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Study of hexamine removal by activated carbon modified with magnetic iron oxide nanoparticles for application in treatment of hexamine industrial wastewater

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ABSTRACT

The industrial wastewater produced by hexamine plants is considered as a major environmental polluting factor, and hence its treatment is required. The adsorption of hexamine from aqueous solutions onto activated carbon modified with magnetic iron oxide nanoparticles (AC-MIONs) was studied in a batch process. Langmuir, Freundlich, and Toth isotherm models were used to fit the experimental data and then isotherm parameters were determined. The effects of activated carbon and AC-MIONs amounts, solution pH, contact time, temperature, and electrolyte concentration on the adsorption capacity were studied. The results indicate that AC-MIONs were a more efficient adsorbent for hexamine than activated carbon and have potential for the adsorption of hexamine from industrial hexamine wastewater. Pseudo-first order rate equation was able to provide realistic description of adsorption kinetics. The rate of adsorption process on AC-MIONs is higher than that on AC. Desorption of hexamine from AC-MIONs is easier than AC. Therefore, the AC-MIONs can be a good reusable and economical sorbent.

Keywords: Activated carbon; Iron oxide nanoparticles; Hexamine; Magnetic separation; Adsorbent

1. Introduction

The most important contaminants of water are organic compounds, microorganisms, and heavy metals which cause many problems for the environment. Consequently, treatment of water for industrial and potable uses is necessary. One of the polluted industrial wastewaters is the hexamine wastewater. Hexamine or hexamethylenetetramine, $(CH_2)_6N_4$, is a non-aromatic heterocyclic amine with a symmetrical three-dimensional molecular structure, as shown in Fig. 1. It is a white, crystalline powder with a slight amine odor, soluble in water (867 g/L at 25°C), alcohol, and chloroform, but it is insoluble in ether and has a melting point of 280°C. The pK_a value of hexamine is 4.89 [1] and pH of 10% aqueous solution

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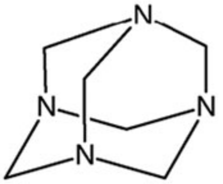


Fig. 1. The molecular structure of hexamine.

is 8–9. Hexamine is used for the production of plastic materials, explosives, phenolic resins, antibacterial pharmaceutics (as a urinary tract antiseptic), disinfecting materials, in the rubber industry as an additive, etc. [2]. The most common production method of hexamine in industrial scale is the reaction of formaldehyde with ammonia or ammonium salts. This reaction produces a considerable amount of heat and water. The soluble hexamine is simultaneously crystallized to produce crystalline hexamine [3]. The wastewater that is formed in the crystallization stage usually contains residual amounts of hexamine. Besides, the use of hexamine as an ammonia or formaldehyde donor may result in it being released to the environment through various waste streams [4].

Hexamine has a very stable structure (Fig. 1) which makes the molecule recalcitrant to oxidation via methylotrophic pathway reactions so that very few micro-organisms in soil can break it for utilization as sole source of carbon, nitrogen, and energy [5]. Therefore, hexamine is resistant to biodegradation [6], even when sludge has been acclimated for a long period [5,7]. Hexamine must be considered as a real wastewater pollutant and should not be allowed to enter water resources and soils. Hexamine is expected to have high mobility in soil based upon an estimated soil sorption coefficients value of 55 [8] and n-octanol-water partition coefficient (log K_{ow}) of –4.2 [9]. Therefore, if this antibacterial substance is discharged into water and soil, it can have potential health risk to human beings and living organisms. Elevated concentrations of antimicrobial pharmaceutical substances in the environment may lead to resistant bacterial strains through chromosomal mutations [10].

The high strength hexamine-containing wastewater is efficiently removed from industrial wastewater by means of a cation exchange resin [11]. This method requires an expensive cation exchanger resin and trace amounts of hexamine remain in wastewater. Therefore, it is necessary to adsorb the remains of hexamine with a complement method. Currently, adsorption by activated carbon (AC) is one of the most widely used and effective physical methods in the industries [12]. Unfortunately, the separation of AC from solutions is difficult. Magnetic separation is a new solid-phase extraction (SPE) method in which non-magnetic target such as organic molecule is adsorbed on magnetic particles and is then separated by an external magnetic field.

This work addresses the adsorption of hexamine solution on activated carbon modified with magnetic iron oxide nanoparticles (AC-MIONs) under a wide range of operating conditions with a combination of experimental and modeling studies. Equilibrium isotherm parameters are used to describe the experimental sorption data. Isotherm and kinetic parameters are determined using the method of non-linear least squares.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals and reagents were of analytical grade, and all dilutions have been carried out with doubly distilled water (DDW). Phosphoric acid (85 wt. %), ammonia solution (25 wt. %), hydrochloric acid (37 wt. %), $FeCl_3 \cdot 6H_2O$ (96%), $FeCl_2 \cdot 4H_2O$ (99.9%), and methanol were purchased from Merck. pH adjustments were performed with HCl and/or NaOH solutions (0.1 M). Phosphate buffer solution (pH 6) was prepared by adding appropriate amounts of sodium hydroxide solution (1 M) to the phosphoric acid solution (0.1 M). A 5% (w/v) aqueous solution of chromotropic acid (disodium salt dihydrate, Merck) was freshly prepared for determination of hexamine. The hexamine powder (99.5%) was from Sina Chemical Industries Co. (SCIC, Iran). It was re-crystallized from ethanol and dried at 60˚C to constant weight and used for preparation of standard solutions of hexamine. Stock solutions of hexamine were prepared by dissolving the powder in DDW. Hexamine solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions. The activated carbon (AC) powder (<100 μm) was supplied by Merck (Ref. 102186). It had a total BET surface area of 775 m^2/g before activation with nitric acid [13].

