Ultrasond-assisted synthesis of Fe₃O₄/SiO₂ core/shell with enhanced adsorption capacity for diazinon removal

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Abstract

Fe₃O₄/SiO₂ core/shell nanocrystals were synthesized by ultrasond-assisted procedure. The core/shell nanocrystals were characterized using XRD, FT-IR spectroscopy, SEM and BET. The BET analysis confirmed that iron oxide nanocrystal with the surface area of 208.0 m²/g can be used as an excellent adsorbent for organic and inorganic pollutants. The core/shell nanocrystal was used as an adsorbent for removal of insecticide O,O-dietethyl-O[2-isopropl-6-methyl[pyridimidinyl] phosphorothioate (diazinon). In continue the influence of different parameters such as pH, adsorbent dosage and shaking time on the adsorption capacity were studied. The experimental data were fitted well with the pseudo-second-order kinetic model (R²=0.9706). The adsorption isotherm was described well by Langmuir isotherm.

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1. Introduction

The development and improvement of agriculture as well as food industry have been made with intensive uses of pesticides [1]. Due to large quantities and inappropriate use of the pesticides caused pollution of natural environment and food commodity [2]. Toxic pesticide can be a potential hazard to the consumers and environment and at a large scale for chemosphere. Pesticide can produces negative impacts on the society and economics [3]. Several Studies have shown that human exposure to these compounds can have adverse health effects like suppressing of the immune system, cancer and neurological disorder [4]. Extensive use of pesticides has resulted in contamination of water and food. Residual pesticide in food causes a consumers’ safety issue and pesticide residue in environment has become an environment safety issue. Next generation of human have the right to have a safe and clean environment. So the removal of pesticide in the environment as well as surface waters is becoming the public issue.

At this time various adsorbents with different maximum adsorption capacity were used for elimination of pesticide. Activated carbon with adsorption capacity between 1–500 mg/g was used for elimination of organic toxic materials. Dhauadi et al. [5] reported a maximum adsorption capacity of 270.3 mg/g for removal of pesticide using a modified activated carbon. El Bakour et al. [6] obtained 94.8% removal efficiency for endosulfan sulfate removal using acid-treated date stones. Memon et al. [7] used calix arene based silica resin for elimination of endosulfan isomers from aqueous solutions. Gupta et al. [8] prepared an activated carbon from waste rubber which has maximum adsorption capacity of 112, 104.9 and 88.9 mg/g for methoxychlor, atrazine and methyl parathion, respectively. Sousa et al [9] used pine bark for removal of pesticides lindane and heptachlor. Moussavi et al. [10] investigated NH₄Cl-induced activated carbon (NAC) for diazinon removal pesticide from water.

Today, much attention has been paid to the synthesis of nanomaterials with improved sorption capacity for removal of toxic organic/inorganic materials.

Fe₃O₄/SiO₂ nanocrystals have shown prominent result for removal of contaminations from water [11–13]. These nanoparticles could become cost-effective nanomaterials for decontamination of chemical pollutions. Using Fe₃O₄/SiO₂ nanocrystals in adsorption process was believed to exhibit a high potential for the adsorption of organic/inorganic materials [14–16]. However, after a saturated sorption process, the separation of the adsorbent-adsorbate from aqueous solution is a time-consuming and complex process. Magnetically assisted separation of adsorbent-adsorbate by applying an appropriate magnetic field is a main key to solve the problem. So, the advantages of Fe₃O₄/SiO₂ nanocrystals such as efficient removal and easy separation by a magnet motivated us to consider this nanomaterial as adsorbent for removal of diazinon. In this study, the adsorption property of Fe₃O₄/SiO₂ nanocrystals for the removal of diazinon from aqueous solution was investigated under optimum experimental conditions. To obtain the adsorption capacity and adsorption mechanism of diazinon onto Fe₃O₄/SiO₂ nanocrystals surface, adsorption kinetics and adsorption isotherms are obtained.

