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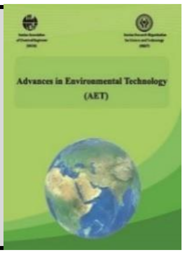

Magnetite nanoparticles coated with methoxy polyethylene glycol as an efficient adsorbent of diazinon pesticide from water

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ABSTRACT

Methoxy polyethylene glycol modified magnetite nanoparticles (PEGMNs) were synthesized and characterized by scanning electron microscopy (SEM), vibrating sample magnetometer (VSM), and X-ray diffraction (XRD). The adsorption of diazinon onto PEGMNs was investigated by UV-Vis spectrophotometry at 236 nm, through batch experiments. The effects of adsorbent dosage, solution pH, contact time, solution temperature and water impurities on the adsorption of diazinon onto PEGMNs were investigated. The process of adsorption was increased rapidly in the first contact period of 10 min. The adsorption at equilibrium (qe) was found to increase with increasing pH. The results of diazinon removal at various PEGMNs dosages demonstrated that the optimum dose of PEGMNs was 1mg. The amount of adsorption of diazinon at equilibrium increased with an increasing temperature from 15°C to 45°C that indicateds an endothermic process. Therefore, PEGMNs were used as an efficient absorbent for the removal of diazinon.

1. Introduction

The use of large quantities of pesticides, which includes insecticides in agriculture, is one of the main sources of pollution of surface and ground water [1]. In fact, 17% of the 2.36 billion kg of pesticides used worldwide was insecticides. The Water Frame work Directive (WFD) (Directive, 2000/60/EC – *European Parliament* and Council of the European Union, 2000) established the environmental quality standards(EQS) for pesticides, their relevant metabolites, degradation and reaction products in 0.1 µg/L for individual compounds and 0.5 µg/L for the sum of pesticides in ground water [2]. Conventional technologies have been used to treat all types of organic and toxic waste by adsorption, biological oxidation, chemical oxidation and incineration. In parallel, advances in nanoscale science and engineering suggest that many of the current problems involving water quality could be resolved or greatly diminished by using nonabsorbent, nanocatalysts, and bioactive nanoparticles. In addition to having high specific surface areas, nanoparticles also have unique adsorption properties due to different distributions of reactive surface sites and disordered surface regions. The mobility of nanomaterials in solution is high and the whole volume can be quickly scanned with small amounts of nanomaterials due to their small size. Magnetic separation has been applied recently in various fields such as analytical biochemistry [3], medical science [4] and biotechnology [5]. From an environmental point of view, on magnetic separation offers advantages due to the easy recovery of the adsorbent without filtration or centrifugation. Several studies have reported magnetic separation using modified magnetite (Fe_3O_4) as an environmentally friendly approach to remove heavy metal ions [7] and organic pollutants [8]. In this work, we attempt to use polyethylene glycol modified magnetic nanoparticles PEGMNs as an adsorbent for the removal of pesticide from aqueous solutions. Diazinon, an organophosphate insecticide, was selected for the present study as it is widely used in pest control, and high

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residual levels had been detected in vegetables contact time, solution temperature, and water impurities were investigated on the adsorption of diazinon.

2. Experimental

2.1. Materials and Methods

Analytical grade diazinon for the experiment was purchased from the Fluka Co. (Germany). A diazinon stock solution of 40 mg/L was prepared in distilled water and kept in a refrigerator at 4 °C until use. All the other chemicals used, were as analytical grade and were purchased from Merck Co. (Germany). The standard solutions and working solutions were prepared by the appropriate dilution of the stock solutions.

2.2. Adsorption experiments and analysis

The adsorption of diazinon on adsorbents such as PEGMNs, Fe_3O_4, Silica-Coated Magnetite Nanoparticles, Iranian natural zeolite, and multiwall carbon nanotubes were investigated by UV-Vis spectrophotometry at 236 nm, through batch experiments. For each adsorption test, 5 mL of diazinon solution was transferred to the beaker, and the solution pH level was adjusted to the desired value; the given amount of adsorbents were added to the solution and the suspensions were subjected to ultrasonic waves to obtain a uniform dispersion. For PEGMNs, Fe_3O_4, and silica-coated magnetite nanoparticles, the mixture was allowed to stand and the adsorbent was precipitated at the bottom of the beaker by a strong magnet and the supernatant was decanted. For Iranian natural zeolite and multiwall carbon nanotubes, the adsorbents were collected by centrifuging and the supernatant was decanted. Then, it was transferred to a cm^{-1} quartz cell and the absorbance at 236 nm was considered for determination of any residual diazinon, using a Cary 100 UV spectrophotometer.

