analyte.

In the recent years, studies on ionic liquids (ILs) have grown exponentially which is due to their unique physicochemical properties such as negligible vapor pressure, wide liquid range, higher ionic conductivity and excellent solubility [11, 12]. Some ILs have been used in liquid-liquid extraction, gas separation, electrochemistry and as catalysts, however their wide application is hindered because of some problems such as their isolation, recovery and use of relatively large amounts of ILs which raise the operation costs [13]. To overcome these problems, supported ILs have recently been put forward which merges the advantages of ILs with those of support materials.

To the best of our knowledge, there is no report on the use of ILs-grafted magnetite for acid dye removal in the literature, so fabrication of a new kind of magnetic sorbent is possible through combination of the advantages of ILs and magnetic nanoparticles. During the functionalization step, ILs have covalently linked to the surface of the magnetic nanoparticles. In this work, we focused on the acid dyes which are among the most widely used commercial dyes in terms of their quantity of production and consumption [14]. For this purpose, C.I. Acid Blue 113 (AB113, Figure 1) was selected as model textile dyes and the effect of magnetic treatment

was evaluated. This dye is generally used in wool dyeing to obtain deep shade of navy blue color. The kinetic data of the adsorption process were analyzed to clarify the mechanism of adsorption of AB113 molecules onto the proposed nanosorbent.

2. Experimental

2.1. Materials

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), acetonitrile, dichloromethane (DCM), methanol, toluene, ether, 2-propanol and ammonia were all of analytical grade from Merck, Germany. Tetraethyl orthosilicate (TEOS), NaPF_6 , N-octylimidazole and 3-chloropropyl-triethoxysilane were purchased from Sigma-Aldrich. AB113 was provided from Institute for Color Science and Technology, Tehran, Iran.

2.2. Equipments

The morphology and the size of the nanoparticles were characterized using a Zeiss 900 TEM at a voltage of 80 kV. The phase characterization was performed by X-ray powder diffraction (XRD) (PW-1840 diffractometer from Philips Co) using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). FTIR spectra were obtained using a Vertex 70 FT-IR spectrophotometer from Bruker Co. pH measurements were performed with a Metrohm 691 pH meter. The AB113 concentration was measured on a Carry 5030 spectrophotometer from Varian Co. at the maximum absorption band i.e. $\lambda_{\text{max}} = 580 \text{ nm}$.

2.3. Sorbent preparation

2.3.1. Synthesis of Fe_3O_4 nanoparticles

According to the improved chemical co-precipitation method reported by Maity et al., $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2:1) were dissolved in deionized water [15].

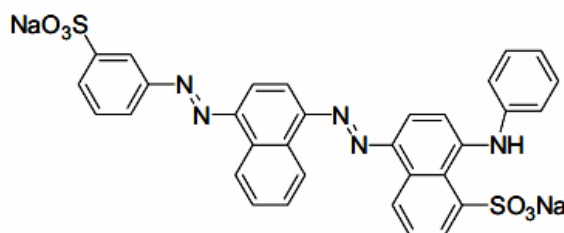


Figure 1: Chemical structure of the Acid Blue 113 dye used.

The mixed solution was stirred under N_2 at $80^\circ C$ for 1 h. Then, ammonia solution was injected into the mixture drop wise, stirred under N_2 for another 1 h and then cooled to room temperature. Finally, the precipitated magnetic nanoparticles (MNPs, Figure 2(a)) were washed with hot water, separated by magnetic decantation and dried.

2.3.2. Synthesis of Fe_3O_4 nanoparticles with silica shell

40mg Fe_3O_4 was diluted with 40 ml of water and 160ml of 2-propanol [16]. This suspension was dispersed under ultrasonication for 10min. 3ml ammonia solution was added at room temperature in the presence of a constant nitrogen flux, followed by the addition of 0.2 ml TEOS with stirring. The mixture was stirred for 12 h to allow the silica shell to grow on the surface of the nanoparticles. The sample ($SiO_2@Fe_3O_4$, Figure 2(b)) was washed with water for several times and dried under vacuum.

