

## **Kinetic and adsorption study of enrofloxacin from aqueous solutions by modified magnetic (Fe<sub>3</sub>O<sub>4</sub>) nano-particles**

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### **ABSTRACT**

A study was conducted to synthesis a novel adsorbent for enrofloxacin (ENR) adsorption from aqueous solution. We investigated the impacts of different pH and temperature on adsorption capacity. The magnetic (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles were prepared by co-precipitation method and modified by 3-mercaptopropyltrimethoxysilane follow by grafting with 1-(N,N-bis-carboxymethyl)amino-3-allylglycerol. The characterizations of prepared magnetic nanoparticles were carried out by Fourier transform infrared spectroscopy and scanning electron microscopy and studied for adsorption and kinetic behavior of enrofloxacin on the grafted nano-adsorbent. It was showed, this nano-adsorbent possess highest adsorption capacity at pH 3. Three kinetics model, pseudo-first-order, pseudo-second-order and intraparticle diffusion were used to study the adsorption mechanism of ENR onto grafted magnetic nanoparticles. The best fitting was obtained by pseudo-second-order model.

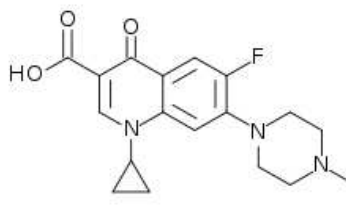
**Key words:** Enrofloxacin, Magnetic nanoparticles, Kinetic study, Modification

### **INTRODUCTION**

Fluoroquinolones are synthetic antimicrobials having significant antibacterial activity against broad spectrum of Gram-negative and Gram-positive bacteria. Enrofloxacin (ENR) (C<sub>19</sub>H<sub>22</sub>FN<sub>3</sub>O<sub>3</sub>) is a fluoroquinolone bacterial antibiotic, which is used for treatment of infections in the respiratory, urinary and alimentary tract, septicemia, or in the last few years, have been widely used as a feed additive to promote animal growth. ENR is a pyridone carboxylic acid derivative (Fig. 1), which acts by inhibiting bacterial DNA gyrase, thereby preventing DNA supercoiling and DNA synthesis [2-6-14-15]. There is evidence that the misuse of quinolones in animals result in adverse health consequences like quinolone-resistant bacteria, allergic hypersensitivity reactions, etc [15]. Hence, in some countries such as the USA, EU and China, public health agencies have regulated maximum residue limits which means allowable maximum concentration of veterinary drugs in animals products [19].

Today, Nano-materials have highly attracted because of their physical and magnetic properties and also their nanosize. Very small size of nanoparticles results in specific properties and a increase of their dispersion and specific surface area which have significant effect on adsorption capacity of nanoparticles. Magnetic separation technology is showing an attractive application prospect due to the laboratory scale synthesis of superparamagnetic magnetic particles (usually Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub>), magnetic behavior and simple applications. These particles introduce magnetic behavior under an external field, but this property disappears once the field is removed. Nowadays, magnetic separation is well known as an appropriate alternative to centrifugal separation of chemical or biological solutions. However, until now, the literatures involving magnetic separation technology were very rare in monitoring drug residue research. Surface charge of nanoparticles has important role in their interaction with other

compounds and environments [8]. Furthermore, it is easy to apply the chemical modification to change the chemical characteristics of the adsorbent's surface [17]. Therefore, the surface modified adsorbents can have higher affinity to some specific substances. In this research, surface modification was made in two steps: first, surface modification with (3-mercaptopropyl)trimethoxy silane and second, modification of these modified nanoparticles with *N,N*-dimethylacrylamide and 1-(*N,N*-bis-carboxymethyl)amino-3-allylglycerol. The objective of this research was to evaluate the adsorption potential of grafted magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles for ENR. The kinetic adsorption studies were processed to understand the adsorption mechanism of ENR onto grafted magnetic ( $\text{Fe}_3\text{O}_4$ ) nanoparticles. Kinetic data can be used to predict the rate at which the target particle is removed from aqueous solutions.