2.2. Apparatus

Weighing of materials was performed using an analytical balance model, Sartorius MCBA 100, with precision of ±0.0001 g. A Jenway 6300 spectrophotometer was used for spectrophotometric measurement of hexamine. For pH measurements, a Metrohm type 781 pH-meter was used. A vibrating sample magnetometer (VSM, Made in Kashan University) was used to characterize the magnetic properties of the nanoparticles at room temperature. The morphology of the nanoparticles was characterized by scanning electron microscope (SEM JXA-840, JEOL, Japan). The size of the nanoparticles was characterized by transmission electronic microscopy (TEM, Zeiss, EM10C, 80 kV). The AC-MIONs powder was dispersed in DDW by Misonix S3000 sonicator. A drop of the resultant suspension was deposited on a Formvar carbon-coated grid Cu (300 Mesh) and then introduced into the microscope column. The structure of AC-MIONs was analyzed by a STOE X-ray diffractometer system at room temperature. The thermogravimetric analysis (TGA) of AC-MIONs was performed on a Rheometric Scientific STA 1500 thermal analyzer. The BET surface area of AC-MIONs was determined from N_2 adsorption isotherm with a Surface Area Analyzer (Quantasorb) and the result was 789 m^2/g.

2.3. Procedures

2.3.1. Preparation of AC

The activated carbon (AC) was extensively washed and activated with 3 M nitric acid solution and DDW to remove impurities and enhance the active surface of carbon particles. Then the AC was filtered and dried overnight at 100℃ and stored in a desiccator until use.

2.3.2. Preparation of AC-MIONs

4.4 mL of $FeCl_3.6H_2O$ (1 M) was mixed with 1.2 mL of $FeCl_2.4H_2O$ (2 M) in a beaker. Then the previously washed activated carbon powder was added and mixed completely using a mechanical stirrer. Ammonia (1 M) solution (50 mL) was added dropwise to the solution with constant stirring. Iron oxide nanoparticles were adsorbed with maximum amount of activated carbon to enhance the adsorption capacity of the particles. The beaker was then placed on the magnet and after complete settlement of AC-MIONs, the solution was decanted. AC-MIONs particles were washed several times with water to remove excess ammonia solution.

2.3.3. Adsorption studies on AC and AC-MIONs

For adsorption study on AC, a weighed amount (0.36 g) of adsorbent was added to 50 ml of hexamine solution (20 mg L^{-1}). All experiments were carried out in 100 mL Erlenmeyer flasks at 25℃ with a stirring speed of 400 rpm. The solutions were centrifuged and then the concentrations of hexamine were determined.

Adsorption of hexamine on AC-MIONs was investigated using a 50 mL solution of hexamine (20 mg L^{-1}) with 3 mL of phosphate buffer (pH 6) in a beaker. Damp AC-MIONs (0.32 g), which was equivalent to 0.037 g of dry AC-MIONs was added to the beaker and the mixture was stirred for different durations at 400 rpm. Hexamine adsorbed AC-MIONs were then collected by placing the beaker on the magnet.

Determination of hexamine was performed spectrophotometrically [14]. The amount of hexamine adsorbed onto the sorbent in mg/g was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_e is the equilibrium concentration of hexamine in the solution in mg/L, C_0 is initial hexamine concentration in mg/L, m is the amount of sorbent mass in grams, and V is the solution volume in L.

2.3.4. Mathematical modeling

The isotherm and kinetic models were used to describe the sorption data generated from hexamine sorption. The isotherm and kinetic parameters were determined by minimizing the error functions using the solver add-in with Microsoft's spreadsheet, Excel. Chi-square statistic was used to evaluate the fitness of isotherm and kinetic equations to the experimental data. The chi-square test statistic is the sum of the squares of the differences between the experimental data and data obtained by calculating from models. The equivalent mathematical statement is:

$$\chi^2 = \sum_{i=1}^{N} \frac{\left(q_{e,\exp.} - q_{e,calc.}\right)^2}{q_{e,calc.}} \tag{2}$$

where $q_{e,\exp.}$ and $q_{e,\mathrm{calc.}}$ are the equilibrium capacity obtained by experimental data and calculating from the model in mg/g, respectively. If data from the model are similar to the experimental data, χ^2 will be a small number; if they are different, χ^2 will be a large number.

3. Results and discussion

3.1. Characterization of AC-MIONs

The magnetic characterization of AC-MIONs and its enlargement near the origin were shown in Fig. 2.

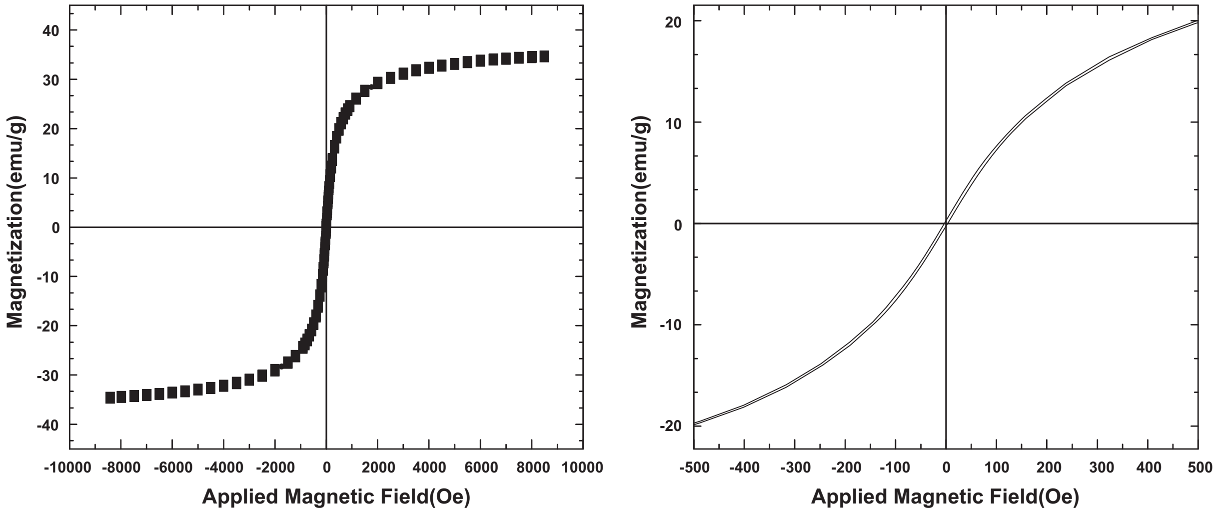


Fig. 2. Magnetization curve of AC-MIONs.