2. Experimental

2.1. Material and methods

All chemicals were of analytical grade and used as received. Diazinon was obtained from Sigma-Aldrich. Ferrous chloride tetrahydrate...
Iron oxide nanocrystals were prepared via an improved chemical co-precipitation method. Briefly, FeCl₃·4H₂O (1.5 mmol) and FeCl₂·6H₂O (3 mmol) prepared in 0.01 M hydrochloric acid was rapidly injected by a plastic tube to 80 mL 2 M ammonia solution. The system was sonicated under N₂ for 1 h at 25 °C. The precipitated was washed with pure ethanol and separated by magnetic decantation. Finally, Fe₃O₄ nanocrystals were dried under vacuum at 70 °C.

3. Ultrasound-assisted synthesis of Fe₃O₄/SiO₂ core/shell nanocrystals

A suspension of iron oxide nanocrystals was sonicated in 30 mL ethanol for 30 min to get uniform dispersion. A solution of 0.7 mL concentrated ammonia in 9.3 mL double distilled water was added to nanocrystal suspension. After 15 min of sonication, a solution of 1.8 mmol TEOS and 5 mL ethanol was injected to the sonicator. Sonocatalytic treatment was aged 2 h at 25 °C. After 1 h of sonication, a very stable black colored magnetic fluid was obtained. The precipitate was collected with a magnet, and washed with ethanol (three times). Finally, Fe₃O₄/SiO₂ nanocrystal was obtained by ethanol evaporation at a reduced pressure chamber.

4. Results and discussions

4.1. Fe₃O₄/SiO₂ core/shell nanocrystals characterization

4.1.1. FT-IR study

The FTIR spectra of superparamagnetic iron oxide nanocrystal, and superparamagnetic iron oxide/SiO₂–NH₃ nanocrystal are presented in Fig. 1. For both nanocrystals, absorption peaks at 581 cm⁻¹ were observed, which are correspond to the Fe–O vibration of the magnetite phase of nanocrystal [20]. The binding of silica shell to iron oxide nanocrystal is apparent from FTIR spectra (Fig. 1) where the following modes are observed: a) vibration and stretching of SiO₂ at 1221, 1046, 991, and 993 cm⁻¹ which is in agreement with that reported by Huang et al. [18], b) bending and stretching vibrations of amino functional groups at 2808, 1603, and 693 cm⁻¹ [17–20], and c) stretching vibration of C–C groups of propyl functional groups at 2800–3025 cm⁻¹ [20]. In comparison between Fig. 1a and b, significant changes in FTIR spectra are observed when the aminopropyl functionalized iron oxide nanocrystals are compared to the bare iron oxide nanocrystals. This indicates a strong binding of SiO₂ groups to the iron oxide nanocrystals and effective aminopropyl functionalization process. Also, a comparison of FTIR spectra of bare iron oxide nanocrystals and iron oxide/SiO₂–NH₃ in Fig. 1 indicates that iron oxide is coated by SiO₂ shell which Fe–O transmittance in Fig. 1b is reduced rather than what is seen in Fig. 1a. The aminopropyl and SiO₂ vibration at 2808 cm⁻¹ and 991–1221 cm⁻¹ which are absent in the bare iron oxide nanocrystals are clearly approved the aminopropyl-triethoxysilanation process [17–20].

4.2. X-ray diffraction pattern

The crystal structure of the nanocrystals was identified with X-ray diffraction pattern. Diffraction peaks 2θ at 30.0, 35.6, 43.8, 54.2, 57.2 and 62.5 shown in Fig. 2 indexed to (220) (311) (400) (422) (511) and (440). This show that the crystal structure of iron oxide nanocrystal is cubic spinel [16]. The particle size of the magnetite was calculated using the Scherrer equation as 11.3 nm.

4.3. Scanning electron microscope

To determine the average particle size and morphology of nanocrystals, Scanning Electron Microscope (SEM) was used. In Fig. 3, the SEM images of nanocrystals show particles with amorph surface.