**Fig.1. Chemical structure of enrofloxacin**

## MATERIALS AND METHODS

### 2.1. Materials

Ammonia, ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ferrous chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), NaOH,  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{CH}_3\text{COONa}$ , iminodiacetic acid (IDA), Anhydrous 1,4-dioxane, KOH and ethanol were purchased from Merck. Allyl glycidyl ether (AGE) was purchased from Fluka. *N,N*-dimethylacrylamide, (3-mercaptopropyl)trimethoxysilane was from Aldrich. 2,2'-Azobis (2-methylpropionitrile) was purchased from Acros Organics. The pH value of the solutions was adjusted via 0.01 M acetate buffer solution 0.01 M (pH 3-6.5) or 0.01 M phosphate buffer (pH 6.5-7.5).

### 2.2. Synthesis and surface grafting of magnetite nanoparticles

Details of the synthesis of the magnetic nanoparticles were reported elsewhere [11]. Briefly, ammonia solution was added to a solution of  $\text{FeCl}_3$  and  $\text{FeCl}_2$  drop wise under Nitrogen gas atmosphere. The solution was agitated mechanically at  $85^\circ\text{C}$  for 2.5 h. The magnetic nanoparticles were washed and dried at room temperature.

The functionalized monomer of 1-(*N,N*-bis-carboxymethyl)amino-3-allylglycerol was prepared through coupling method [3]. At first the iminodiacetic acid was neutralized and reacted with allyl glycidyl ether at  $67^\circ\text{C}$  for 90 min under stirring. The resultant yellowish liquid monomer was purified by acetone and characterized by FT-IR,  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$ .

The next step is silylation of magnetic nanoparticles. The magnetic nanoparticles (2.5 g) were reacted by 50 ml solution of 5% of (3-mercaptopropyl)trimethoxysilane in anhydrous 1, 4-dioxane in the boiling state for 40 h. Then, the silylated magnetic nanoparticles were washed with 1, 4-dioxane and dried at room temperature.

The final step is polymerization and grafting of functionalized monomer onto the silylated magnetic nanoparticles. The mixture of 10 ml of 1-(*N,N*-bis-carboxymethyl)amino-3-allylglycerol and 2 ml *N,N*-dimethylacrylamide as the monomers, 0.1 g 2, 2'-azobis (2-methylpropionitrile) as initiator, 20 ml ethanol as solvent and 2.5 g the silylated magnetic nanoparticles were poured in a temperature-controlled reactor and heated for 6.5 h at  $70^\circ\text{C}$  under a nitrogen atmosphere. The grafted magnetic nanoparticles was separated from the solution magnetically, and washed with ethanol and dried under ambient condition. The methodology used to synthesis of grafted magnetic nanoparticles is summarized in Fig. 2. The grafted magnetic nanoparticles were characterized by FT-IR and scanning electron microscopy.