As can be seen, the resultant magnetic nanoparticles have high magnetism and superparamagnetic behavior with saturation magnetization (Ms) of 34.6 emu/g (in the magnetic field equal to ±8.5 kOe). Fig. 3 shows that the particles of AC-MIONs can be easily separated by an external magnet. The change of solution from black to clear can be quickly obtained within a few minutes. The TEM image of AC-MIONs (Fig. 4) revealed that iron oxide nanoparticles (darker particles) were distributed at the surface of AC and assigned its magnetic properties. As can be seen, these particles have a nanometric size. In order to confirm the type of iron oxide particles at the surface of AC to be Fe_3O_4, the AC-MIONs sample was measured by X-ray powder diffraction. From the XRD pattern of AC-MIONs (Fig. 5), the typical peaks of Fe_3O_4 can be observed [$2\theta = 30.13^\circ$ (220, $d = 2.96$ Å), 35.46° (311, $d = 2.53$ Å), 43.16° (400, $d = 2.09$ Å), 56.89° (511, $d = 1.61$ Å), and 62.43° (440, $d = 1.48$ Å)]. The typical peaks at $2\theta = 28.64^\circ$ (111, $d = 3.11$ Å) and 46.63° (220, $d = 1.95$ Å) are from AC. TGA was used to calculate the loading of the magnetic component on AC. TGA curve of AC-MIONs that provided the maximum adsorption capacity was shown in Fig. 6. This curve indicates that there was about 65 wt. % of Fe_3O_4 in AC-MIONs nanocomposite. The weight loss from 360 to 550°C is related to the oxidation of the carbon [15]. The morphology of AC-MIONs was evaluated by SEM and compared with the morphology of AC (Fig. 7).

Fig. 3. Photograph of magnetic separation of AC-MIONs from solution.

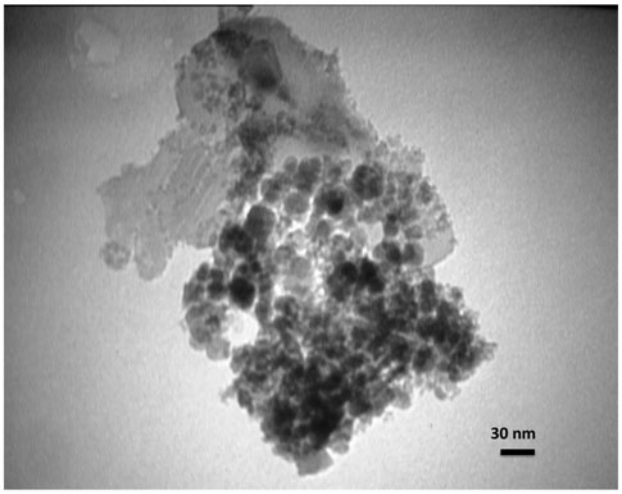


Fig. 4. TEM image of AC-MIONs.

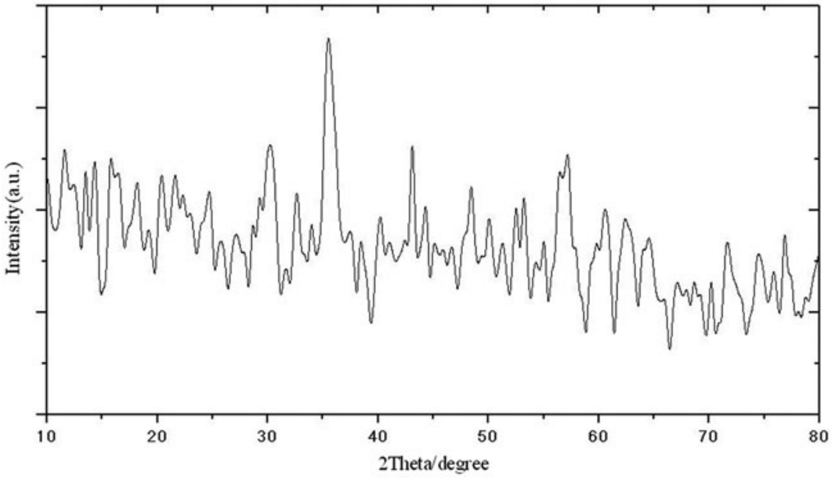


Fig. 5. XRD pattern of AC-MIONs.

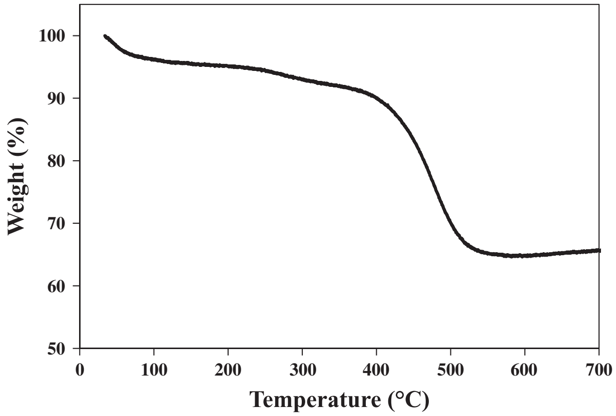


Fig. 6. TGA curve of AC-MIONs (AC amount in AC-MIONs = 0.24 g).

