



Adsorption of Acid Red 114 onto Fe₃O₄@Caffeic acid Recyclable Magnetic Nanocomposite

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Abstract: In this study, the adsorption capacity of caffeic acid (CFA) functionalized Fe₃O₄ magnetic recyclable nanocomposite (Fe₃O₄@CFA MNC) for removal of industrial dye Acid Red 114 (AR 114) was investigated. The maximum adsorption (q_m) of the Fe₃O₄@CFA MNC for AR114 was 333 mg/g without pH correction of the solution. Compared with other studies these adsorbent possess high adsorption capacity for AR114 dye. The adsorption isotherm data and the process of adsorption kinetics were fitted using the Langmuir equation and a pseudo-second-order kinetic model that showed chemisorption may be the rate controlling step in the adsorption processes. It was proved that the magnetic NMs technology was contributed by this study which can be a new and covetable alternative for organic contaminant adsorption. Furthermore, the reusability of the Fe₃O₄@CFA MNC was investigated and significant removal of AR114 obtained even after five cycles.

Keywords: Waste water treatment; Magnetic nanocomposite; Adsorption; Acid Red 114.

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INTRODUCTION

The textile industry is the main source of today's industrial wastewater due to its high water consumption. These types of wastewater are produced at the end of dyeing and finishing processes which release large amount of dyes to the environment. There are over 100,000 kinds of dyes commercially available (1). A serious number of these dyes are synthetic which contain carcinogenic and mutagenic aromatic rings (2). The presence of large amount of these stable organic compounds in industrial wastewater make their degradation/removal difficult for many methods which are coagulation, adsorption, precipitation, flocculation and ozonization (3,4). However, the adsorption is inexpensive and readily available. Due to its low maintenance, adsorption is an effective method for the dye removal (5-8).

Due to the potential for human exposure during production of bisazobiphenyl dyes which contains benzidine, a carcinogen chemical, Acid Red 114 was nominated for this study (9).

Since the presented $\text{Fe}_3\text{O}_4@\text{CFA}$ MNC contains either carboxylate groups or magnetic component, it can be an excellent candidate for the application of adsorption of various different dyes (10). Zhang *et al.* studied the adsorption of methylene blue onto HA-coated Fe_3O_4 MNC. They reported typical superparamagnetic characteristics and great reactive activity for MB adsorption of $\text{Fe}_3\text{O}_4@\text{CFA}$ MNC (11). Cao *et al.* studied the high adsorption capacity of magnetic $\text{Fe}_3\text{O}_4/\text{chitosan}$ nanoparticles and removal of brilliant red (X-3B) (12). In another study, Chang *et al.* synthesized the $\text{Fe}_3\text{O}_4/\text{activated montmorillonite}$ ($\text{Fe}_3\text{O}_4/\text{Mt}$) nanocomposite with co-precipitation method and found out over 83.73% color removal of MB (13). Mesoporous graphene/ $\text{Fe}_3\text{O}_4/\text{chitosan}$ nanocomposite was also used for the adsorption capacity for a textile dye (methylene blue) and found out that the adsorption capacity reached 98% within a contact time of 5 min at pH 9 and an initial dye concentration of 25 mg/L (14). Tan *et al.* used the activated maize cob impregnated with magnetic nanoparticles (Fe_3O_4 nanoparticles) for methylene blue (MB) adsorption found out 99.63% (15). Lee and Thinakaran *et al.* also reported on the removal of AR 114 by different techniques (16, 17). However, none of the studies reported on the remediation of AR 114 by adsorption method.

In this study, an inexpensive magnetic adsorbent, $\text{Fe}_3\text{O}_4@\text{CFA}$ MNC, was easily synthesized (18, 19). The adsorption of the Acid Red 114 (Fig 1a) dye onto $\text{Fe}_3\text{O}_4@\text{CFA}$ MNC (Fig 1b) has been studied, and the adsorption reactions were argued. Reutilizing the adsorbents saturated with dyes were evaluated and an efficient method was introduced.