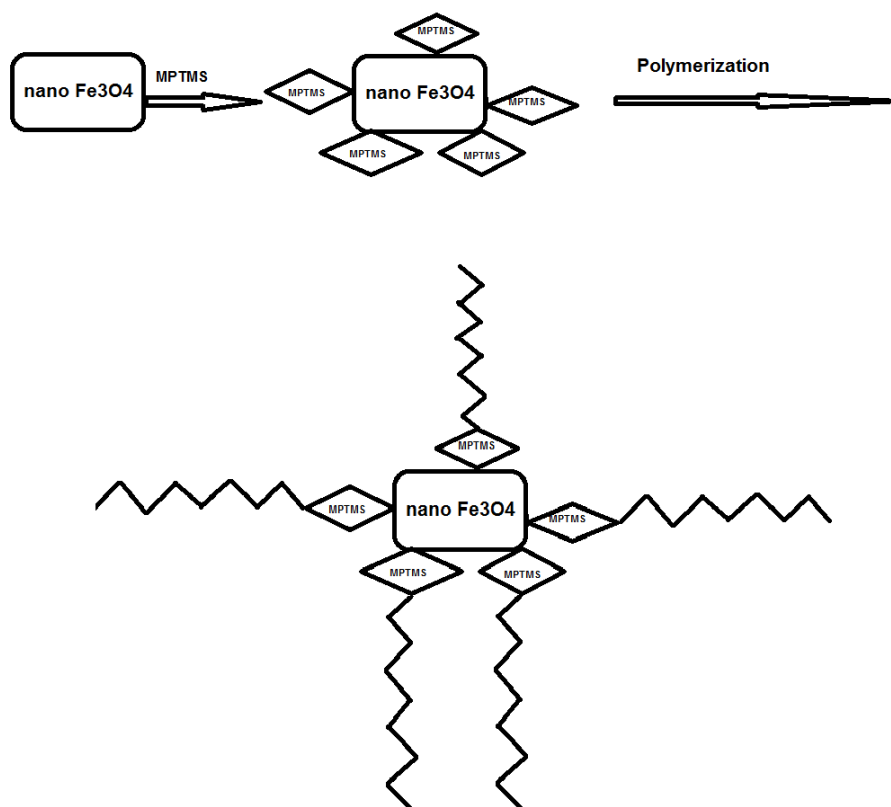


Fig. 2. Schematic presentation of silylation and graft polymerization of grafted magnetic nanoparticles

### 2.3. Adsorption studies

The adsorption experiments of ENR were investigated in aqueous solutions at pH 3-7.5. Firstly, stock solution ( $500 \text{ mg l}^{-1}$ ) was prepared by dissolving the appropriate amounts of ENR in distilled water. Then, 100 ml of working solution ( $20 \text{ } \mu\text{g ml}^{-1}$ ) was prepared. Because of critical role of pH in the adsorption process, the effect of pH in the ENR adsorption was examined. For each pH, 0.02 g grafted magnetic adsorbent was taken into a beaker and mixed with 10 ml of working solution. The pH values were adjusted to the desired value in the range of 3 to 7.5 with buffer solutions (0.01M acetate and/or 0.01M phosphate). The resultant mixture was then equilibrated for 2 h by shaking at room temperature. The supernatant was filtered and the concentration of ENR in the solution was measured at wavelength of ENR (271 nm) using UV/Vis spectrophotometer (Cary 5o UV/Vis1601 Spectrophotometer). The amount of adsorbed ENR onto adsorbent was determined as following:

$$q_e = (C_0 - C_e) V/W \quad (1)$$

where  $C_0$  and  $C_e$  (mg/l) are ENR concentrations at initial and equilibrium, respectively,  $V$  (l) is the volume of the ENR solution and  $W$  (g) is the mass adsorbent.

In kinetics study, the effect of the contact time on ENR adsorption by adsorbent was determined by the same process mentioned above. A set of beakers containing ENR solution and 0.02 g magnetic adsorbent were taken and then shaken at different time intervals at optimum pH (pH=3). Then, the amount of ENR adsorption was calculated from the following equation:

$$q_t = (C_0 - C_t) V/W \quad (2)$$

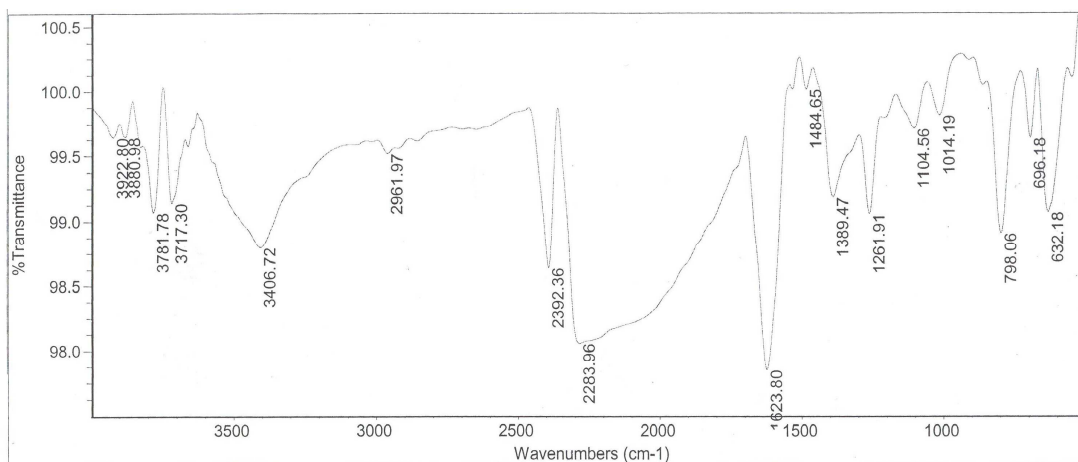
where  $C_0$  and  $C_t$  (mg/l) are ENR concentrations at initial and any time, respectively,  $V$  (l) is the volume of the ENR solution and  $W$  (g) is the mass adsorbent.