3.2. Effect of the amount of activated carbon

The amount of activated carbon that was used for the preparation of AC-MIONs by the above mentioned procedure was optimized. As it is shown in Fig. 8(a), the optimum amount of activated carbon coated with the magnetic iron oxide nanoparticles is 0.24 g, i.e. about 65 wt. % of Fe_3O_4 in AC-MIONs (Fig. 8(b)). Without using activated carbon there was no significant adsorption and hence removal of hexamine. The AC-MIONs adsorb more amounts of hexamine in comparison with AC alone (Fig. 8(a)). This increase can be attributed to large surface area and the availability of more adsorption sites in AC-MIONs and this is confirmed in SEM images (Fig. 7) and in the result of the BET surface area of AC-MIONs (789 m^2/g).

3.3. Effect of the AC-MIONs amount

The adsorption of hexamine by AC-MIONs was studied using varying quantities of damped AC-MIONs from 0.08 to 0.56 g, for removal of hexamine from 50 mL of the test solution (20 mg/L), while other variables were kept constant. Maximum adsorption was obtained when the amount of AC-MIONs was 0.32 g (Fig. 9), and therefore 0.32 g of damp AC-MIONs (equivalent to 0.037 g of dry AC-MIONs) was used for further experiments.

3.4. Effect of solution pH

To investigate the role of surface chemistry of AC-MIONs on the adsorption capacity of hexamine and comparison with AC, the effect of solution pH was studied. The experiments were carried out by varying the initial pH under a constant initial hexamine concentration of 20 mg/L. The effect of solution pH on the adsorption of hexamine (Fig. 10) shows that the amount of adsorption increases when the pH is between 3 and 6 for AC-MIONs and 12 and 14 for AC. The pH value of 6 can be used for the removal of hexamine from real wastewater by AC-MIONs. It is clear that medium pH ranges for AC-MIONs is more of an advantage than high pH values for AC because the pH of industrial hexamine wastewater is about 8 [16,17]. In low pH values, the solution became dark brown because of dissolution of nanoparticles. On the other hand, in solutions with high pH values, the particles were converted to colloidal form and did not settle by the applied magnetic field.

The charge of the surface can be important for understanding the adsorption of ionic species. A

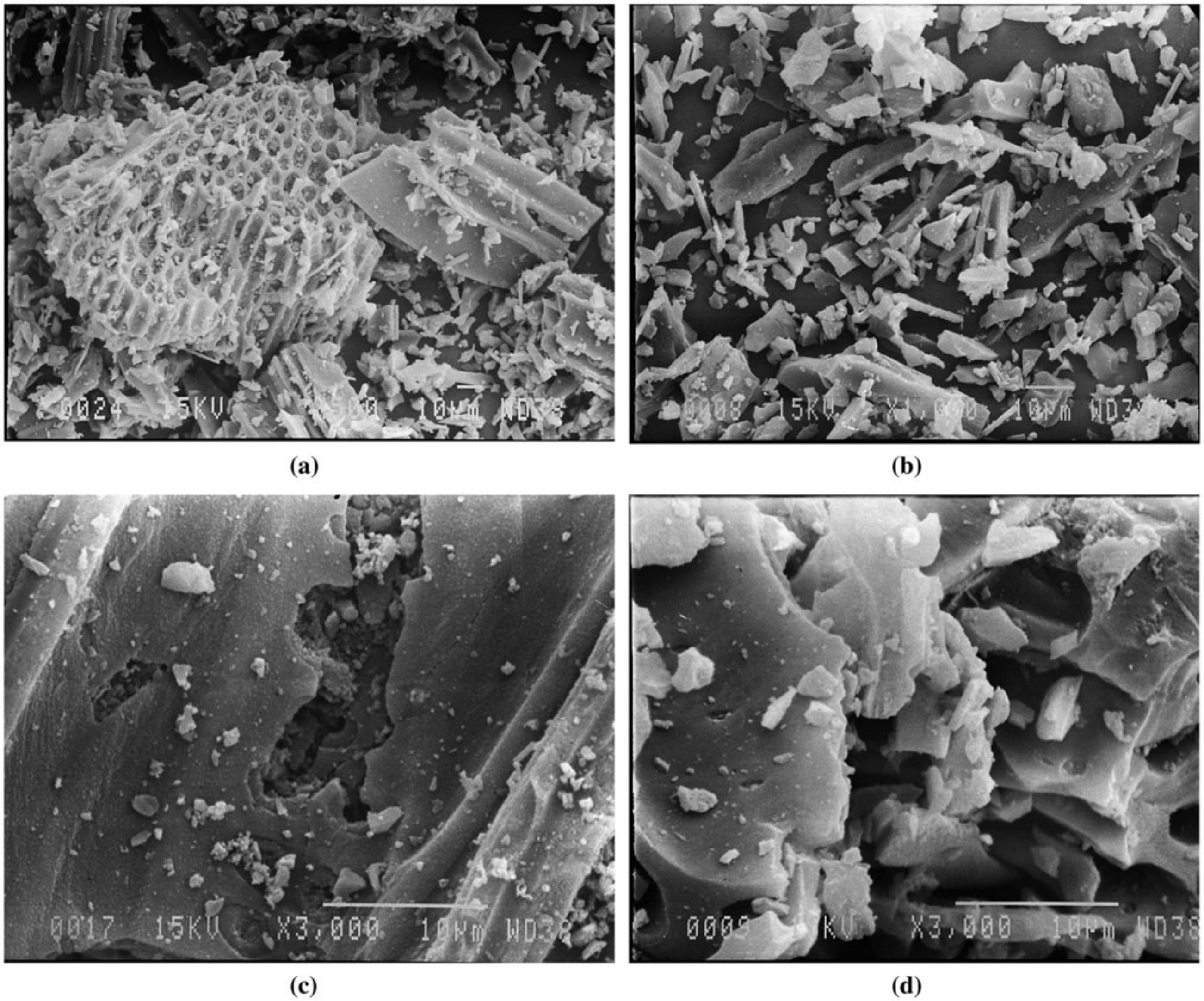


Fig. 7. SEM images of AC-MIONs (a, c) and AC (b, d).