2.3. Synthesis of Magnetite Nanoparticles (Fe_3O_4, MNP)

A solution of $FeCl_2$ (5.40 g) and $FeCl_3$ (2.00 g) in aqueous hydrochloride acid (2.00 M, 25.00 mL) at room temperature, was sonicated until the salts dissolved completely. Aqueous ammonia (25%, 40.00 mL) was added slowly over 20 min to the mixture under Ar atmosphere at room temperature followed by stirring for about 30 min with a mechanical stirrer. The Fe_3O_4 nanoparticles were separated by an external magnet and washed three times with deionized water and ethanol. The final product was obtained after drying under a vacuum [16-17].

2.4. Synthesis of Silica-Coated Magnetite Nanoparticles (SMNP)

The synthesized Fe_3O_4 was suspended in 35.00 mL of ethanol and 6 mL of deionized water and sonicated for 15 min. 1.50 mL of tetraethyl orthosilicate (TEOS) was slowly added to the mixture and sonicated for 10 min. Then, aqueous ammonia (10%, 1.40 mL) was added slowly over 10 min under mechanical stirrer. The mixture was heated at 40 °C for 12 h. The iron oxide nanoparticles with a thin layer of silica ($Fe_3O_4@SiO_2$, SMNP) were separated by an external magnet and washed three times with ethanol and dried under a vacuum [16-17].

2.5. Synthesis of methoxy polyethylene glycol attached to amino-silane modified magnetic nanoparticles (PEGMNs)

1 eq of methoxy polyethylene glycol (1100 g/mol) was added in the dichloromethane. Then, 1 eq of triethylamine and acryloyl chloride were added to the reaction. After 24h, the mixture of the reaction was filtered to remove the triethylamine hydrochloride. By adding diethylether, Acrylated methoxy polyethylene glycol (AmPEG) was obtained. AmPEG and (3-aminopropyl) triethoxysilane were added to dry DMF. After 48h, 0.5 gr of Magnetite Nanoparticles was added and stirred for another 48h. The final sample was separated by an external magnet and washed three times with DMF and dried under a vacuum.

3. Results and discussion

Initially, Fe_3O_4 NPs were synthesized by a chemical co-precipitation technique of ferric and ferrous ions in an alkali solution and was coated by tetraethyl orthosilicate to obtained the SMNPs. The AmPEG was then allowed to react with an appropriate concentration of 3-aminopropyltrimethoxysilane to give amino-functionalized AmPEG. Then, SMNPs and amino functionlized AmPEG were reacted together to obtained PEGMNs. The size and structure of PEGMNs were evaluated using scanning electron microscopy (SEM). The SEM image (Figure 1) showed uniformity and spherical-like morphology of the nanoparticles with an average diameter from 20-30 nm.

FT-IR spectra of the PEGMNs are shown in Figure 1. The band at around 627–648 cm^{-1} was assigned to the stretching vibrations of the Fe-O bond in these compounds [35]. The peaks positioned at 3424 cm^{-1} and 2922 cm^{-1} in the FT-IR spectrum of the PEGMNs was related to the stretching and bending of the OH and CH bonds, respectively [18]. The SiO stretching bond was observed at about 1000–1110 cm^{-1} [18].