## RESULTS AND DISCUSSION

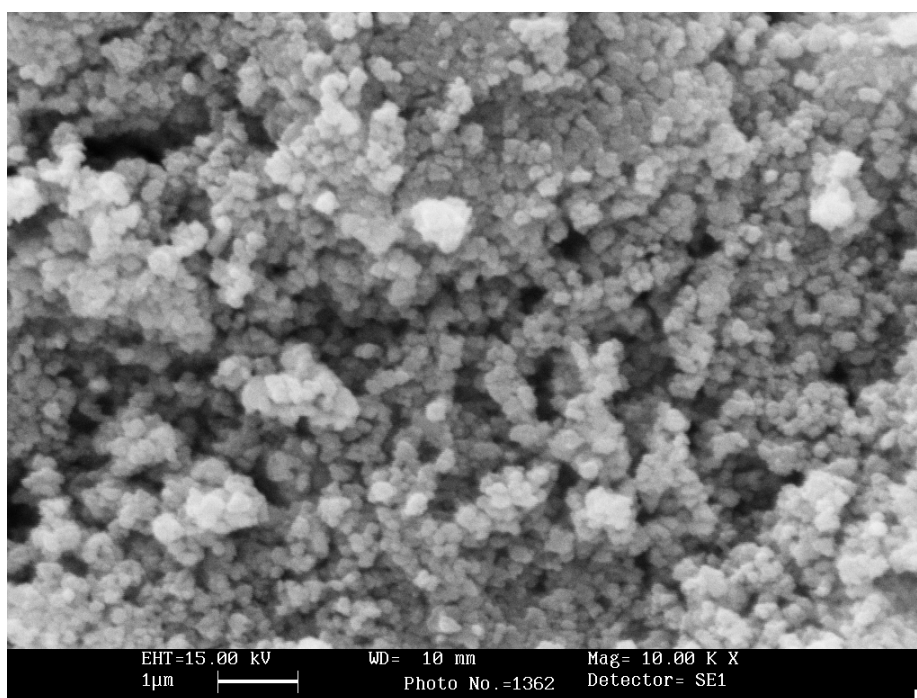
### 3.1. The characterization of copolymer-grafted Magnetic nanoparticles

Magnetic nanoparticles showed the peaks at  $632 \text{ cm}^{-1}$  (Fe-O) and  $3717 \text{ cm}^{-1}$  (O-H) in FT- IR spectrum. There is an additional band at  $2961$ ,  $1104$ ,  $1623$  and  $3406 \text{ cm}^{-1}$  in FT-IR spectrum of grafted magnetic nanoparticles related to

C-H, C-O, C=O and O-H groups in modified nano-sorbent indicated (see Fig. 3) that grafting was performed successfully. The morphology of grafted magnetic nanoparticles were analyzed by using scanning electron microscopy. Fig. 4 shows the spherical agglomerated particles with an average diameter fewer than 150 nm. The scanning electron microscopy image also indicates that the surface of agglomerated grafted magnetic nanoparticles is not smooth.



**Fig. 3.** FTIR spectra of the grafted magnetic nanoparticles



**Fig. 4.** Scanning electron micrograph of the grafted magnetic nanoparticles

### 3.2. Effect of pH on ENR adsorption

pH of solutions has an important effect on adsorption processes. In this work, the wide range of pH between pH 3 to 7.5 was examined. As shown in Fig. 5 the highest adsorption capacity results at pH 3 while with increase the pH value, the adsorption capacity decreases greatly. From this, it is concluded that the optimal pH value is 3. In this pH, the hydrogen bonding occurs between COOH groups exists on the surface of the superparamagnetic adsorbent and the oxygen of ENR. Regardless of the type of the adsorbate and modification, in other research, highest adsorption of Cu (II) by micro-size magnetic polymer adsorbent was attained at pH 4.5 [16]. In other studies about sorption of Pb (II) and Cu (II) onto magnetic eggshells-Fe<sub>3</sub>O<sub>4</sub> powder [13] and sorption of Ni (II) ions by dead biomass of fresh water green algae *Cosmarium panamense* [5], this pH was around 5.5 and 6, respectively. The pH did not affect the adsorption of imidacloprid by magnetic activated carbon and powdered activated carbon [18]. The adsorption of Cd

(II) and Zn (II) using magnetic hydroxyapatite nanoparticles showed that the optimum pH was in the range of 4 to 8 [7].