2.3.3. Synthesis of ionic liquid

N-octylimidazole (50 mmol) and 3-chloropropyl-triethoxy-silane (50 mmol) were stirred at $95^\circ C$ for 24 h.

The product (Figure 2(c)) was washed with ether and dried under vacuum at room temperature [17]. The ionic liquid with desired anion (PF_6^-) was obtained by ion exchange with anion salt according to Mehnert et al. [18]. IL with chloride ion (50 mmol) was dissolved in 300 ml acetonitrile. Sodium hexafluorophosphate (50 mmol) was added and the mixture was stirred for 5 days at $30^\circ C$. Then the precipitate was filtrated and the solvent was evaporated in vacuum. DCM was used to wash the slurry and then was evaporated to get the final product (Figure 2(d)).

2.3.4. Grafting of ILs at the surface of $SiO_2@Fe_3O_4$

In order to prepare ionic liquids linked- magnetic nanoparticles ($IL@Fe_3O_4$, Figure 2(e)), 100mg $SiO_2@Fe_3O_4$ was dispersed in toluene by ultrasonication [17, 18]. 1 g IL, PF_6^- was then added to the system and the mixture was stirred at $90^\circ C$ for 24 h. After reaction, the solid product was isolated by a magnet, washed with acetonitrile and methanol, and dried under vacuum. The yield of this step was 89.3%. A scheme of the magnetite surface modification process is shown in Figure 2 [19-22].

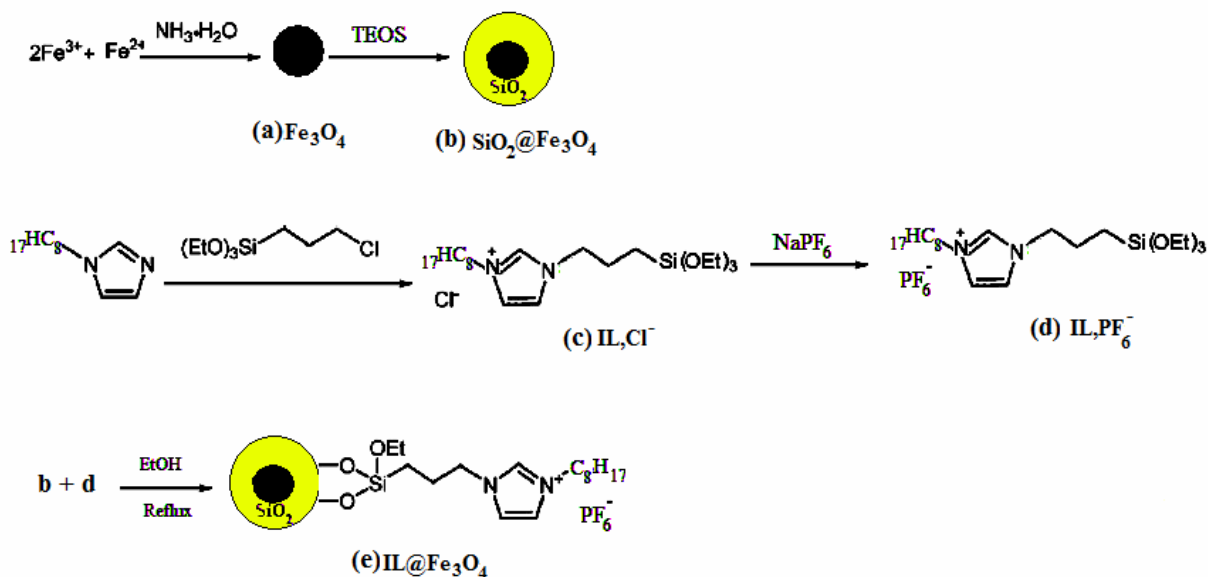


Figure 2: Synthesis route of ionic liquid linked- Fe_3O_4 nanoparticles.