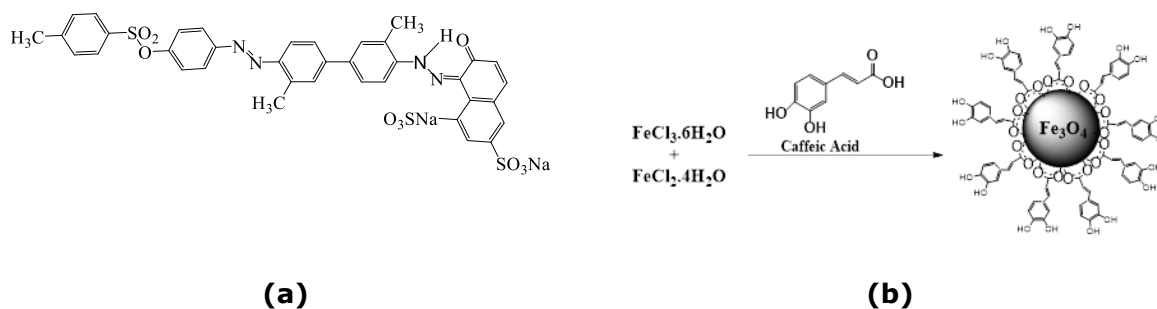


Figure 1. The chemical structure of **a)** Acid Red 114 and **b)** Fe₃O₄@CFA MNC

MATERIALS AND METHODS

Materials

FeCl₃.6H₂O, FeCl₂.4H₂O, Magnetite (Fe₃O₄) Caffeic acid (CFA), NH₃, Acetic Acid, NaOH, Methanol, and HCl were purchased from Merck and used without further purification. The adsorbate AR 114 was purchased from Sigma–Aldrich.

Instrumentations

Thermo Spectronic Aquamate Visible Light Spectrophotometer 315 to 1100 nm wavelength range; 50/60 Hz. Light source was a Tungsten lamp.

Biosan PSU-10i Orbital Shaker was used to stir Fe₃O₄@CFA MNC with Acid Red 114.

EXPERIMENTAL PROCEDURE

Preparation of Adsorbate

For the synthesis of Fe₃O₄@CFA MNC, 10 mL of 0.4 M iron chloride solution (FeCl₃ 6H₂O) and 10 mL of 0.2 M of iron chloride solution (FeCl₂ 4H₂O) were mixed in distilled water. A specified amount of caffeic acid was added to the solution as a surfactant and coating material. A 1.5 M solution of sodium hydroxide (NaOH) was prepared and slowly added to the salt solution dropwise. The pH of the solution was constantly monitored as the NaOH solution was added. The reactants were constantly stirred using a magnetic stirrer until a pH level of 7–8 was reached. The liquid precipitate was then brought to a reaction temperature of 80 °C and stirred for 5 h. The product was then cooled to room temperature. To get particles free from sodium and chlorine compounds, the precipitate was washed twice with distilled water and then with ethanol to remove the excess surfactant from the solution. The obtained products were dried at 80 °C for 3 hrs. (18) AR114 stock solution (Stock solution) (200 mg/L) was prepared by dissolving 200 mg of

AR114 dye into 1 L of distilled water. Solutions of the required concentrations (20-200 mg/L) were prepared by consecutive dilution of this stock solution. Physical and chemical features of Acid Red 114 are given in Table 1 (2).

Table 1. Physical and chemical features of AR 144

Commercial name	Acid Red 114
Molecular formula	$C_{37}H_{28}N_4O_{10}S_3Na_2$
Purity	80%
Chromophore	Diazo
Molecular weight (g/mole)	830
λ_{max} (nm)	522
View	Dark red powder

Batch adsorption study

Adsorption studies were applied at various initial concentrations (10, 20, 40, 60, 80, 100 and 200 mg/L) and different pH conditions (pH: 3, 5, without pH correction (7.3) and 11) which were applied at locked adsorbent dosage (0.03 g/50 mL) in the aqueous solution at room temperature. pH adjustment was done with 0.1 N HCl and 0.1 N NaOH. The effect of contact time (1, 5, 10, 15, 30, 45, 60, 90, 120 and 150 min) on color removal were also applied at a series of kinetic experiments. After adsorption process $Fe_3O_4@CFA$ MNC were removed from the solution with a magnet and the concentration of the dye was evaluated at a wavelength which is maximum absorbance of AR114 by using a spectrophotometer.