![Fig. 1. FT-IR spectra of a) Fe₃O₄, b) Fe₃O₄/SiO₂–NH₃.](image1)

![Fig. 2. XRD-pattern of Fe₃O₄.](image2)

![Fig. 3. SEM micrograph of Fe₃O₄.](image3)
4.4. BET and zeta potential

Surface areas of Fe$_3$O$_4$ nanocrystal and Fe$_3$O$_4$/SiO$_2$–NH$_2$ were measured according to BET procedure [21]. The results show that surface areas of Fe$_3$O$_4$ nanocrystal and Fe$_3$O$_4$ nanocrystal/SiO$_2$–NH$_2$ are 112.3, and 208.0 m$^2$/g, respectively. (Scheme 1)

The respective zeta potential of nanocrystals was measured in the pH range of 2–12. The pH of zero charge pH (p$\text{H}_{\text{ZPC}}$) of nanocrystals was determined as 2.8 which is in agreement with the literature [22]. The results of this study shows that the surface of nanocrystals was slightly negative charged at pH>2.8. This implies that the deprotonation of amine groups on the nanocrystals will occur at pH>2.8.

4.5. Magnetic behavior

The magnetic behavior of the nanocrystals was studied using VSM. The magnetization hysteresis loop of Fe$_3$O$_4$/SiO$_2$–NH$_2$ is shown in Fig. 4. The results show that the magnetic behavior of nanocrystals is similar to that of superparamagnetic materials. The saturated magnetization of the superparamagnetic nanocrystals at room temperature was 40 emu/g. This result is in agreement with the results of Majeed et al. [17].

4.6. Adsorption experiments

Adsorption experiments were conducted using batch approach. Briefly, at room temperature, 50 mL solution contains 0.4 mg/L diazinon and 0.2 mg nanocrystal added into a 30 mL flask. The pH of mixture fixed to 6. The suspension was mixed by a shaker for 25 min.

The removal sorption capacity of sorbent was calculated using Eq. (1)

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

(1)

where $q_e$(mg/g) is the sorption capacity of the sorbent. $C_0$(mg/L) is the initial diazinon concentration, $C_e$(mg/L) is the equilibrium diazinon concentration, $m$(g) and $V$(L) are sorbent mass and solution volume, respectively.

4.7. Optimization of adsorption parameters

The optimization of experimental parameters was carried out for diazinon adsorption. The pH of the solution affects the surface charge of the nanocrystal, degree of ionization of the materials, and dissociation of functional groups on the adsorbent. As well, it affects on the both structure of the diazinon molecule and nanocrystal surface [23]. The sorption capacity of nanocrystal as a function of pH is plotted in Fig. 5. The sorption capacity increased from 8–28 when pH was increased from 2–6. This was because the diazinon molecule adsorbed easily even in inert media. As the initial solution pH decreased, the number of positively charged active sites increased due to the protonation of the amine groups (–NH$_2$) in the nanocrystal chain. Consequently, the electrostatic interaction between the positively charged adsorbent and the diazinon A increased, which resulted in increased adsorption. Therefore, higher adsorption capacities were observed at inert pH value. The effect of adsorbent dosage (varied from 0.001 to 0.3 g) on the sorption capacity of 0.4 mg/L diazinon solution was studied. The sorption capacity of diazinon from the solution in-

Scheme 1. Fe$_3$O$_4$/SiO$_2$ core/shell nanocrystals have a maximum adsorption capacity for removal of diazinon in environment.
Fig. 4. Magnetization hysteresis loop of Fe$_3$O$_4$/SiO$_2$–NH$_2$ nanocrystals at room temperature.

Fig. 5. Effect of pH on the adsorption of diazinon onto Fe$_3$O$_4$/SiO$_2$–NH$_2$.

Fig. 6. Effect of shaking time on the adsorption of diazinon onto Fe$_3$O$_4$/SiO$_2$–NH$_2$.

The sorption capacity increased from 7–30 when time was increased from 5 to 50 min, this due to saturation of active sites which do not allow further adsorption to take place [25].

4.8. Adsorption kinetics

To obtain the sorption process model, kinetic of adsorption was studied [26,28–30]. In this study, main sorption kinetic models such as first order and pseudo-second-order kinetics were employed to analysis the adsorption data. The results of kinetic study of the sorption process are given in Table 1 and Fig. 7. The results showed that the adsorption kinetic of diazinon onto the nanocrystal followed the pseudo-second-order kinetic model. As shown in Fig. 6 and Table 1, the correlation coefficient of the pseudo-second order ($R^2=0.9706$) is higher than of the first order (0.9518) kinetic model.