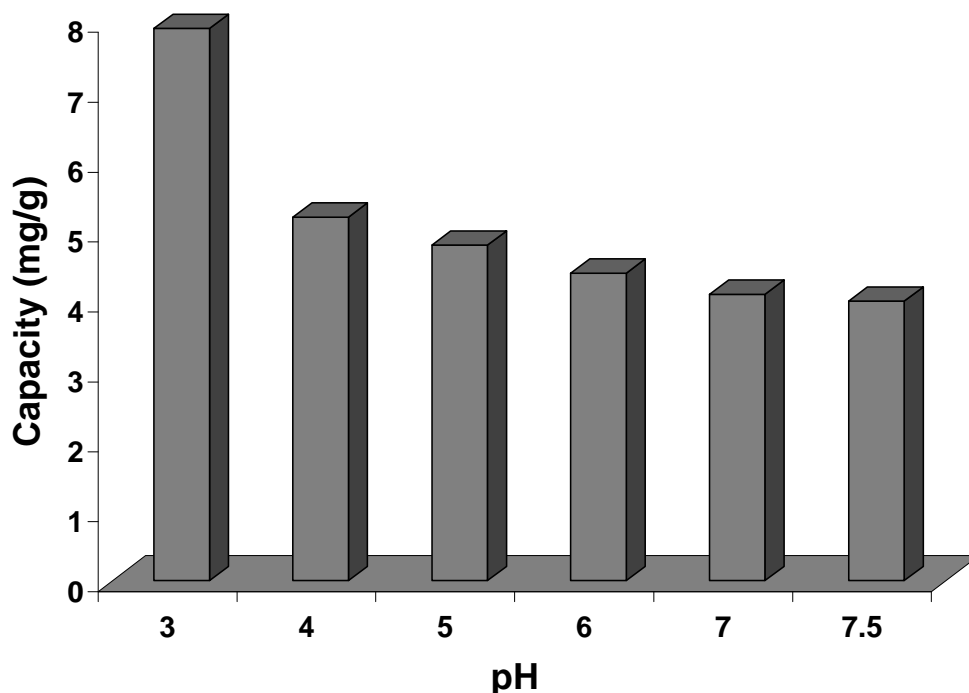


Fig. 5. Effect of solution pH on the adsorption of ENR onto grafted magnetic nanoparticles

### 3.3. Adsorption kinetics

Fig. 6 shows the adsorption kinetics of ENR onto grafted magnetic nanoparticles. Based on Fig. 6, the necessary time to attain the adsorption equilibrium of ENR onto magnetic particles is 15 min. It means the ENR adsorption onto adsorbent surface was performed in a short time. One reason of rapid adsorption is good accessibility of the binding sites in the grafted magnetic nanoparticles. Other possible reasons for this are adsorbent high surface area, short diffusion path [13] or nonporous structure of this adsorbent that result in happening adsorption on the external surface [4]. Further, the study of adsorption kinetics of ENR onto magnetic adsorbents was performed using various equations such as pseudo-first-order and pseudo-second-order kinetic equations.

The pseudo-first-order equation is represented as:

$$\log (q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (3)$$

where  $q_e$  and  $q_t$  (mg/g) are the amount of adsorbed ENR onto adsorbent at equilibrium and at time  $t$ , respectively, and  $k_1$  is the rate constant of pseudo-first-order (1/min). A straight line was resulted from the plot of  $\log (q_e - q_t)$  versus  $t$  (Fig. 7). The slope of this line is  $k_1$ . The values of  $k_1$ , the calculated and experimental  $q_e$  and the correlation coefficients  $R^2$  are shown in Table 1.