The amount of adsorbed AR114 was calculated (Equation 1):

$$q_e = V(C_0 - C_e) / W \quad (\text{Eq 1})$$

q_e is the amount adsorbed (mg/g); C_0 and C_e are the initial and equilibrium AR114 concentrations in the solution (mg/L); V is the solution volume (L); and W is the mass of adsorbent (g).

Regeneration and reuse experiments

The practical applications of adsorbents are significantly dependent to the recycling and regeneration ability (11). Such adsorbents not only have an excellent adsorption capacity but also large desorption feature which will reduce secondary pollution and the overall cost. The optimum regeneration ability was found to be the mixture of methanol and acetic acid. 0.03 g of AR114-loaded adsorbents were added to 50 mL of a mixture of methanol and acetic acid (volume ratio of 9:1). After that $Fe_3O_4@CFA$ MNC was prepared with a magnetic stirrer for 10 min. When the regeneration was complete $Fe_3O_4@CFA$ MNC was separated with an external magnet. 5 g of $Fe_3O_4@CFA$ MNC was added into the 1 L mixture of

methanol - acetic acid, and the final solution was shaken for 1 h to reach desorption equilibrium. To estimate the desorbed amount of AR114 in the concentration, a Thermospectronic spectrometer was used for the measurement at a wavelength of 522 nm. The experiment was repeated for three times (wavelength of 522 nm) until the AR114 concentration in the liquid decreased below 0.002 mmol/L (11). After the experiment was completed, the NPs were washed with ultrapure water. Next the NPs dried with air in oven. The adsorption and desorption of the AR114 on/from the $\text{Fe}_3\text{O}_4@\text{CFA}$ MNC were evaluated for five times.

RESULTS AND DISCUSSION

The impact of initial pH, initial dye concentration and contact time on adsorption

To determine the impact of pH the adsorption experiments were applied for different pHs which were pH: 3, 5, without pH correction (7.3) and 11, at fixed adsorbent dosage (0.03 g/50 mL) in the aqueous solution and at room temperature (Fig. 2). It is seen from Fig. 2 that a high q_e values was achieved for AR114 at natural pH (without pH correction-pH:7.3). This can be explained by low solubility of $\text{Fe}_3\text{O}_4@\text{CFA}$ MNC at neutral pH. The lower adsorption capacity may be because of the solubility of adsorbent in strong acid or base. (20). It can be seen from Figure 2 that lower AR114 removal was obtained at alkaline pH values than at acidic pH values. This is caused by the fact that surplus OH^- anions compete with the dye anions for the available adsorption sites at alkaline pH values. Since color removal was maximum without pH correction, the original solution pH (7.3) was selected for all adsorption experiments. It is known that colored dye anions are released from the acid dyes, into the solutions during the dissolutions. (2).