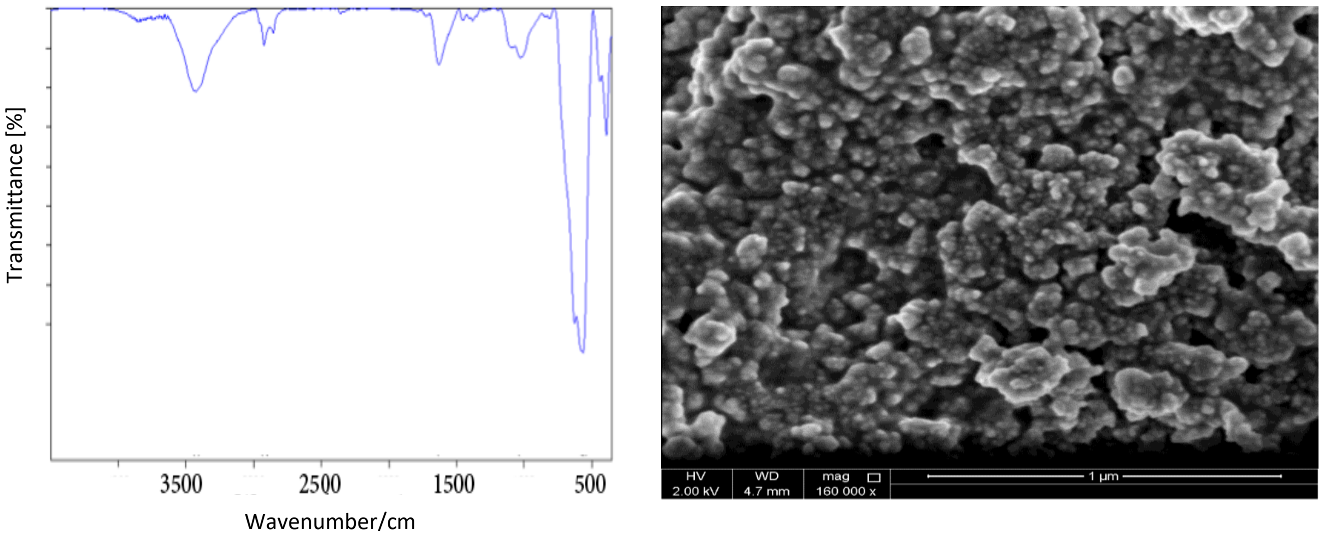

Fig. 1. IR and SEM of PEGMNs

3.1. Effect of adsorbent dosage

The adsorbent dosage is an important parameter because it determines the capacity of the adsorbent for a given diazinon concentration, and it also determines adsorbent–adsorbate equilibrium of the system [2]. Therefore, the effect of adsorbent dosage in the range of 0.1-20 mg on the diazinon adsorption was studied using a solution containing 5 mg/L diazinon. The percentage of the removal of diazinon increased from 55.1% at 0.1 mg to 72.7% at 2.5 mg of adsorbent dosage (Figure 2). The optimum dosage was found to be 1 mg, because after 1 mg, no significantly changes occurred. The improvement of diazinon removal with an increased dose of PEGMNs as an adsorbent can be attributed to the increased adsorbent surface area and the availability of active adsorption sites for a fixed number of diazinon molecules in the solution [12].

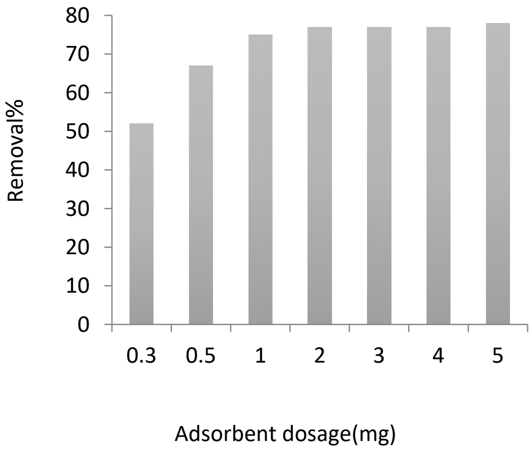

Fig. 2. Effect of adsorbent dosage on removal of diazinon onto (PEGMNs) (diazinon concentration: 5 mg /L PEGMNs dosage: 0.1–20 mg; contact time: 30 min)

3.2. Effect of pH on the diazinon removal

The adjustment of the pH has an important role for the removal of the compounds that can be protonated. In this study, the effect of pH on diazinon adsorption was investigated using a 5 mg/L of initial concentration of diazinon. The pH value varied from 2 to 10 to evaluate the effect of pH on the removal of diazinon onto PEGMNs. As shown in Figure 3, the equilibrium adsorption (q_e) increased by increasing the pH. This behavior suggested that the adsorption was dominated by the van der Waals interaction between the diazinon and adsorbent surface [3]. The existent –OH groups on the surface of PEGMNs were predominantly – OH_3^+ in the aqueous medium. So a double layer with negative electric charge could be formed around the PEGMNs. On the other hand, diazinon molecules have positive electric charge in a pH of 2 because of the pK_a=2.6. Thus the van der Waals interaction between the cationic diazinon molecules and negative surface of the nanoparticles could not be improved at this pH level [13].