2.4. Dye removal procedure

The mixture of IL@Fe₃O₄ nanoparticles and AB113 aqueous solution were used in batch experiments. 50 mL aqueous solution of AB113 (100 mg/L) and various amounts (25-150 mg) of dry powder of the nanosorbent were added to a stoppered flask, which was shaken at 200 rpm and room temperature for a predefined time. The sorbent was separated before measurement. The residual AB113 concentration of aqueous solution was determined and the removal efficiency was calculated according to Eq. (1):

$$\text{AB113 removal efficiency (\%)} = \left[\frac{C_0 - C_r}{C_0} \right] \times 100 \quad (1)$$

where C_0 and C_r are the initial and final concentrations of the AB113 before and after the sorption, respectively.

2.5. Adsorption isotherms

In order for designing an adsorption process, it is necessary to have information about the adsorption isotherms of the adsorbent [23]. To obtain the AB113 adsorption isotherms onto the IL@Fe₃O₄ surface, various amounts (25 to 150 mg) of IL@Fe₃O₄ was added to the beakers containing 50 mL of 100 mgL⁻¹ AB113 solution at pH 2.5. To reach equilibrium condition, the solutions were stirred for 15 min. After magnetic separation of nanoparticles the AB113 residual was determined in aqueous solution. The amount of the adsorbed AB113 onto IL@Fe₃O₄ was calculated based on the following mass balanced equation (Eq. (2)).

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

where q_e (mg g⁻¹) is the adsorption capacity, V is the volume of the AB113 solution (L), C_0 and C_e are the initial and equilibrium AB113 concentrations (mg L⁻¹), and m is the mass (g) of the dry IL@Fe₃O₄ added.

Several isotherm models are developed to evaluate the equilibrium adsorption; however, Langmuir [24] and Freundlich [25] are the most common ones. Assuming

monolayer adsorption occurring on a homogeneous adsorbent surface, the linearized form of the Langmuir isotherm is expressed as Eq. (3).

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{C_e}{q_{\max}} \quad (3)$$

where $q_{\max}$ (mg g⁻¹) is the surface concentration at monolayer coverage, illustrating the maximum attainable value of q_e with C_e increments. b which increases with the strength of the adsorption bond, is the coefficient related to the energy of adsorption. Values of $q_{\max}$ and b could be obtained from the linear regression plot of (C_e/q_e) versus C_e .

The linearized form of the Freundlich equation [25] is expressed as Eq. (4).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where K_F and n are the Freundlich equation constants. K_F represents the capacity of the adsorbent for the adsorbate and n is the reaction order while $1/n$ is a function of the strength of adsorption.

3. Results and discussion

3.1. Characterization of IL@Fe₃O₄ nanoparticles

3.1.1. Structure and particle size determination

The identity and the phase purity of the IL@Fe₃O₄ nanoparticles were checked by XRD (Figure 3). The Joint Committee on Powder Diffraction Standards (JCPDS) reference pattern of magnetite (No. 19-629) was used for comparison. As can be seen, although the magnetic nanoparticle surfaces were coated with ionic liquid, the XRD pattern of IL@Fe₃O₄ nanoparticles was in good agreement with that of the standard Fe₃O₄ structure indicated that these particles have phase stability and the structural integrity was preserved [26].

The introduction of IL into the magnetite nanoparticles was evident from TEM results. The dark nano-Fe₃O₄ cores surrounded by a gray shell could be observed in Figure 4. Moreover, the naked Fe₃O₄ nanoparticles had a mean diameter of about 10 nm, much smaller than the functionalized ones (28 nm). The

particles modified with ionic liquids show some aggregations which might be due to the self-interaction of the surrounding layer of ionic liquids [27]. Another reason is that the ionic liquids could reduce the surface charges of nanoparticles which is a case similar to what can be observed for colloidal particles when an inert electrolyte is added to their aqueous solutions [28].

3.1.2. FT-IR studies

To warrant the successful functionalization of Fe_3O_4 with IL, we employed IR to give detailed investigations of the obtained sorbent (Figure 5).