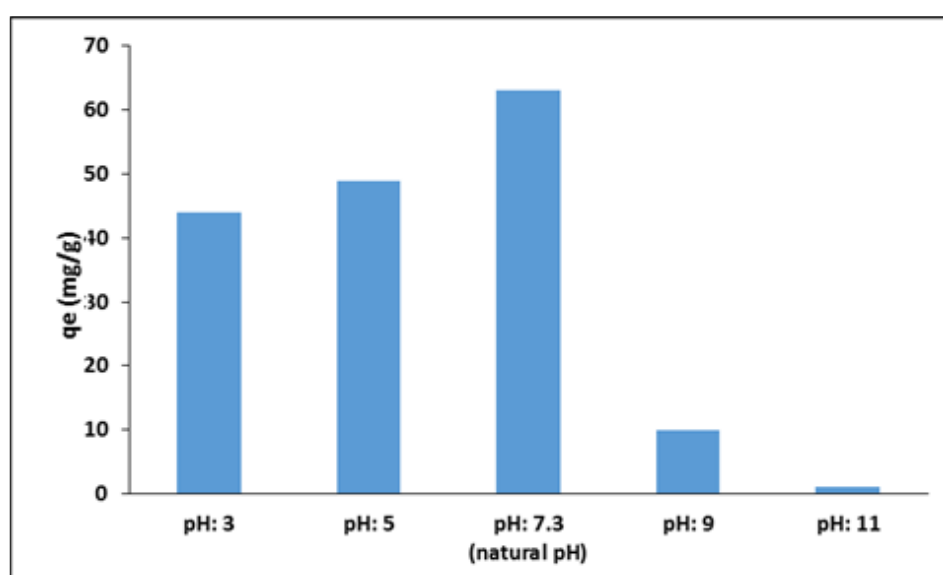


Figure 2. The variation of q_e values depending on pH values

The impact of initial dye concentration for the adsorption of AR 114 onto $\text{Fe}_3\text{O}_4@\text{CFA MNC}$ is shown in Figure 3. The increase in the dye concentration from 10 mg/L to 200 mg/L resulted the increase of (mg/g) values from 12.65 mg/g to 214.92 mg/g. As it is shown in Figure 3 that the adsorption capacity increases with an increase in the initial concentration of AR114 which shows the favorable adsorption at high concentration (21). As it is known eliminate the mass change of dye between the liquid and solid phases are eliminated by a driving force which is provided by the initial dye concentration So the interaction between the adsorbent and dye increases along with initial dye concentration (22).

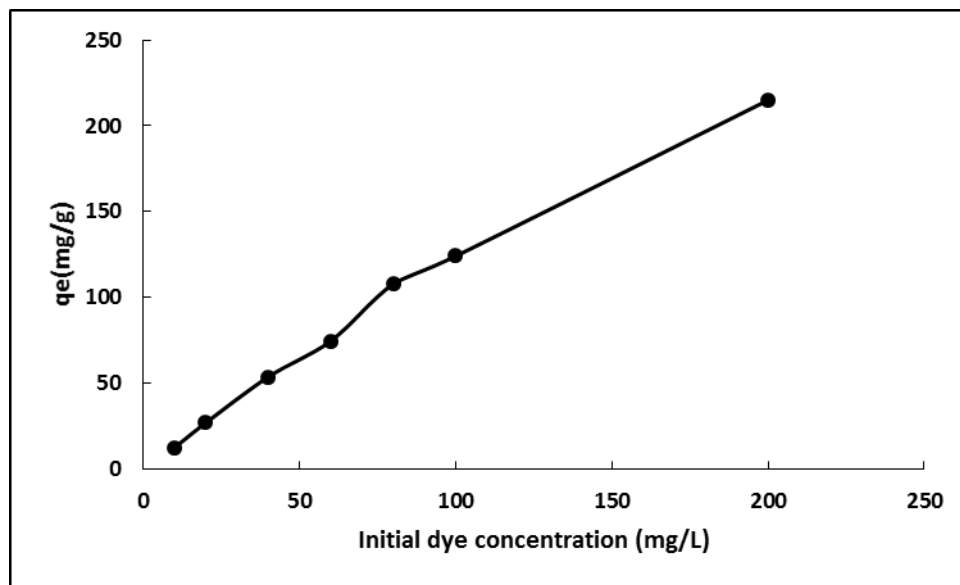


Figure 3. The impact of initial dye concentration on q_e values

Fig.4 presents the effects of contact time according to initial dye concentration for the adsorption of AR 114. The adsorption equilibriums of anionic dye on $\text{Fe}_3\text{O}_4@\text{CFA MNC}$ are reached within 150 min as it is shown in Fig.4.