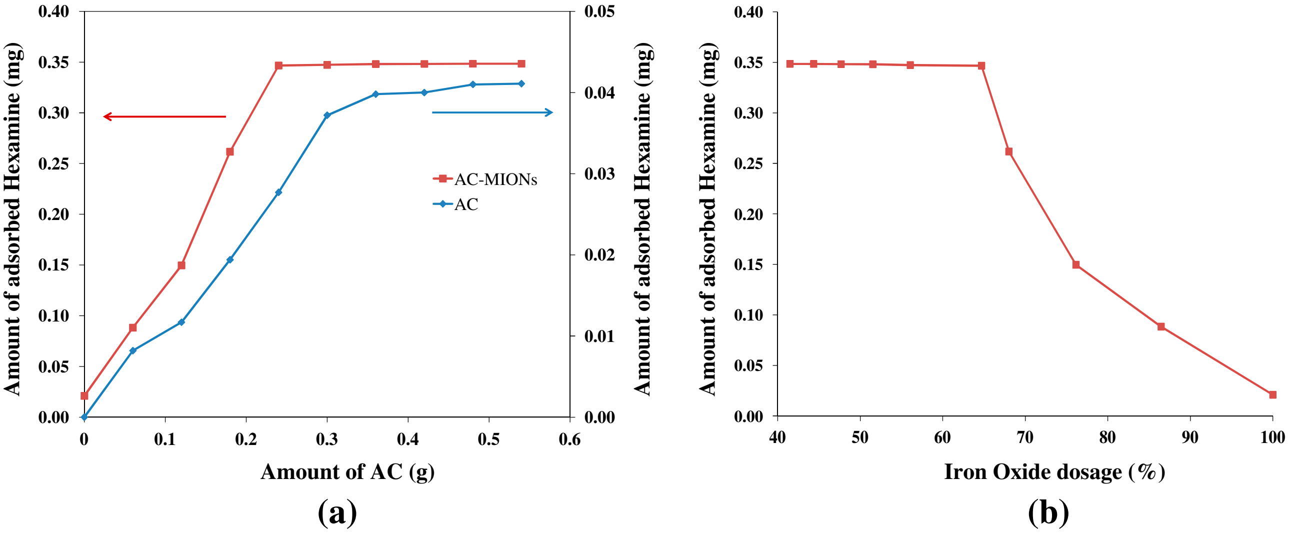
common indicator of the surface acidity is the value of the potential of zero charge (pzc) defined as the value of pH at which the net surface charge is zero. If the adsorption pH is equal to the pzc the surface will be neutral, but if the adsorption pH is lower than the pzc the surface is positively charged. The pH_{pzc} of AC-MIONs in aqueous solution is 6.4 [18]. When pH is lower than 3, hexamine ($pK_a = 4.89$) is cationic and electrostatic repulsion with surface exists. At pH 3–6, hexamine approaches to neutral form and electrostatic attraction exists between partial negatively charged nitrogen atoms of hexamine (due to the existence of the nonbonding electron pairs) and the positively charged surface of AC-MIONs. It is maintained until pH is about 6. When pH is greater than 6, the surface charge is negative and hexamine is repulsed.

3.5. Effect of contact time (kinetic studies)

For evaluating the adsorption kinetic of hexamine, the effect of stirring time was studied (Fig. 11). Then, pseudo-first order and pseudo-second order kinetic models were used. The conformity between experimental data and the model-predicted values was expressed by nonlinear Chi-square statistic. The Lagergren pseudo-first order kinetic model is expressed as Eq. (3) [19]:

$$q_t = q_e - q_e 10^{\frac{-k_1 t}{2.303}} \tag{3}$$

where q_t and q_e are the amount of hexamine adsorbed (mg/g) at any time and equilibrium time, respectively, and k_1 is the rate constant in $\min^{-1}$.



(a)

(b)

Fig. 8. (a) Effect of different amounts of AC and (b) effect of iron oxide dosage on the adsorptive removal of hexamine ($C_0 = 20$ mg/L, $V = 50$ mL, damp AC-MIONs dosage = 0.3 g, pH 8.5, contact time = 1 h and $T = 25$°C).

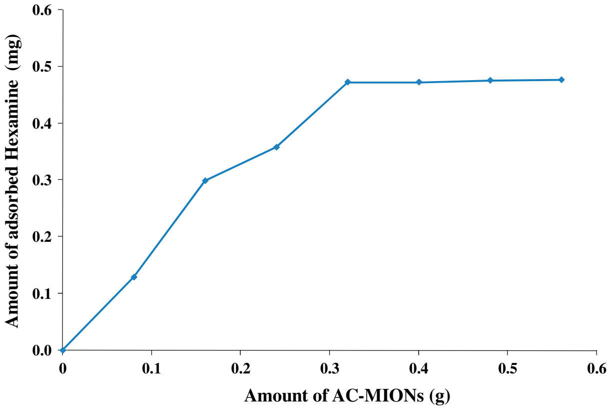


Fig. 9. Effect of different amounts of AC-MIONs on the adsorptive removal of hexamine ($C_0 = 20$ mg/L, $V = 50$ mL, AC amount in AC-MIONs = 0.24 g, pH 8.5, contact time = 1 h and $T = 25$°C).