The IR spectrum of ionic liquids modified magnetic silica (Figure 5(a)) shows a strong bond at 580cm^{-1}

which corresponds to Fe-O vibrations of the magnetite core. The bond at 1100cm^{-1} represents Si-O bonds, and the weak bond at 800cm^{-1} is the characteristic of Si-O-Fe and implies that SiO_2 is chemically bonded to Fe_3O_4 . As a result of ionic liquid attachment, the IR curve shows typical bands at 3170 and 3121cm^{-1} (C-H stretching vibration of imidazole ring), 2980 and 2936cm^{-1} ($-\text{CH}_3$ and $-\text{CH}_2$ stretching vibration, respectively), 2815cm^{-1} (N- CH_2 stretching vibration), 1572cm^{-1} (C-C and C-N stretching vibration of imidazole ring) and 844cm^{-1} (P-F stretching vibration). The FTIR spectrum of pure IL is appended for comparison (Figure 5(b)). FTIR spectrum proves that magnetic silica particles are bonded to ionic liquids.

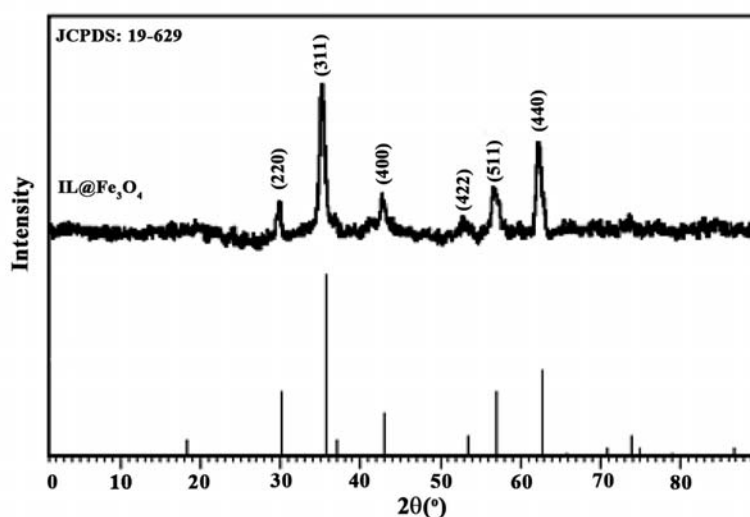


Figure 3: XRD patterns of IL@ Fe_3O_4 nanoadsorbents.

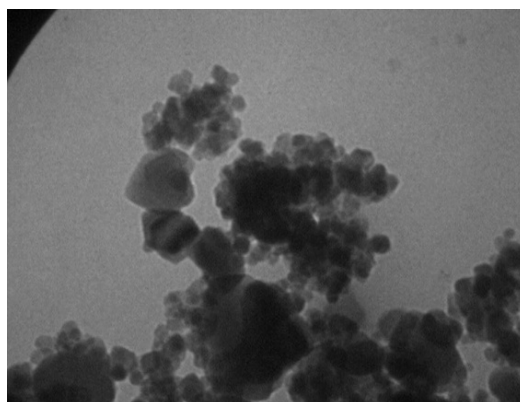


Figure 4: TEM image of IL@ Fe_3O_4 nanoadsorbents.

3.1.3. Immersion technique studies

The experimental curves corresponding to the immersion technique [29, 30] were obtained for the proposed nanosorbent and are presented in Figure 6. Suspension of 5.5 g L^{-1} of nanosorbent was prepared and was put into contact with NaCl solution (0.1 M) at different pH values. The aqueous suspension was

agitated for 48 h until the equilibrium pH was achieved. The pH value at the point of zero charge (pH_{pzc}) was determined by plotting the difference of final and initial pH (ΔpH) values versus the initial pH. As it is shown in Figure 6, the pH_{pzc} values of IL@ Fe_3O_4 nanoadsorbent is 8.0, which means that IL@ Fe_3O_4 nanoadsorbent is positively charged at $\text{pH} < 8.0$.