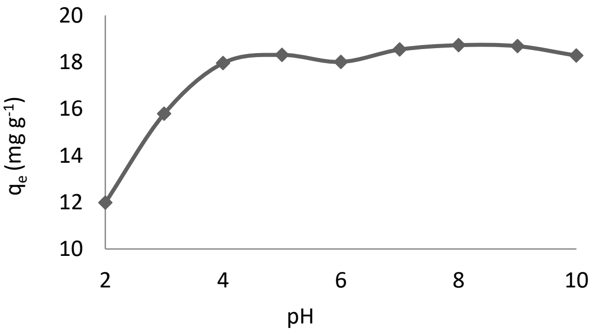

Fig. 3. Effect of solution pH on removal of diazinon onto (PEGMNs). (diazinon concentration: 5 mg/L; solution pH: 2–10; PEGMNs dosage: 1 mg; contact time: 30 min).

3.3. Effect of contact time on the diazinon removal

Another important parameter in the adsorption process is the contact time between adsorbate and adsorbent. The contact time study was performed with initial diazinon concentrations of 5 mg/L, a pH value of 2 and a contact time of 2-60 min. Figure 4 represents the amount of equilibrium adsorption of diazinon onto PEGMNs as a function of contact time. The adsorption process increased rapidly in the first contact period of 10 min, It appeareds that the fast adsorption at the initial stage may be due to the fact that a large number of surface sites were available for adsorption. It was difficult to occupy the remaining vacant surface sites due to the formation of repulsive forces between the diazinon molecules on the solid surface and in the bulk phase [2].

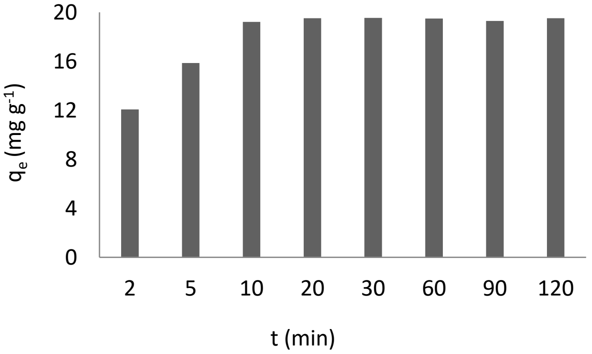

Fig. 4. Effect of contact time on removal of diazinon onto PEGMNs (diazinon concentration: 5 mg /L; solution pH: 7; PEGMNs dosage: 1 mg; contact time: 2-60 min).

3.4 Effect of temperature on the diazinon removal

The effect of temperature on the diazinon adsorption onto PEGMNs was carried out at the range of 15°C to 45°C. The amount of adsorption of diazinon at equilibrium was plotted against the temperature (Figure 5). The amount of the adsorption of diazinon at equilibrium increased with an increasing temperature from 15°C to 45°C indicating an endothermic process. This finding could be due to a tendency for the target molecules to escape from the solid phase to the bulk phase with a decrease in the temperature of the solution [14].

3.5 Effect of water impurities

The effect of several important water impurities including NaCl and ammonia on the adsorption of diazinon onto PEGMNs was investigated. The concentrations of NaCl, and ammonia used were 0–1.5 mg/L and 0–20 mg/L were used respectively [18]. These results showd that the percentage of diazinon adsorption improved in the presence of NaCl (Figure 6(A)). This could be due to the electrostatic interaction that is the main mechanism of diazinon adsorption onto PEGMNs. The increased adsorption of organic molecules with a NaCl concentration of up to 0.1 M has been reported in other research such as Al-Degs et al. [18-19]. In addition, the diazinon adsorption was enhanced in the presence of ammonia (Figure 6(B)). The ammonia molecules in pH<7 have NH_4^+ and OH^- ions and the existent OH^- ions in the aqueous medium could form a double layer with a negative electric charge around the PEGMNs. Therefore, the electrostatic interaction between the cationic diazinon molecules and the negative surface of nanoparticles was confirmed again.

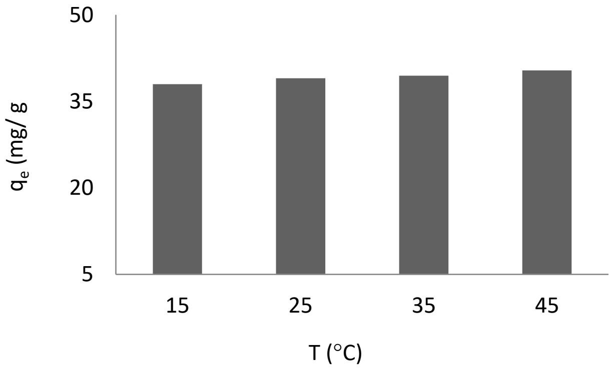

Fig. 5. Effect of temperature on removal of diazinon onto PEGMNs. (diazinon concentration: 5 mg/L; solution pH: 7; PEGMNs dosage: 1 mg; contact time: 10 min, Temperature; 15-45°C).