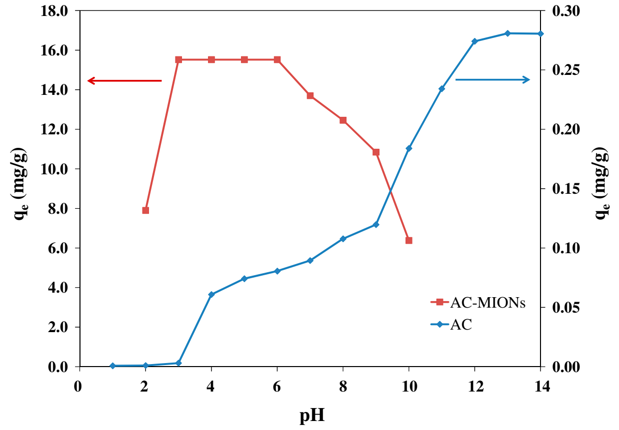


Fig. 10. Effect of solution pH on the adsorptive removal of hexamine by AC-MIONs and AC ($C_0 = 20$ mg/L, $V = 50$ mL, dry AC-MIONs dosage = 0.037 g, AC dosage = 0.36 g, contact time = 1 h and $T = 25$°C).

The Ho pseudo-second order rate equation is expressed as Eq. (4) [19]:

$$q_t = \frac{q_e^2 k_2 t}{q_e k_2 t + 1} \tag{4}$$

where k_2 is the rate constant of pseudo-second order model in g/mg.min. The values of chi-square statistic and rate constants of the pseudo-first order and pseudo-second order models for AC and AC-MIONs are shown in Table 1. As can be seen, the values of chi-square statistic of the first-order model for AC and AC-MIONs are lower than corresponding values for the pseudo-second order model. These results show that pseudo-first order equation of Lagergren could fit well over the range of contact times and suitably describe the kinetic of hexamine sorption onto AC and AC-MIONs. The adsorption rate and equilibrium sorption capacity (q_e) on AC-MIONs is higher than these on AC. It should be noted that the pseudo-second order kinetic model considers the rate-limiting step as the formation of a chemisorptive bond involving sharing or exchange of electrons between the sorbate and the sorbent [18]. Therefore, the good agreement

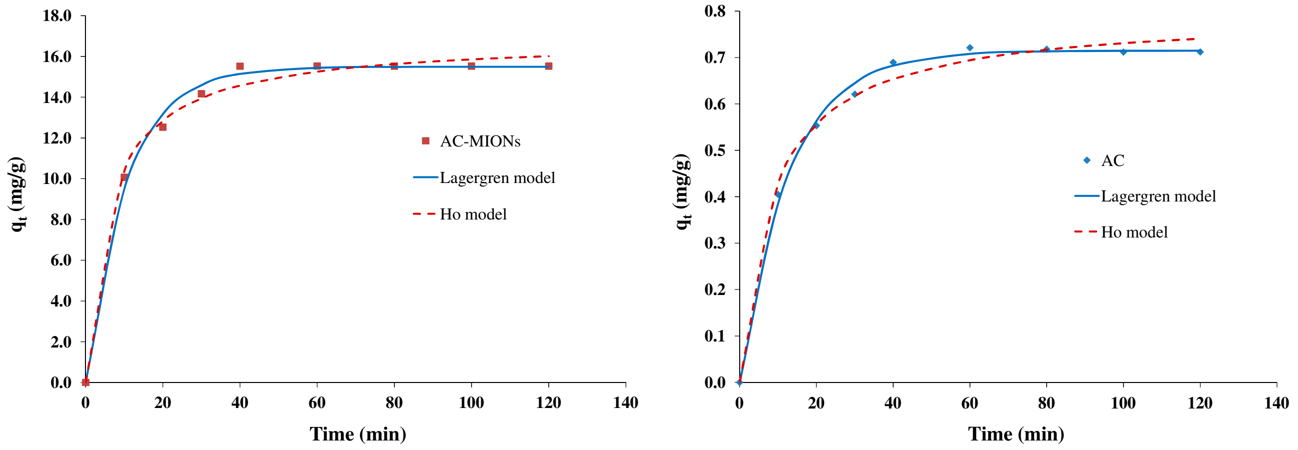


Fig. 11. Kinetic experimental data, pseudo-first order and pseudo-second order models of hexamine sorption onto AC and AC-MIONs. The lines indicate the fit to kinetic models (C_0=20 mg/L, V = 50 mL, dry AC-MIONs dosage = 0.037 g, AC dosage = 0.36 g, T = 25˚C, pH 13 for AC and pH 6 for AC-MIONs).

Table 1
Parameters of the kinetic models for the adsorption of hexamine onto AC and AC-MIONs

Model	Parameter	Value	
		AC	AC-MIONs
Pseudo-first order	k_1	0.077	0.095
	q_e	0.715	15.492
	χ^2	0.002	0.089
Pseudo-second order	k_2	0.1466	0.0094
	q_e	0.794	16.853
	χ^2	0.006	0.108

between experimental data and pseudo-first order model (Fig. 11) indicates that the controlling mechanism of adsorption process onto AC and AC-MIONs is not chemical interaction.

3.6. Effect of temperature and thermodynamic parameters

Fig. 12 shows the experimental results of hexamine adsorption on AC and AC-MIONs when temperature was increased from 5 to 50˚C. Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process. Plot of the adsorption capacity as a function of temperature (see Fig. 12) showed that the adsorption of hexamine on AC was decreased as a result of an increase in the solution temperature. This can be explained by the exothermic adsorption process ($\Delta H < 0$, Table 2) and the weakening of bonds between hexamine molecules and active sites of adsorbent at high temperatures.