Table 1: Comparison of the pseudo-first-order, pseudo-second-order and intraparticle diffusion models calculated equilibrium, rate constants and correlation coefficients

| Kinetic models                   |        |
|----------------------------------|--------|
| pseudo-first-order               |        |
| $q_{e,cal}$ (mg/g)               | 2.82   |
| $k_1$ (1/min)                    | 0.197  |
| $R^2$                            | 0.9370 |
| pseudo-second-order              |        |
| $q_{e,cal}$ (mg/g)               | 4.08   |
| $K_2$ (g/mg min)                 | 0.114  |
| $R^2$                            | 0.9952 |
| intraparticle diffusion          |        |
| $k_p$ (mg/g min <sup>0.5</sup> ) | 0.7462 |
| $C$                              | 0.8776 |
| $R^2$                            | 0.9363 |

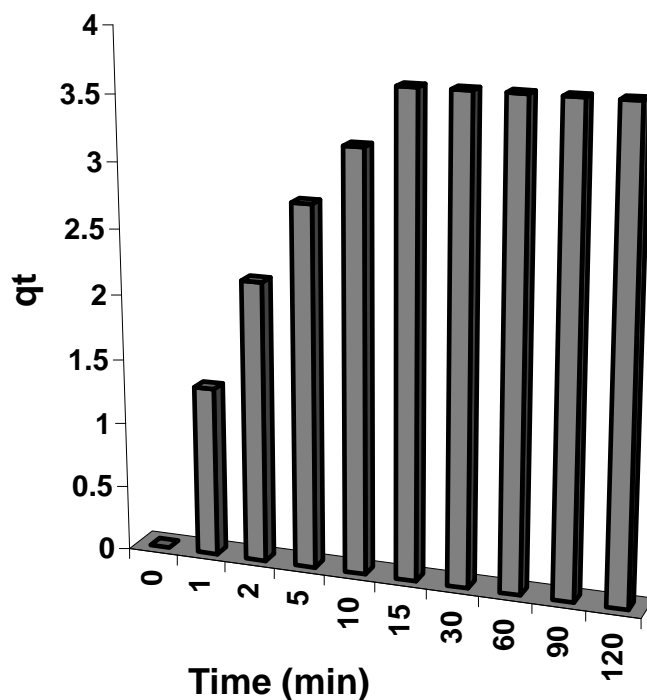


Fig. 6. Kinetics of enrofloxacin sorption on the grafted magnetic nanoparticles

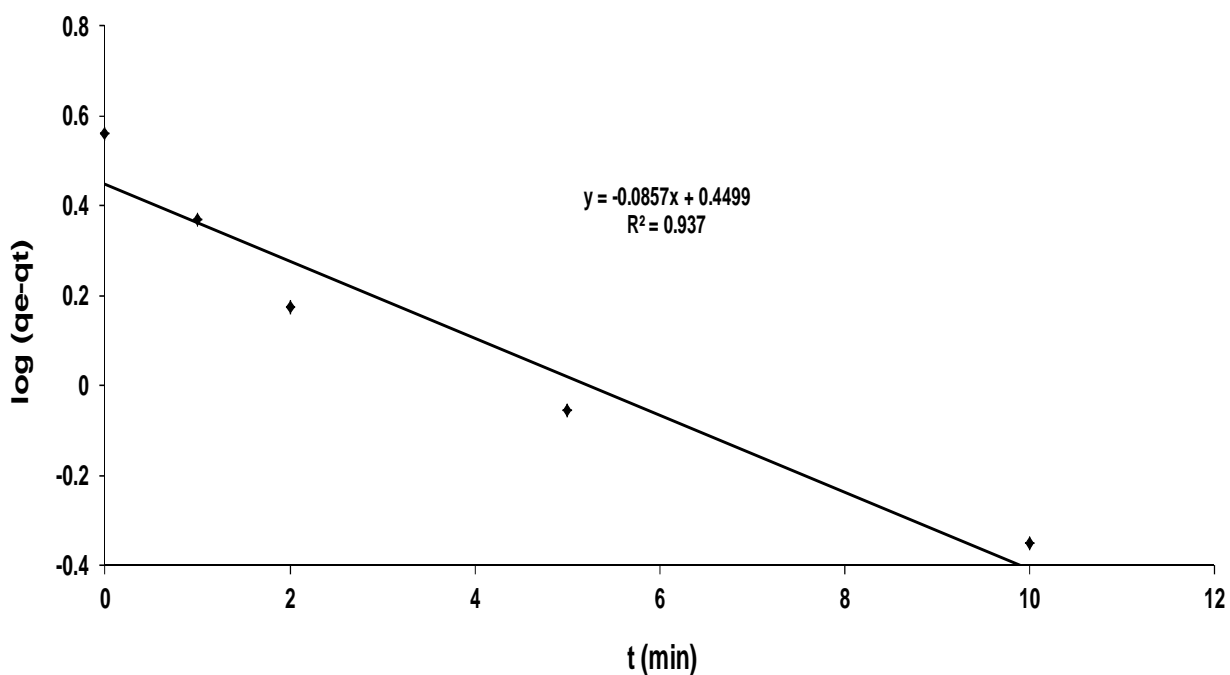


Fig. 7. The pseudo-first-order kinetics for ENR adsorption by grafted magnetic nanoparticles