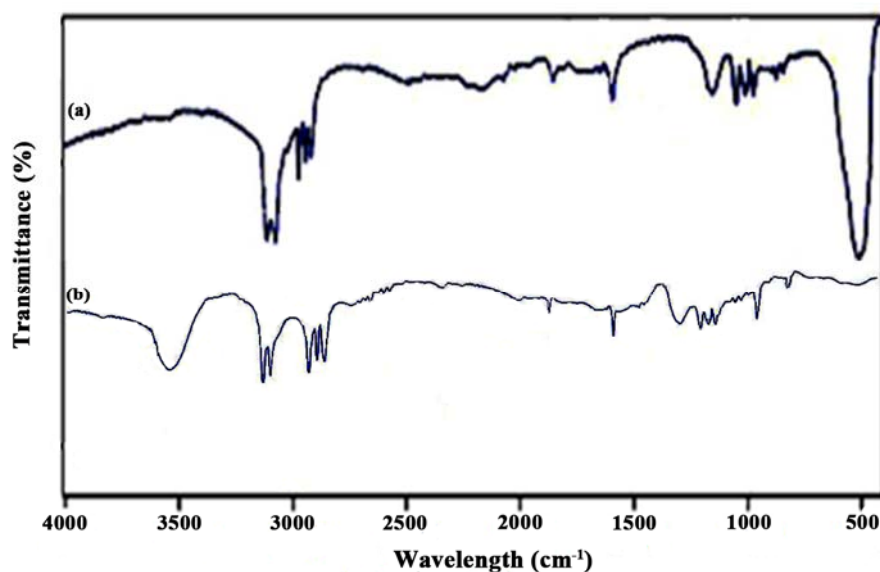


Figure 5: FTIR spectra of IL@ Fe_3O_4 nanoadsorbents (a) and pure IL (b).

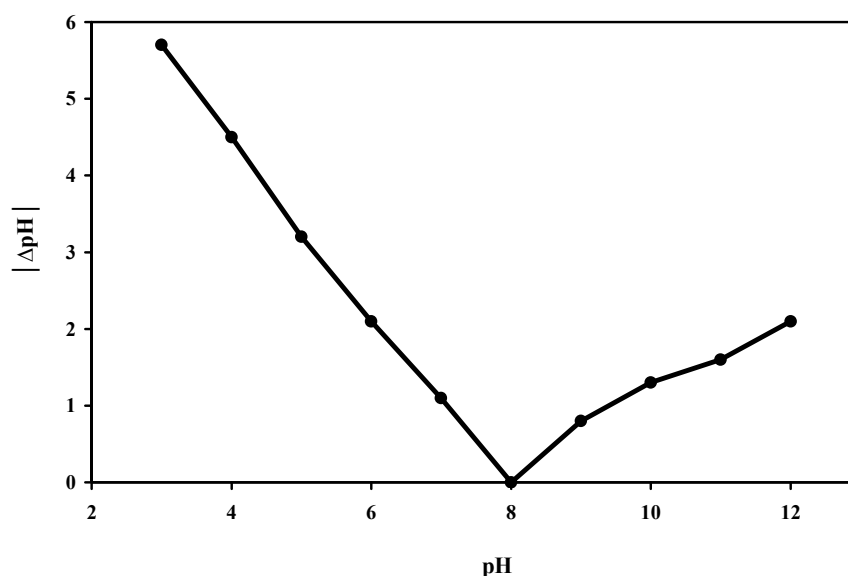


Figure 6: Immersion technique curves of IL@ Fe_3O_4 nanoadsorbents.

3.2.1. Effect of solution pH

The efficiency of sorption processes is strongly dependent on the pH, which affects the degree of ionization of the dye as well as the surface properties of the sorbent. Therefore the effect of the pH of the solution on the adsorption of AB113 onto IL@ Fe₃O₄ nanoparticles was assessed at different pH values, ranging from 1.0 to 11.0. Figure 7 clearly shows that the pH of the sample solution could affect the adsorption of AB113. It is evident that the sorption of AB113 initially increased with pH until pH 2.5, then decreased until pH 8 and further sloped down at pH 8.