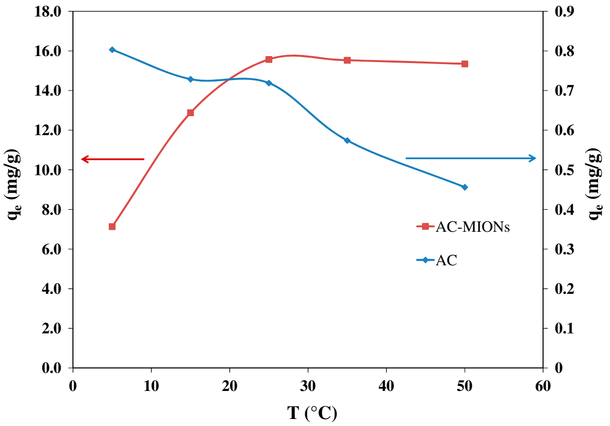


Fig. 12. Effect of temperature on the adsorptive removal of hexamine (C_0 = 20 mg/L, V = 50 mL, dry AC-MIONs dosage = 0.037 g, AC dosage = 0.36 g, contact time = 1 h, pH 13 for AC and pH 6 for AC-MIONs).

On the other hand, the observed increase in adsorption hexamine by AC-MIONs can be explained by the endothermic adsorption process ($\Delta H > 0$, Table 2). The observed small decrease in the adsorption at much higher temperature could be attributed to the weakening of the attractive forces between hexamine and active sites on the magnetic beads.

The maximum adsorption capacity is at 5 and 25˚C for AC and AC-MIONs, respectively. It is clear that ambient temperature for AC-MIONs is more of an advantage than low temperature for AC.

The thermodynamic parameters for the adsorption process, ΔH° and ΔS°, were evaluated using the Van't Hoff equation:

Table 2
Thermodynamic parameters for the adsorption of hexamine on AC-MIONs and AC

Adsorbent	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol) @ 298 °K
AC-MIONs	79.4	292.7	−7.8
AC	−8.0	−21.1	−1.7

$$\log K_c = -\frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R} \tag{5}$$

where ΔH° and ΔS° are enthalpy (kJ/mol) and the entropy (kJ/mol K) change of adsorption, respectively, R is universal gas constant (8.314 J/mol K), and T is the absolute temperature (°K).

The values of log K_c were defined as follow [20]:

$$\log K_c = \frac{F_e}{1 - F_e} \tag{6}$$

where F_e is the fraction of hexamine adsorbed at equilibrium.

The values of ΔH° and ΔS° were calculated from the slope and intercept of linear regression of log K_c vs. 1,000/T. The value of ΔG° was estimated by:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{7}$$

The calculated thermodynamic parameters are given in Table 2. The values of ΔG° indicate that the adsorption process on AC-MIONs is more desirable than that on AC, i.e. $\Delta G^\circ_{\text{AC-MIONs}} < \Delta G^\circ_{\text{AC}}$.

3.7. Effect of electrolyte concentration

The effect of adding 1×10^{-4}–5×10^{-4} M NaCl salt to solutions of hexamine prior to adsorption onto AC and AC-MIONs is shown in Fig. 13. The results found from the effect of added salt showed the presence of NaCl in the range of 1×10^{-4}–5×10^{-4} M had no effective influence on the adsorption capacity of hexamine onto AC-MIONs but significantly increased the adsorption capacity of hexamine onto AC and then decreased it. It seems the physical process is dominant over the chemisorption process in the adsorption of hexamine onto AC-MIONs since the adsorption capacity is not influenced by electrostatic forces (various concentrations of NaCl). But in the case of AC, the chemisorption process is dominant over the physical process.

3.8. Adsorption isotherm models

Equilibrium isotherm equations are used to describe the experimental sorption data. The most common isotherms for describing solid–liquid sorption systems are the Langmuir, the Freundlich, and the Toth isotherms. Fig. 14 shows the experimental aqueous-phase adsorption isotherms for hexamine/AC-MIONs system along with the curve fitted by isotherm models. The isotherm parameters and values of chi-square are also shown in Table 3. Examination of isotherm plots (Fig. 14) shows that Toth and Langmuir isotherms more accurately describe the sorption behavior of hexamine on AC-MIONs. Since the method used to derive the isotherm parameters minimizes the chi-square statistic, the Toth and Langmuir isotherms exhibit low values that produce a better fit. The values of maximum adsorption capacity (q_m) and K_a determined using Langmuir model are 18.199 mg/g and 0.283 L/mg, respectively. The q_m value for AC-MIONs is about 17 times larger than AC [12]. The value of K_a is the constant representing the affinity of sorbate to sorbent. The larger K_a value of AC-MIONs indicates that hexamine has a relatively higher affinity for AC-MIONs surface than AC surface ($K_a = 0.011$ [12]). The adsorption data obeyed Langmuir and Toth models exhibiting heterogeneous surface conditions and monolayer adsorption. Therefore, the adsorbate has a high affinity for the surface at low surface coverage. However, as coverage increases, the affinity of the adsorbate for the surface decreases (Fig. 14). The order of adsorption isotherm models for AC are Langmuir > Toth > Freundlich [12].