The pseudo-second-order equation is represented as:

$$t/q_t = 1/k_2q_e^2 + t/q_e \quad (4)$$

where  $q_e$  and  $q_t$  (mg/g) are the amount of adsorbed ENR onto adsorbent at equilibrium and at time  $t$ , respectively, and  $k_2$  is the rate constant of pseudo-second-order (g/mg min). A straight line was resulted from the plot of  $t/q_t$  versus  $t$  (Fig. 8). The slope and intercept of this line are  $k_2$  and  $q_e$ , respectively. The values of  $k_2$ , the calculated and experimental  $q_e$  and the correlation coefficients  $R^2$  are shown in Table 1.

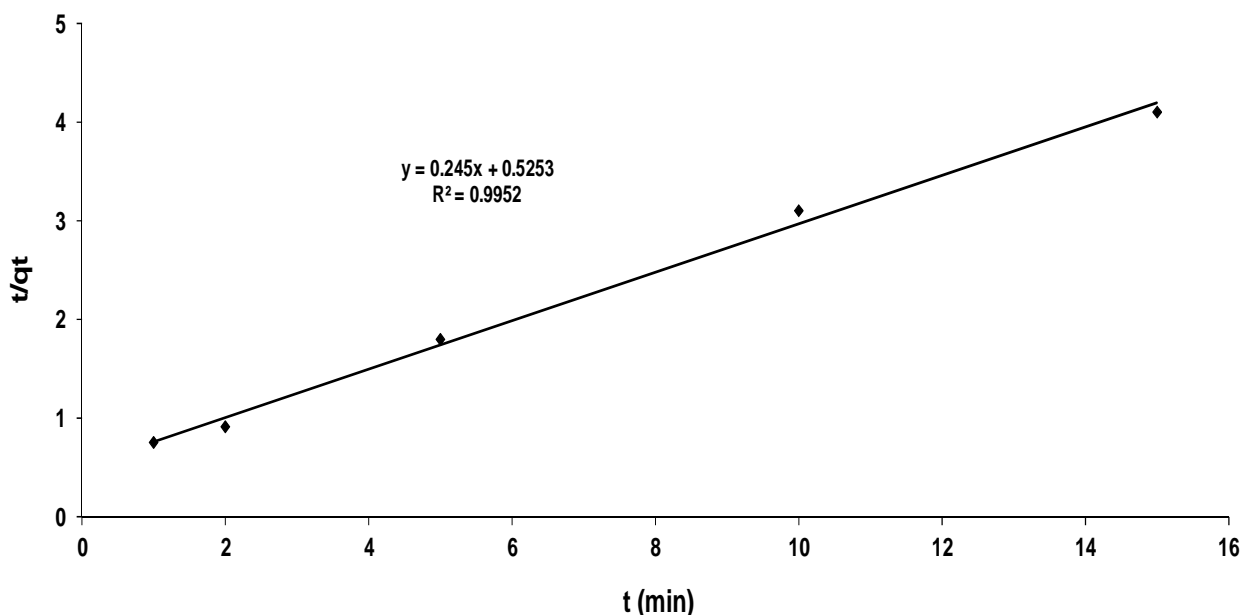


Fig. 8. The pseudo-second-order kinetics for ENR adsorption by grafted magnetic nanoparticles

Because of the possibility of intraparticle diffusion, the intraparticle diffusion model was used to study the diffusion mechanism of adsorption. This model is given as following equation:

$$q_t = k_p t^{0.5} + C \quad (5)$$

where  $C$  is the intercept and  $k_p$  is the rate constant of intraparticle diffusion ( $\text{mg/g min}^{0.5}$ ). A straight line was resulted from the plot of  $q_t$  versus  $t^{0.5}$  (Fig. 6). The values of  $k_p$ ,  $C$  and the correlation coefficients  $R^2$  are shown in Table 1. If the line does not pass through the origin, it means intraparticle diffusion is not the only rate-limiting process, so relationship between  $q_t$  and  $t^{0.5}$  is not linear. Other rate-controlling step can be explained by the boundary layer effect [18].