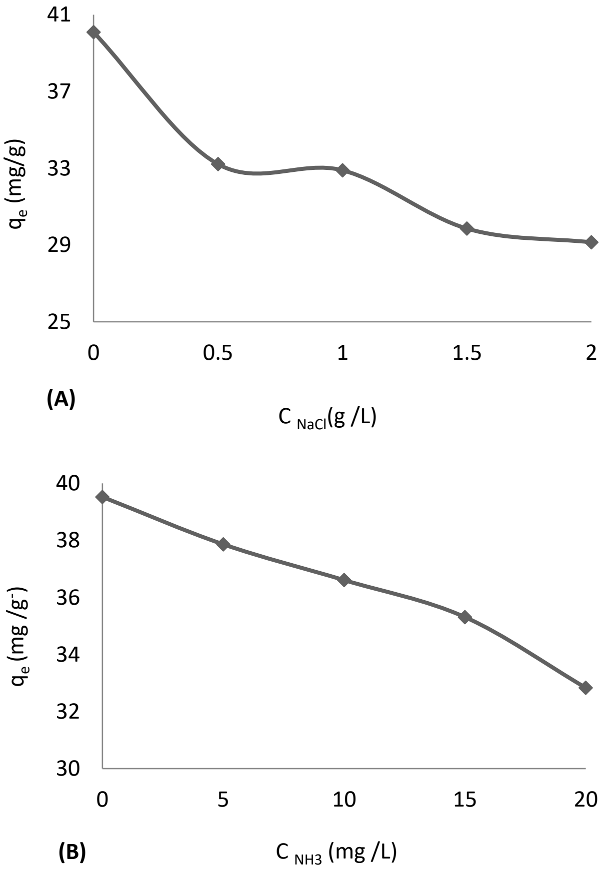

Fig. 6. The effect of different concentration of NaCl and NH_3 on removal f diazinon on PEGMNs.

Finally, in order to investigate the applicability of the proposed method for the removal of diazinon in water samples, adsorption tests were performed on tap, mineral and well water samples spiked with diazinon (5 mg/L). The experiment was conducted at the optimum condition including 1 mg adsorbent, a pH value of 7, and a contact time of 10 min. The obtained results are presented in Table 1. A low amount of PEGMNs could remove diazinon from an aqueous solution at a relatively short contact time with an acceptable percentage. These findings demonstrate the feasibility of PEGMNs in the removal of diazinon from actual contaminated water samples (Table 1).

Table 1. The applicability of the proposed method for removal of diazinon in water samples: Tap, Mineral, Well water

Entry	C_0 (mg/ L)	C_e (mg/ L)	%R
Tap	10	3.53	67.79
Mineral Water	10	3.05	70.69
Well	10	3.84	70.75

Diazinon concentration: 5 mg/ L; solution pH: 7; PEGMNs dosage: 1 mg; contact time: 10 min, temperature

3.6. Isotherm adsorption

Freundlich and Temkin isotherms described the adsorption behavior of diazinon onto PEGMNs. In fact, the Freundlich equation explained the equilibrium adsorption, which is commonly written as [20]:

$$\ln q_e = \ln k_f + (1/n)\ln C_e \tag{1}$$

where the equilibrium adsorption capacity of the PEGMNs is qe (mg diazinon/g PEGMNs), the equilibrium concentration of diazinon is Ce (mg/L) and sorption capacity and intensity are Kf (mg/L) and 1/n, respectively.

The effects of indirect adsorbate/adsorbate interactions on adsorption isotherms were considered by Temkin and Pyzhev. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions. This isotherm can be shown as Equation 4:

$$q_e = RT\ln(AC_e)/b \tag{2}$$

where the Temkin isotherm constant is A (L/g), the gas constant is R (8.314 J mol^{-1} K^{-1}), the heat of adsorption is the Temkin constant (J/mol), and the absolute temperature is T (K)[21]. The linear form of the Temkin isotherm is as follows:

$$q_e = B\ln A + B\ln C_e \tag{3}$$

Where B = RT/b [22-23]. The A and B constants can be determined by plotting q_e against lnC_e.