The Freundlich exponent, $1/n$, should have values lying in the range of 0.1–1 for classification as favorable adsorption [21] and it has been shown that this value between 0.1 and 0.5 indicate beneficial adsorption [22]. The adsorption system approaches to chemical process and distances from physical process whenever the value of n approaches to unity and below unity [20]. The value of n in AC-MIONs system (8.47) indicates that the adsorption process is physical as dominant but the adsorption process of hexamine onto AC is a combination of chemisorption as dominant and physical adsorption [12]. These explanations

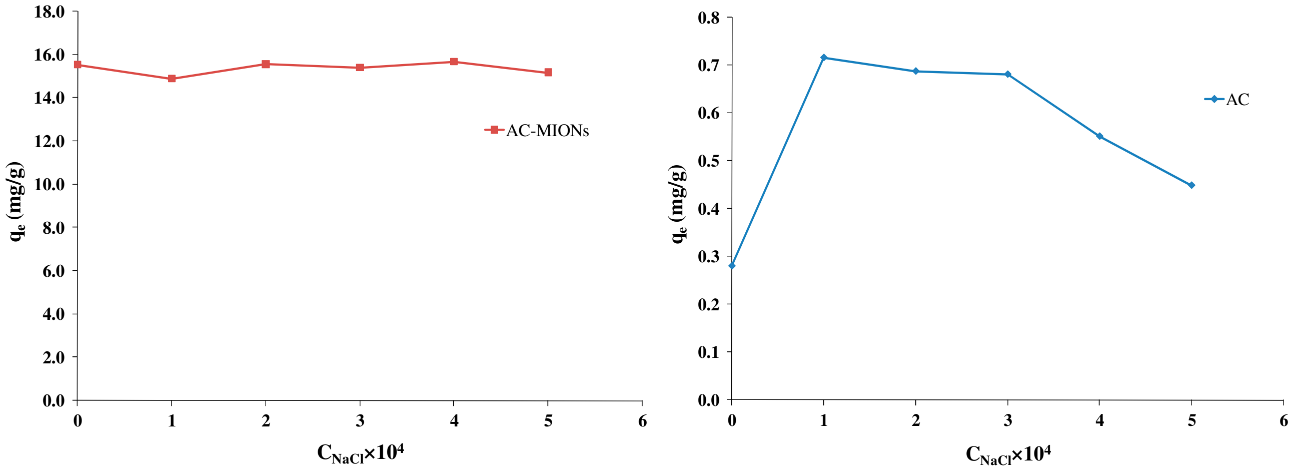


Fig. 13. Effect of electrolyte concentration on the adsorptive removal of hexamine ($C_0 = 20$ mg/L, $V = 50$ mL, dry AC-MIONs dosage = 0.037 g, AC dosage = 0.36 g, contact time = 1 h, pH 13 for AC and pH 6 for AC-MIONs and $T = 25$°C).

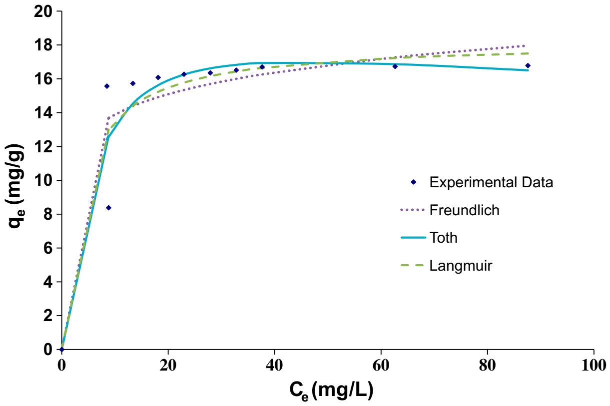


Fig. 14. Langmuir, Freundlich and Toth isotherms for the adsorption of hexamine by AC-MIONs ($V = 50$ mL, sorbent dosage = 0.037 g, pH 6 and $T = 25$°C).

Table 3
Parameters of the isotherm models for the adsorption of hexamine onto AC-MIONs

Model	Equation	Parameter	Value	χ^2
Toth	$q_e = \frac{K_t C_e}{(a_t + C_e)^{1/t}}$	K_t	43.401	2.350
		a_t	8.743	
		$1/t$	1.191	
Langmuir	$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$	q_m	18.199	2.446
		K_a	0.283	
Freundlich	$q_e = K_F C_e^{1/n}$	K_F	10.597	2.763
		$1/n$	0.118	

are consistent with the solution pH and electrolyte concentration effects that imply the adsorption process is different between AC-MIONs and AC.

3.9. Desorption and reuse studies

The ability of reusing the adsorbents in several successive adsorption and desorption processes is very important for practical applications. Desorption process was conducted by washing hexamine loaded on adsorbent using 50 mL of methanol. Then, the adsorbent was reused for removal of hexamine. The results of efficiency of adsorption (calculated based on the initial adsorption amount) are shown in Table 4. The obtained results (Table 4) show that the AC (at least 2 cycles with performance >66%) and AC-MIONs (at least 4 cycles with performance >81%) can be reused using the same experimental studies. Hexamine desorption from AC-MIONs is easier than AC because the adsorption process is physical for AC-MIONs. This observation is the other confirmation for previous results. The effectiveness of regeneration for AC adsorbent is significantly less. This suggests that the AC-MIONs adsorbent is considerably stable during the adsorption of hexamine and can be a good reusable and economical sorbent.

Table 4
The ability of reusing the adsorbents (AC and AC-MIONs) on adsorption removal of hexamine in the optimal reaction conditions

Cycles	AC Efficiency (%)	AC-MIONs Efficiency (%)
1	96	98
2	66	91
3	45	84
4	13	81

4. Conclusions

The results of the present investigation showed that the activated carbon modified with magnetic iron oxide nanoparticles has higher potential for the adsorption of hexamine than lone activated carbon and can be used for removing low concentrations of hexamine from industrial hexamine wastewater. The prepared magnetic adsorbent can be well dispersed into the water and be easily separated magnetically from the medium after adsorption. The adsorption rate is more rapid than AC which is mainly attributed to the large surface area of adsorbent and good affinity for the facile and fast adsorption of hexamine molecules.

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