Efficient removal of deltamethrin from polluted aquatic media by modified iron oxide magnetic nanoparticles

Bahareh Ghafari^a, Elham Moniri^{b,*}, Homayon Ahmad Panahi^c, Abdolreza Karbassi^d, Shaban Najafpour^e

^aDepartment of Environmental Science, Faculty of Environment and Energy, Science and Research Branch, Islamic Azad University, Tehran, Iran, email: bahare.ghafari@gmail.com

^bDepartment of Chemistry, Varamin (Pishva) Branch, Islamic Azad University, Tehran, Iran, Tel. +989125011003; email: moniri30003000@yahoo.com

^cDepartment of Chemistry, Central Tehran Branch, Islamic Azad University, Tehran, Iran, email: h.ahmadpanahi@iauctb.ac.ir ^dDepartment of Environmental Engineering, Faculty of Environment, University of Tehran, Tehran, Iran, email: akarbasi@ut.ac.ir ^eDepartment of Ecology, Caspian Sea Ecology Research Center (CSERC), Sari, Iran, email: najafpour_s@yahoo.com

Received 22 April 2016; Accepted 2 July 2016

ABSTRACT

In the present study, iron oxide magnetic nanoparticles were synthesized by co-precipitation method. Iron oxide magnetic nanoparticles were modified with 3-mercaptopropyltrimethoxysilane and grafted with 2-dimethylacrylamid, allylglycidylether and then coupled with 3-hydroxytyramine. The characterization of nanoparticles was confirmed by Fourier Transform Infrared spectroscopy, thermogravimetric analysis, elemental analysis, transmission electron microscopy, scanning electron microscope, and surface area determination. This was shortly followed by efficient removal of deltamethrin pesticide in environmental water as a real sample, using a modified nanoadsorbent. Optimum conditions for the removal of deltamethrin were obtained by examining important variables such as temperature, contact time, agitation speed and pH. The optimum condition for deltamethrin removal is obtained at 20°C with 200 rpm in pH 7 after 45 min. Different models of adsorption isotherms such as Langmuir, Freundlich and Temkin were studied, and relevant constants were determined and compared with previous studies. These studies showed that the Langmuir isotherm model adjusted well to the adsorption data. The optimum adsorption capacity of deltamethrin was 27.5 mg/g. The nanoadsorbent can be reused for 13 cycles of sorption-desorption with only maximum 17% changes in reducing sorption capacity. The practicality of the procedure is its usefulness in the removal of deltamethrin pesticide in agricultural wastewater with reasonable efficiency.

Keywords: Iron oxide magnetic nanoparticles; Deltamethrin; Agricultural wastewater; Adsorption isotherms; 3-hydroxytyramine

1. Introduction

The contamination of water sources by different pollutants, such as agricultural pesticides, is considered as a serious problem and a threat to human health due to their high toxicity [1,2]. Deltamethrin, with chemical formula $C_{22}H_{19}Br_2No_{37}$

*Corresponding author.

is a type of pyrethroid pesticide (Table 1) [3,4]. This pesticide is one of the main pesticides used all over the world, and its toxicology was assessed in water and wastewater samples [5,6]. Deltamethrin is a stable compound with low solubility in water and is one of the most widely and frequently used pyrethroids against a broad of insect pests [7]. Its presence in agricultural water and wastewater is a major concern, as a result of toxicity to nature and the environment as a whole [8,9]. The effects of exposure to deltamethrin, like Dichloro-Diphenyl-Trichloro-ethane (DDT), and many types of pesticides

1944-3994 / 1944-3986 © 2017 Desalination Publications. All rights reserved.

Table 1 Some properties of deltamethrin



on humans include, abdominal pain, headache, dizziness, skin and eye problems, memory disorders, severe neural disorders, cancer and infertility [10,11]. The special area of its effect is still unknown, but DDT and deltamethrin are known to affect the brain, spinal cord and peripheral nervous system [12,13]. Deltamethrin is widely used in the spraying of fruit tree, cultivation of wheat, beet and so on, and is extremely toxic to the aquatic environment, especially fishes [4]. Besides the inorganic adsorbents used to remove pollution from aquatic solutions, some recent studies have revealed other materials with good efficiency and adsorption capacity for the removal of hazardous substances from wastewater; examples include hen feathers [14-17], egg shell [18,19], bottom ash, de-oiled soya [20,21], white rot fungi [22] and fungal biomass composite [23]. Some recent adsorbents have been improved for increasing capacity [24].