The surface chemistry could explain this pH dependent trend. The surface of the adsorbent changes its polarization according to the value of the pH of the solution and the pH_{pzc} of the sorbent [31]. Thus, the pH influences both the surface state of the adsorbent and the ionization state of ionizable organic molecules. At $pH < pH_{pzc}$ (~8), the surface of IL@ Fe₃O₄ nanoparticles is positively charged. Since AB113 exposes negatively charged sulfonate SO₃⁻ groups and the pK value for hydrolysis of the sulfonate groups is 2.1, in the pH values lower than ~2.0 the dye molecules are presented in their positive or neutral forms; so it is conceivable that at low pH values, its adsorption is not favorable as a result of electrostatic repulsion between both positively charged nanosorbent and AB113 molecules. At $pH > 2.5$, the anionic form of AB113 predominates and the populations of negatively

charged nanoparticles are expected to be increased by pH; so there is a decrease in dye removal percent. Since the IL@Fe₃O₄ is negatively charged at $pH > 8.0$, the drop-off of the removal percent continues with larger slopes from pH 8 onwards. The observed pH trend is a good solution for the recovery of acid dye and regeneration of nanosorbent after extraction. For all subsequent experiments, pH 2.5 was employed.

3.2.2 Effect of contact time

The time dependence of AB113 removal was monitored for 60 min. It was seen that the maximum AB113 removal was obtained within the first 15 min, and then gently reached equilibrium in 30 min with no significant changes for the following 30 min.

3.2.3 Effect of adsorbent dosage

The optimum amount of the sorbent which can remove AB113 from aqueous solution was found via a batch-mode sorption. In due course the effect of various amounts (25–150 mg) of IL@ Fe₃O₄ nanoparticles was examined and the AB113 removal efficiency as a function of nanosorbents dosage is monitored. It was found that the AB113 removal percentage increases with the increases of nanosorbent dosage and 75 mg of nanoadsorbents has the best extracting ability to remove AB113 and the removal percent reached steady state.

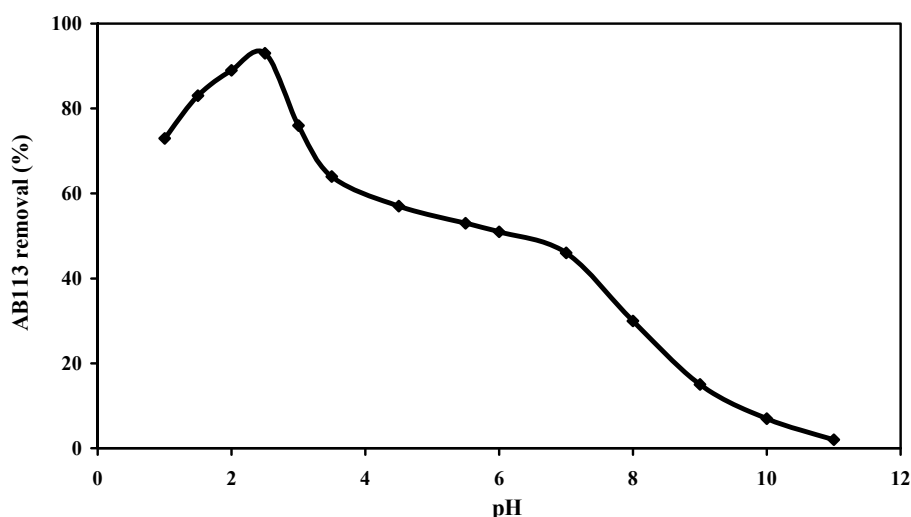


Figure 7: Effect of solution pH on the adsorption of AB113 by IL@ Fe₃O₄ nanoadsorbents.

3.2.4 Stripping and regeneration

In the evaluation of the performance of the sorbents, regeneration is an important factor to make an economic process. Due to their magnetic core, the nanosorbent could be easily separated by applying an external magnetic field and could then be recycled. In this work, NaOH was chosen as the stripping reagent for the recovery of Ab113 from the adsorbents. The concentration of the NaOH solution (1-20mM) was optimized and the results indicated that the highest recovery was obtained by using NaOH 10 mM solution (Table 1).