The result of the curve was fitted with the Freundlich equation (Table 2) instead of the Temkin equation, because the value of R^2 in this isotherm is higher than the other one (R^2=0.9658). Fitting the results with the Freundlich model reflected a heterogeneous surface and the adsorption into a porous material. Therefore, this system apeared to be porous adsorption.

Table 2. Freundlich equation and temkin equation constants[a]

Freundlich		
n	K_F	R^2
1.25	21.84	0.9920
temkin		
A	B	R^2
1.28	48.67	0.9658

a) diazinon concentration: 5 mg/L solution pH: 7; PEGMNs dosage: 1 mg; contact time: 10 min

To better understand diazinon adsorption on PEGMNs, the thermodynamic of this process was investigated. ΔG° is negative and ΔH° and ΔS° were positive during the diazinon adsorption process (Table 3). The negative value of ΔG° showeds that the adsorption of diazinon onto PEGMNs was a spontaneous and favorable process [22]. The positive value of ΔS° indicateds an increase in the state of disorderness in the molecules during the adsorption of diazinon onto adsorbent, which was due to the binding of molecules with the adsorbent surface [23]. The positive value of ΔH° showeds the endothermic nature of the adsorption process. Typically, physisorption, which is mainly driven by the van der Waals interaction forces, is usually lower than 20 kJ/mol; the electrostatic interaction forces range from 20 to 80 kJ/mol and these kind of interaction forces are, frequently, classified as physisorption. Also, the chemisorption bond strengths can be 80–450 kJ/mol [24]. According to the obtained value for ΔH° (+ 6.79 kj/mol), it can be concluded that the adsorption process of diazinon onto PEGMNs was based on the van der Waals interactions.

Table 3. The thermodynamic information of diazinon adsorption onto PEGMNs

Solution temperature (K)	K (mL/g)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J (K mol)$^{-1}$)
288	15.81	-7.12	+6.79	+46.68
298	17.71			
308	18.67			
318	20.91			

In order to evaluate the potential of adsorption of diazinon on PEGMNs, different kind of sorbents were studied. Hence, Fe_3O_4, SMNP, Iranian natural zeolite, and MWCNT which are used in heavy metal removal [24], were checked as adsorbents. According to the obtained results, the time of the proposed method is much shorter (10 min) and the amount of sorbent is significantly lower than other ones

(0.001g), which is indicative of the efficiency of PEGMNs (Table 4).

Table 4. The effect of different sorbents on removal of diazinon[a]

Sorbent	Time (h)	Sorbent dosage (g)	Removal%
Fe_3O_4	1	0.002	23
MWCNTs	8	0.25	1.12
SMNP	1	0.25	39
Iranian natural zeolite	7	0.25	12
PEGMNs	0.16	0.001	83

[a] diazinon concentration: 5 mg/L solution pH: 7

In 2015, F. Chan investigated the effectiveness of chlorine dioxide (CD) to remove phorate and diazinon residues on fresh lettuce and in an aqueous solution. At their optimum condition, 60% of diazinon was remained after 20 min [25]. In 2013, K. S. Ryoo reported fly ash, loess, and activated carbon as adsorbents for the removal of diazinon from water. The equilibrium adsorption times of diazinon by activated carbon and loess were found within 24 h of contact time. Activated carbon showed the best adsorption under the same condition. After 4 hours, approximately 75-85% of the diazinon was removed by the activated carbon. The adsorption data shows that fly ash is not effective for the adsorption of diazinon [24]. The batch removal of diazinon from an aqueous solution by granular-activated carbon was reported by Pirsaheb *et al*. in 2014. After 50 min, the highest removal efficiency of 88% for diazinon was obtained in a 50-min contact time [26]. To our knowledge, the maximum diazinon removed in the minimum contact time was obtained by ASMNPs.

4. Conclusions

The prepared PEGMNs were used for the removal of diazinon from aqueous solutions. For this purpose, the adsorption of diazinon onto PEGMNs was investigated by UV-Vis spectrophotometry at 236 nm, through batch experiments. The effects of adsorbent dosage, solution pH, contact time, and solution temperature were optimized. The results showed that at a natural pH, within 10 min, and the presence of 1mg of PEGMNs, the maximum removal of diazinon was achieved. The isotherm adsorption indicated that this system was fitted with the Freundlich equation but the Temkin equation. Therefore, the application of PEGMNs in the removal of diazinon in environmental remediation could provide lower costs and shorter process times.

Acknowledgements

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