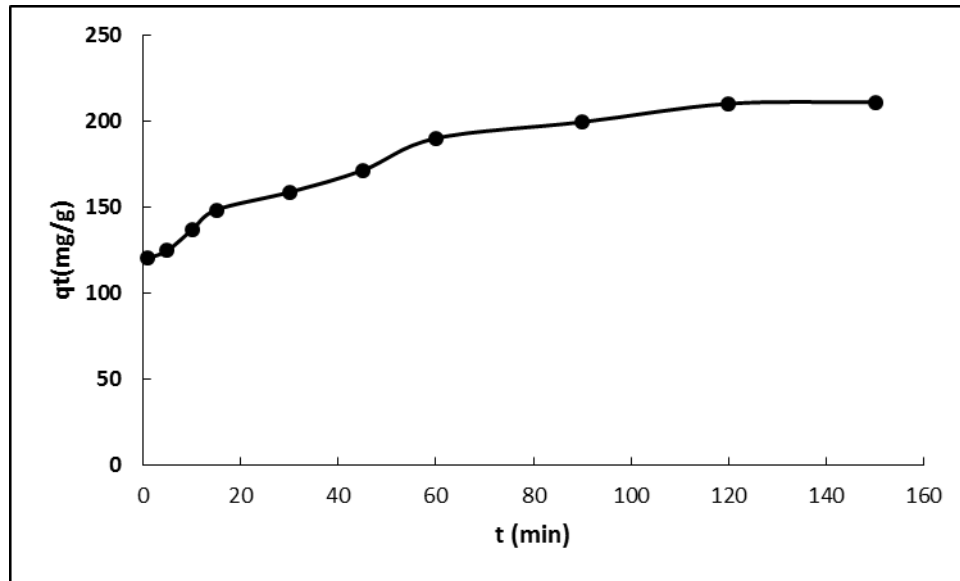


Figure 4. The impact of contact time for the adsorption of AR 114 onto Fe₃O₄@CFA MNC

Adsorption isotherms

For the determination of the adsorption capacity of the adsorbents, adsorption equilibrium studies were utilized by using Langmuir and Freundlich isotherm models. Adsorption isotherm experiments were employed by agitating dye solutions of various concentrations (10, 20, 40, 60, 80, 100 and 200 mg/L) with 0.03 g/50 mL Fe₃O₄@CFA MNC at room temperature.

The expression for the Langmuir isotherm is given below (23) (Equation 2):

$$\frac{C_e}{q_m} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (\text{Eq. 2})$$

The expression for the Freundlich isotherm is given below (24) (Eq. 3):

$$\log q_e = \frac{1}{n} \log c_e + \log K_f \quad (\text{Eq. 3})$$

Where, q_e (mg/g) expresses the AR 114 amount that each unit adsorbent adsorbs in the equilibrium condition, C_e (mg/L) stands for the AR 114 concentration that remains in the solution after the adsorption when the equilibrium condition is reached, K_L (L/mg) is the Langmuir constant, and q_m is the maximum adsorption capacity of the adsorbents (mg/g), K_f is the adsorption capacity that is calculated in the experiments, n is the adsorption density. q_m and K_L values were calculated by plotting of $1/q_e$ against $1/C_e$ by using Langmuir isotherm and n and K_f can be calculated from the slope and intercept by using Freundlich isotherm.

Langmuir and Freundlich isotherm plots and experimental values are shown in Fig 5. The adsorption constants derived from the Langmuir and Freundlich adsorption models are given in Table 2. As indicated from R^2 values given on Table 2, Langmuir model yielded a better fit than the Freundlich model for the adsorption of AR114 on $\text{Fe}_3\text{O}_4\text{@CFA MNC}$. According to this model adsorption appears at particular homogeneous sites within the adsorbent. Once an adsorbate molecule occupies a site, no further adsorption can be observed at the same site (23).

Table 2. The kinetic parameters of Freundlich and Langmuir isothermal equation (Natural pH:7.3, $C_0=10, 20, 40, 60, 80, 100, 200$ mg/L, $m=0.03$ g/50 mL)

Adsorbent	Langmuir model			Freundlich model		
	q_{\max} (mg/g)	K_L (L/g)	R^2	K_f (mg/g)	$1/n$	R^2
$\text{Fe}_3\text{O}_4\text{@CFA MNC}$	333.3	0.025	0.9958	17.02	0.60	0.9818