Finally, several consecutive adsorption-desorption cycles were performed and a change of -5% in the AB113 removal efficiency was defined as tolerance limit. The results show that after six adsorption-desorption cycles, the efficiency of nanosorbent for the AB113 removal was remained within the tolerance limit but after seven runs a 13% decrease in its performance was observed; therefore the reuse limit of the proposed sorbent was six cycles. It is the chemical bonding between IL and sorbent which makes the reuse of the sorbent possible.

3.2.5. Adsorption isotherm modeling

Langmuir and Freundlich models were used for the equilibrium adsorption data analysis of AB113 on IL@Fe₃O₄. The fitted experimental data with both models are shown in Figure 8. Table 2 summarizes the models constants and determination coefficients (R²).

Adsorption of the AB113 on IL@Fe₃O₄ is better described by Langmuir model with the greater R². Therefore, the adsorption occurs as the monolayer AB113 adsorb onto the homogeneous IL@Fe₃O₄ surface. The maximum predictable adsorption capacity is 92.59 mg AB113 per gram IL@Fe₃O₄.

Compared with other adsorbents, the adsorption capacity of 92.59 mg/g is much higher than that of obtained for magnetic molecularly imprinted polymer (water-soluble acid dyes, 71.12 mg/g) [32], activated carbon (Acid Red 97, 54.35mg/g) [33], macroporous anion exchanger (acid blue 29, 21.40 mg/g) [34], chitosan (acid red 73, 27.5 mg/g) [35], magnetic CuFe₂O₄ powder (Acid Red B ,86.8 mg/g) [36] and surfactant-modified mesoporous FSM-16 (acid blue , 55 mg/g) [37]. Although 92.59 mg/g is lower than that 133.30 mg/g obtained for non-living aerobic granular sludge toward acid yellow [38] and poly (amidoamine-co-acrylic acid) copolymer (Acid Blue 25, 3500 mg/g) [39], the proposed magnetic nanosorbent exhibits the advantages of ease of recovery by application of external magnetic fields instead of centrifuging or filtering the solution samples which provide the ability of treating large amounts of wastewater within a short time.

3.2.6. AB113 removal from synthetic wastewater

In order to evaluate the performance of the proposed nanomagnet for AB113 removal, solid-phase extraction was used under optimal conditions.

Table 1: Desorption data of AB113 using different eluents.

NaOH concentration (mM)	Recovery percent of AB113
1	92.3
5	94.2
10	98.3
15	98.3
20	98.3

Table2: Adsorption isotherms parameters of AB113 onto the IL@Fe₃O₄ nanoparticles.

Langmuir model			Freundlich model		
q _{max}	b	R ²	Log K _F	1/n	R ²
92.59	0.31	0.9974	1.5	0.28	0.79

The deionized water was spiked with AB113 to make a 100 mgL^{-1} solution. The batch adsorption experiment was carried out on 50 mL of this spiked sample under optimal conditions; i.e. contact time of 15 minutes, pH 2.5 and sorbent dosage of 75 mg. It was found that the Ab113 content decreased from 100 mgL^{-1} to 1.4 mgL^{-1} (98.6% removal efficiency). In this

test, the Ab113 removal efficiency of the proposed nanosorbent was also compared with the naked magnetite, Fe_3O_4 nanoparticles with silica shell and a pure ionic liquid, i.e. 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM]PF₆. Table 3 shows the enhanced AB113 removal efficiency of magnetic nanoparticles as a result of IL surface modification.