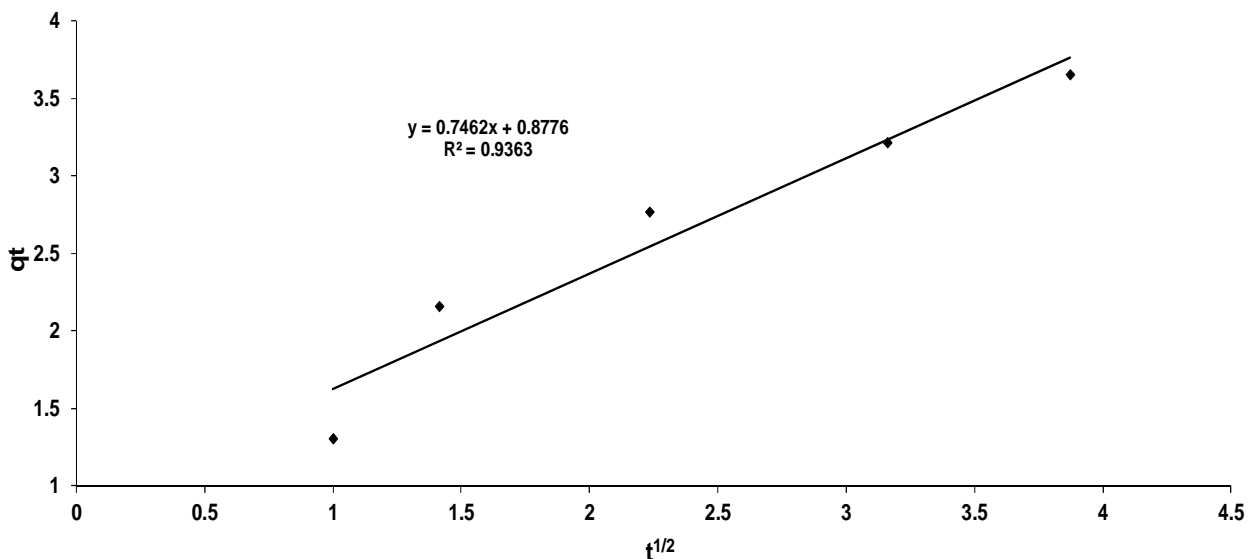


Fig. 9. Intraparticle diffusion kinetics for ENR adsorption by grafted magnetic nanoparticles

As seen in Table 1 the calculated  $q_e$  value for the pseudo-second-order kinetics agrees with experimental  $q_e$  value and its correlation coefficients was greater than 0.99. This shows that the pseudo-second-order kinetics model could well described the adsorption kinetics. Similar results were also reported in other works [9-16]. In other researches about imidacloprid adsorption by two form of activated carbon (*i.e.* powdered and magnetic form) [18], adsorption of reactive yellow 21 dye on flamboyant shells activated carbon [10] and adsorption of Lead(II) and Nickel(II) ions

by activated carbon [12], best discussion was also obtained by pseudo-second-order kinetic model. Furthermore, the results of other research revealed that kinetic data were properly fitted by a pseudo second-order model [7].

It can be concluded that this kind of grafted magnetic adsorbent at low amounts has selectivity to the ENR. Moreover, comparing with the conventional adsorption process, magnetic separation method has the advantages such as easy operation, cost effective, high selectivity, rapid separation and *etc.*

### CONCLUSION

In this research, the ability of grafted magnetic nanoparticles for adsorption of ENR was studied. Co-precipitation method was used to synthesize magnetic adsorbents. Then, this nanoparticle was modified in two steps. The SEM analysis revealed that the modified nanoparticles had spherical shape with an average diameter about 150 nm. Highest adsorption capacity was attained at pH 3. It takes 15 min to obtain the adsorption equilibrium of ENR onto magnetic adsorbents. In this study, three kinetics models consist of pseudo-first-order; pseudo-second-order and intraparticle diffusion were used to study the adsorption mechanism of ENR onto grafted magnetic nanoparticles. Best fitting was obtained by pseudo-second-order model. Therefore, this type of modified nanoparticles can be introduced as low-cost and effective adsorbent for ENR adsorption from Aqueous Solutions.

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