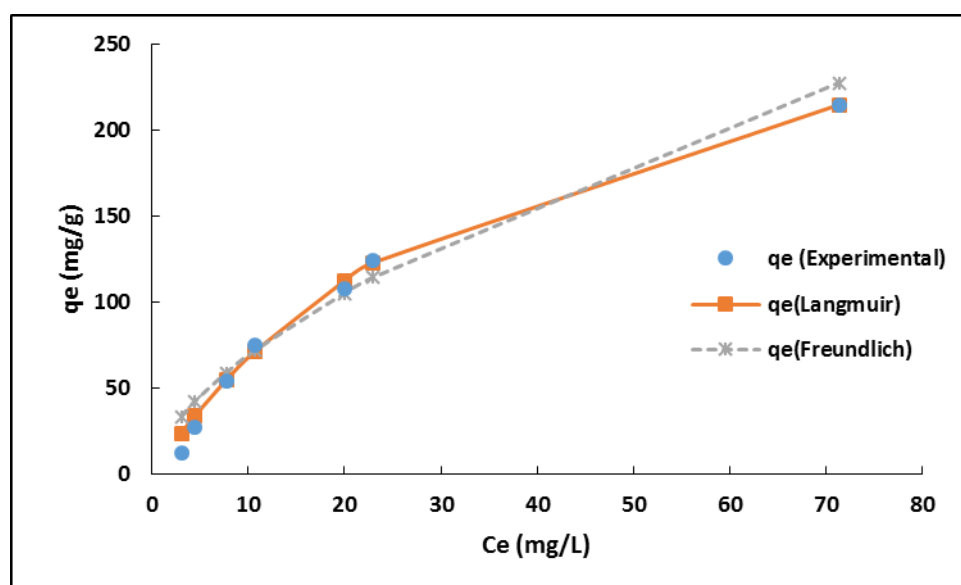


Figure 5. The fit of experimental adsorption data to Langmuir, Freundlich for the removal of AR 114 by $\text{Fe}_3\text{O}_4\text{@CFA MNC}$ ($t = 150$ min, $m = 0.03$ g/50 mL).

The Langmuir isotherm could be indicated by a separation factor, R_L which is defined by McKay *et al.* (1989) as given below (25) (Equation 4):

$$R_L = 1/(1 + K_L C_0) \quad (\text{Eq. 4})$$

Favorable adsorption is demonstrated by $0 < R_L < 1$. The R_L values were found to be between 0.16 and 0.8 for initial dye concentrations of 10-200 mg/L. R_L values between 0-1 show favorable adsorption of AR114 on $\text{Fe}_3\text{O}_4\text{@CFA MNC}$.

Table 3 shows the q_{max} value for AR114 adsorption obtained in this study in comparison with the q_{max} values obtained in the other studies carried out with various adsorbents. As it can be seen from Table 3, the maximum adsorption capacity (q_{max}) of Fe₃O₄@CFA MNC has the value of 333 mg/g for adsorption of AR114. It can be understood that these adsorbent possess high good adsorption capacity for AR114 dye.

Table 3. Adsorption capacities obtained from present study and other studies for the removal of AR114.

Adsorbent	Q_{max} (mg/g)	Reference
Activated pongam seed shells	204.08	(2)
Activated cotton seed shells	153.85	(2)
Activated sesame seed shells	102.04	(2)
Activated carbon-charcoal	101	(26)
Magnetic nanoparticle impregnated rice husk ash	111	(27)
Fe ₃ O ₄ @CFA MNC	333.3	This study

Adsorption kinetics

Pseudo-first order and pseudo-second order models were utilized to analyze the adsorption kinetics of AR 114 on Fe₃O₄@CFA MNC. The equations are integrated into form (Equation 5 and 6), using the boundary conditions $t = 0, q_t = 0$ and $t = t, q_t = q_t$. The linearized form of pseudo-first-order (Equation 5) and pseudo-second-order kinetic models (Equation 6) were expressed as follows (28):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (\text{Eq.5})$$

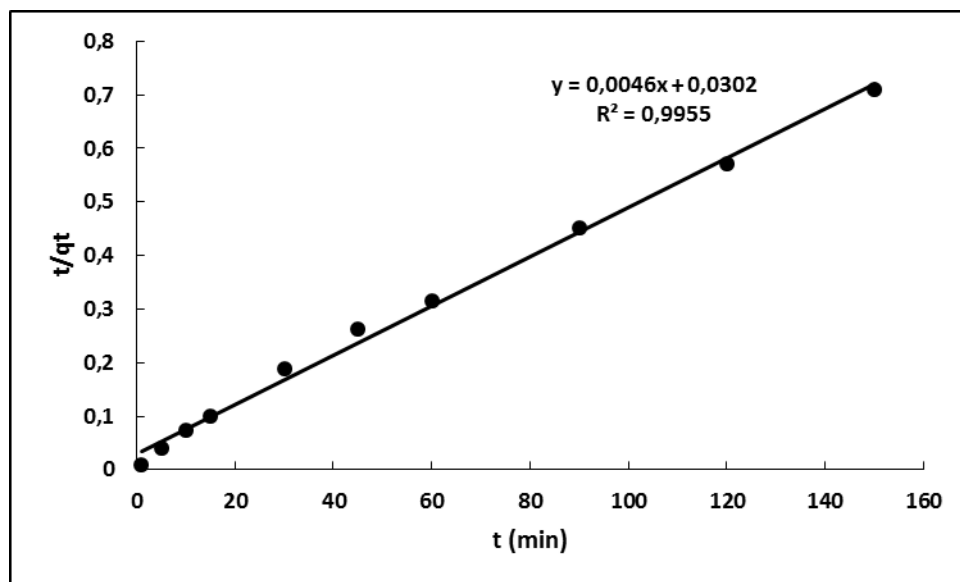
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (\text{Eq. 6})$$