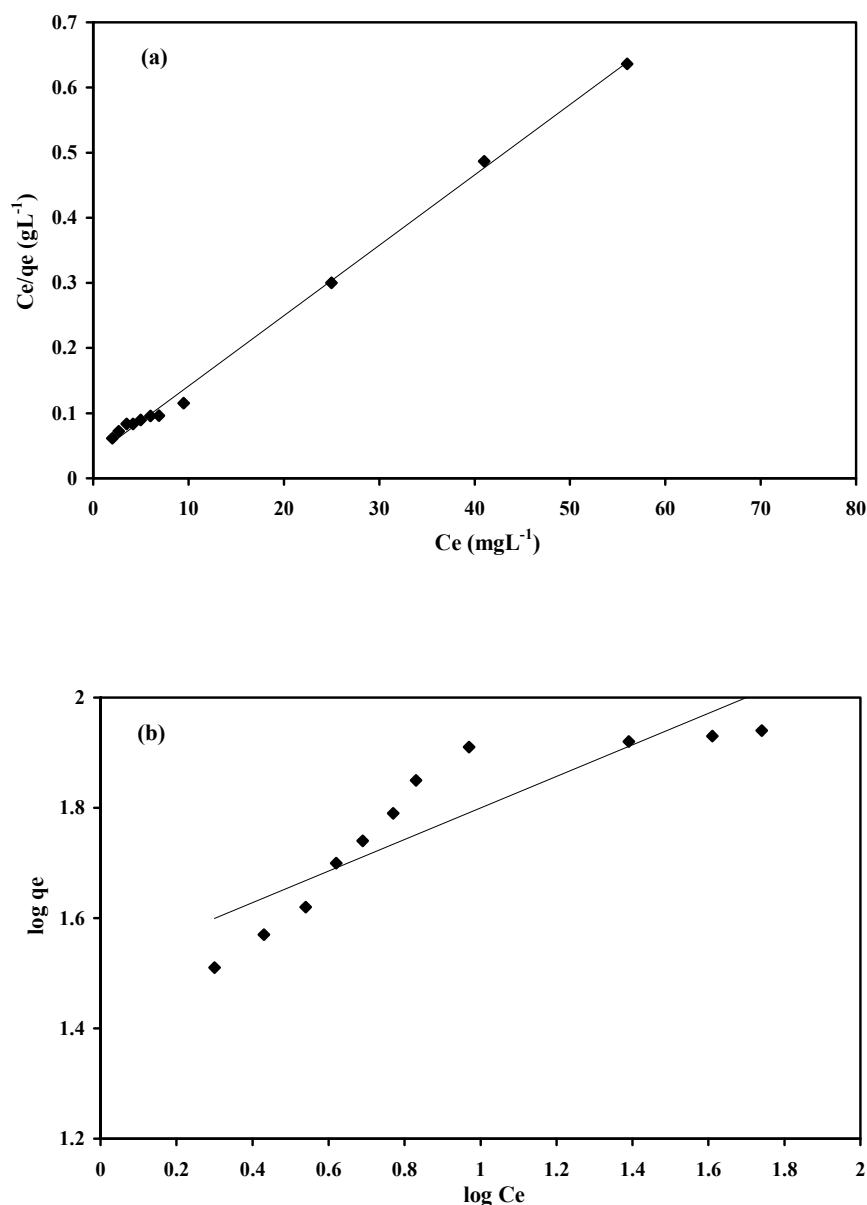


Figure 8: Isotherm plots of AB113 adsorption onto IL@Fe₃O₄ nanoparticles: (a) Langmuir isotherm and (b) Freundlich isotherm. Experimental conditions: IL@Fe₃O₄ dosage 25-150 mg, initial pH 2.5, stirring time 15 min, initial AB113 concentration 100 mg L^{-1} .

Table 3: AB113 removal efficiency for magnetite and surface modified magnetites.

Material	Removal efficiency (%)
Fe ₃ O ₄	53.3
Fe ₃ O ₄ nanoparticles with silica shell	67.2
Pure IL	85.1
IL@ Fe ₃ O ₄ nanoparticles	98.6

4. Conclusions

A new magnetic nanosorbents with the ability of acid dyes removal from wastewater is presented. FTIR spectra proved that IL molecules were covalently bonded to the surface of the magnetite. Some parameters such as contact time, sorbent dosage, pH and stripping reagent were optimized and under optimal conditions, 98.6% of AB113 after a single

extraction was removed. The adsorption data followed the Langmuir isotherm equation. The maximum predicted adsorption capacity was 92.59 mg of AB113 per gram of IL@ Fe₃O₄. The advantages of this product are the ease of separation by an external magnetic field, possibility of simple recovery after washing with a basic aqueous solution. It could be also reused for six successive removal cycles.

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