4.9. Adsorption isotherms

In a batch setup, molecular distribution at the equilibrium state between liquid and solid phases as adsorbent and adsorbed molecules can be obtained in the adsorption isotherms representation. Langmuir and Freundlich isotherms as main adsorption isotherms are widely applied to obtain the equilibrium sorption isotherm model of batch systems. In the Langmuir system of adsorption the monolayer adsorption occurs on a homogeneous surface of the adsorbent without any interaction between the absorbed molecules [26]. The Langmuir isotherm can be shown by Eq. (2):

$$\frac{C_e}{q_e} = \left( \frac{K_L}{q_m} \right) + \frac{1}{K_L q_m}$$

(2)

where $K_L$, $C_e$ and $q_e$ are adsorption constant (Lmg$^{-1}$), diazinon concentration at equilibrium state (mgL$^{-1}$), and the amount of diazinon adsorbed per unit of adsorbent (mgg$^{-1}$) at equilibrium concentration $C_e$, respectively. In Eq. (2) $q_m$ represents the maximum adsorption capacity (mgg$^{-1}$). Note that $q_m$ is depends on the number of adsorption sites of adsorbent nanocrystals.

Table 1

| Isotherm model parameters for diazinon sorption on Fe$_3$O$_4$/SiO$_2$–NH$_2$. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Langmuir model  | Freundlich model |
| $q_{max}$       | $K_L$           | $R^2$           | $K_f$           | $n$             | $R^2$           |
| 206.18          | 3.233           | 0.9966          | 12.5            | 26.63           | 0.9886          |

Fig. 7. Pseudo-second order model of adsorption of diazinon onto Fe$_3$O$_4$/SiO$_2$–NH$_2$ core/shell nanocrystal.

creased from 5 to 29 as the adsorbent dosage increased from 0.001 to 0.3 g [24].

To study the effect of shaking time on the sorption capacity, 0.4 mg/L of diazinon was taken in conical flasks and treated with 0.2 mg adsorbent (nanocrystal) at several times (5–50 min.). The variation in sorption capacity of nanocrystal with the time was shown in
The Freundlich isotherm model is [27–30]:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{3}$$

where $b$ (L/mmol) is the affinity coefficient. Langmuir and Freundlich isotherm parameters and correlation coefficient ($R^2$) are presented in Table 2 and Fig. 8. A comparison between correlation coefficient of Langmuir and Freundlich isotherm show that the Langmuir correlation coefficient ($R^2 = 0.9966$) was lower than of Freundlich ($R^2 = 0.9886$) in.

### Table 2

Kinetic model parameters for diazinon sorption on Fe$_3$O$_4$/SiO$_2$–NH$_2$.

<table>
<thead>
<tr>
<th>Model</th>
<th>$K_2$</th>
<th>$q_{e,\text{Cal}}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-second order</td>
<td>0.00126</td>
<td>46.89</td>
<td>0.9706</td>
</tr>
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</table>

![Figure 8](image-url)

**Fig. 8.** (a) Adsorption isotherm (Langmuir) of diazinon on Fe$_3$O$_4$/SiO$_2$–NH$_2$. (b) Adsorption isotherm (Freundlich) of diazinon on Fe$_3$O$_4$/SiO$_2$–NH$_2$.

indicating that the Freundlich model fitted the experimental data better than other isotherm model.

### 5. Conclusion

Removal of diazinon in environmental water samples is very important today. In this paper Fe$_3$O$_4$/SiO$_2$–NH$_2$ core/shell was synthesized via ultrasound-assisted method. The results of this study showed that the synthesized nanocrystal has a maximum adsorption capacity for removal of diazinon in aqua’s solutions. SiO$_2$ reduces the serious stacking of iron oxide and prevents the agglomeration of nanocrystals, and also produces a high tunable surface area, which enables to high binding capability and excellent adsorption properties for diazinon. The superparamagnetic property of nanocrystals resulted in the fast separation of adsorbent-adsorbate from aqueous solution in the presence of a magnet. This adsorbent is stable, low-cost, and environmentally friendly and shows potential application in the removal of diazinon.

### References


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