Where, k_1 is pseudo-first order adsorption rate constant (min^{-1}), k_2 is pseudo-first order adsorption rate constant (g/mg.min), q_e , the amount that is adsorbed in equilibrium condition (mg/g), q_t is the adsorbed amount at time t (mg/g). The values of $q_{e1,calc}$ and k_1 (for pseudo-first order equation) were determined from linear plots of $\log(q_e - q_t)$ versus t . The values of $q_{e2,calc}$ and k_2 (for pseudo-second order equation) were determined from linear plots of t/q_t versus t .

Table 4 presents the kinetic parameters for the removal of AR114 by Fe₃O₄@CFA MNC. As given in Table 4 and Fig 6, R^2 of the pseudo-second order equation were 0.9955 and bigger than pseudo-first order kinetic model. As it could be seen from the Table 4 the calculated data ($q_{e2,cal}$) agreed well with the experimental data ($q_{e,exp}$) for second order kinetics showing chemisorption that may be the rate controlling step in the adsorption processes (29). These results showed that adsorption was related to the amount of solute adsorbed on the adsorbent surface as well as the amount adsorbed at equilibrium (30).

Table 4. Kinetic parameters for the adsorption of AR 114 on Fe₃O₄@CFA MNC (C₀= 200 mg/L, natural pH)

q _{e,exp} (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	k ₁ (min ⁻¹)	q _{e1,calc} (mg/g)	R ²	k ₂ (g/mg.min)	q _{e2,calc} (mg/g)	R ²
211.17	0.035	124.53	0.8993	0.0007	217.39	0.9955

**Figure 6.** Plot of pseudo-second-order model for AR114 adsorption by Fe₃O₄@CFA MNC (Natural pH, C₀=200 mg/L, m= 0.03 g/50 ml)

Regeneration and reuse

Owing to economic and resource reasons, reuse of the adsorbents is significant. Eluting with organic solutions (The mixture of methanol:acetic acid as the volume ratio of 9:1) were examined in this study. The optimum regeneration ability was found to be the mixture of methanol and acetic acid. The recycling adsorption efficiency is shown in Figure 7 from which the adsorbed amount of AR114 onto the Fe₃O₄@CFA MNC was 74.7 mg/g, and the adsorbed amount of AR114 on the regenerated Fe₃O₄@CFA MNC, decreased each cycle from 74.7 mg/g to 45.5 mg/g.

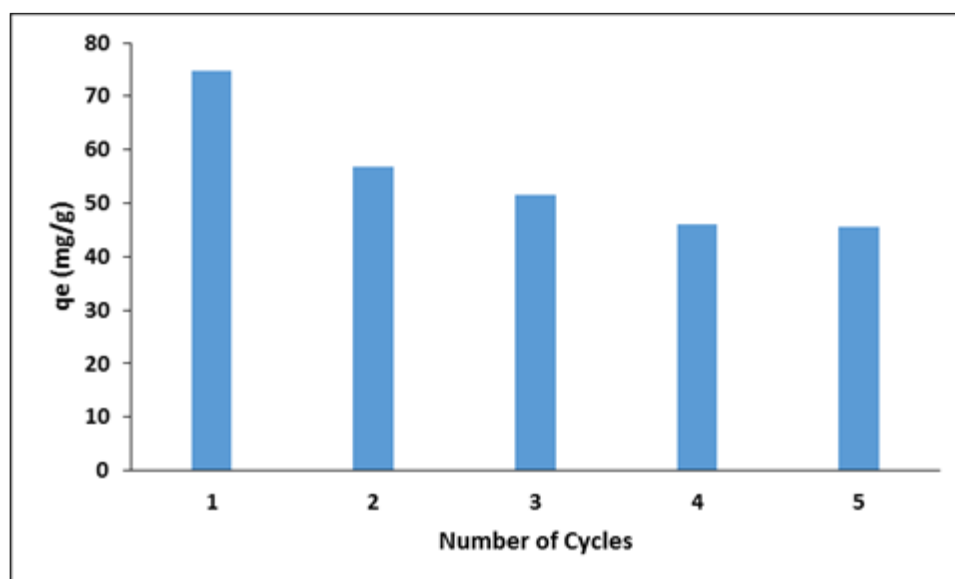


Figure 7. The recyclable adsorption of AR114 Fe₃O₄@CFA MNCs (C₀:60 mg/L, natural pH)

CONCLUSION

In the study the removal of AR114 by adsorption process, using the magnetic nanoparticle Fe₃O₄@CFA MNC were studied. Caffeic acid coated Fe₃O₄ MNC (Fe₃O₄@CFA MNC) were synthesized successfully by the simple chemical refluxing method. The MNC were proved and confirmed that it was covalently bonded to the Fe₃O₄ nanoparticle surface via carboxyl groups. The maximum q_e values for each adsorbent were obtained without correcting pH (pH=7.3). The Langmuir model well described equilibrium data. The maximum adsorption capacity of the Fe₃O₄@CFA MNC for AR114 was 333 mg/g at natural pH. Kinetic data were sufficiently adapted by the pseudo-second order kinetic model. The adsorbed amount of AR114 onto the regenerated Fe₃O₄@CFA MNC, for initial concentration of 60 mg/L, decreased from 74.7 mg/g to 45.5 mg/g after five cycles. This study showed that magnetic nanomaterials supported adsorbent are very attractive and can be a good alternative solution for waste water treatment due to its very efficient adsorbent capability and stability for reusable adsorbing materials used in the removal of hazardous dye. This work also showed that Fe₃O₄@CFA MNC has suitable adsorption ability towards the removal of AR 114 from the wastewater. Finally, Fe₃O₄@CFA MNC can be considered as an alternatives and efficient adsorbents for dye removal in wastewater treatment.

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Türkçe Öz ve Anahtar Kelimeler**Asit Kırmızı 114'ün Fe₃O₄@Kafeik asit Geri Dönüştürülebilir Manyetik Nanokompoziti Üzerine Adsorpsiyonu**

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Öz: Bu çalışmada, kafeik asit (CFA) ile fonksiyonlandırılmış Fe₃O₄ manyetik geri dönüştürülebilir nanokompozitinin (Fe₃O₄@CFA MNC) endüstriyel bir boyar madde olan Asit Kırmızı 114 (AR 114) için adsorpsiyon kapasitesi incelenmiştir. Fe₃O₄@CFA MNC'nin AR114 için maksimum adsorpsiyonu (q_m), çözeltide pH düzeltilmesi yapılmadan 333 mg/g olarak bulunmuştur. Diğer çalışmalarla karşılaştırıldığında, bu adsorbanın AR114 boyar maddesini yüksek bir adsorpsiyon kapasitesi ile tuttuğu görülmüştür. Adsorpsiyon izoterm verileri ve adsorpsiyon kinetik süreci Langmuir eşitliğine uydurulmuştur ve yalancı ikinci mertebe kinetik modele göre de adsorpsiyon sürecinde kemisorpsiyonun hız belirleyen basamak olduğu görülmüştür. Manyetik NM teknolojisinin bu çalışmada kullanılmasıyla organik kirleticilerin adsorpsiyonuna yeni bir boyut katacağına inanılmaktadır. Bunun ötesinde, Fe₃O₄@CFA MNC'nin beş çevrimde bile belirgin giderme sağladığı bulunmuştur.

Anahtar kelimeler: Atıksu islahı; manyetik nanokompozit; adsorpsiyon; Asit Kırmızı 114.

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