Today, nanotechnology plays a very important role in the removal of contaminants from agricultural water and wastewater [25,26], and this technology is based on synthesis [27,28]. In previous studies, methods applied for the removal of deltamethrin include oil shale ash (OSA) [29], acid treated oil shale ash (ATOSA) [30] and membrane processes [31]. These processes mostly encountered failure and were accompanied with decreased efficiency. The magnetic separation method has been widely used because of its low cost, simplicity, optimal speed, as well as high efficiency [32,33]. These iron magnetic nanoparticles are widely used to solve environmental problems (removal of chemical compounds, pesticides, dyes and gases) due to chemical stability without creating secondary pollution [34,35]. Among the nanoparticles, iron oxide magnetic nanoparticles are of particular interest because they are easily separated by an external magnetic field and can be used in various fields owing to their non-toxicity. Also, with the use of surface modification, these nanoparticles can be functionalized by particular groups to make them suitable for more attachment to bioactive molecules with various applications [36]. In comparison with usual micron sized adsorbents, nanomaterials are of high interest because of their physical and magnetic qualities and nanosize [37]. The small size of these nanoparticles gives them special properties together with the expansion of their dispersal and special surface area, which have important effect on their adsorption capacity. The magnetic separation method has become an attractive application, as a result of the laboratory scale synthesis of super-paramagnetic particles (usually Fe₂O₃ or Fe₂O₄), magnetic actions and easy applications [38]. However, until now, literatures on magnetic separation method in monitoring pesticide residue research have been uncommon. The surface charge of nanoparticles plays a significant role in their interaction with other compounds and the environment [39,40]. In addition, it is easier to utilize chemical modification to exchange the chemical characteristics of the adsorbent's surface [41]. Thus, the surface modified adsorbents can have larger attraction to some special substances, especially pesticides. The novelty and significance of this study is in the synthesis of efficient magnetic nanosorbents, for the removal of toxic pesticide from aqueous media. The co-precipitation method was applied in the synthesis of magnetic nanoadsorbents. Then, this nanoparticle was grafted by polymer containing 2-dimethylacrylamide and 3-hydroxytyraminium chloride as a ligand for maximum interaction with deltamethrin. This magnetic nanosorbent can be easily separated from aqueous media by magnetic field and also has an excellent sorption capacity for deltamethrin as a case study.

The purpose of this study is to estimate the adsorption potential of the polymer containing 3-hydroxytyraminium chloride grafted magnetic nanoparticles (PCH-MNP) for deltamethrin. The data can be useful in forecasting the rate at which the target particle is removed from aquatic media in optimum parameters.

2. Materials and methods

2.1. Instruments

Analytical methods for deltamethrin detection focus on a combination of high-performance liquid chromatography-UV detection (HPLC-UV) and ultraviolet-visible spectrophotometry (UV/Vis). Chromatographic separations were performed on an Agilent HPLC, 1200 series, qualified with a UV/Vis detector. Separations were performed on a Zorbax Extend C18 column (15 cm, with 3 mm particle size) from the Agilent Company (Wilmington, DE, USA). The acetonitrile/ water (74/26, v/v, 10% methanol was included in water) was used as the mobile phase. The detection wavelength was 210 nm with an injection volume of 20 µl. The UV-visible spectrum was recorded using the Cary 50 UV/Vis1601 spectrophotometer (Shimadzu, Japan). The pH measurements were made with a Metrohm meter, model 744 (Zofingen, Switzerland). Fourier Transform Infrared spectroscopy (FT-IR) spectra were reported on a FT-IR spectrometer Jasco/FT-IR-410 using the KBr pellet method (Easton, Maryland). Thermal gravimetric analysis (TGA) was performed using a TGA-50H (Shimadzu Corporation, Japan). The samples were characterized with a transmission electron microscope (TEM) model-EM208 (Philips Company, Amsterdam), scanning electron microscope (SEM) model EM-3200 (KYKY Company, China), elemental analysis (Carbon, Hydrogen, Nitrogen, and Sulphur (CHNS)) model VARRIO El (Linseis Company, Germany), and surface area determination (Brunauer-Emmett-Teller (BET)) model Belsorp-mini II (Shimadzu, Japan).

2.2. Reagents and solutions

The products used were all from Merck (Darmstadt, Germany) namely: 3-mercptotrimethoxysilane (MTPMS), nitrate, acetone, ethanol, allylglycidylether (AGE), ammonia, 2, 2'-azoisobutyronitrile (AIBN), 3-hydroxytyraminium chloride, toluene, NaCl, sodium dihydrogen phosphate, disodium

hydrogen phosphate, sodium acetate, acetic acid, FeCl₂.4H₂O, and FeCl₃.6H₂O. 2-dimethyl acrylamide, technical grade of deltamethrin (98%), was supplied by Aldrich (Steinheim, Germany). Deltamethrin stored at +4°C, due to the low solubility of deltamethrin, the first stock solution (500 mg/L) was prepared by dissolving a suitable amount of deltamethrin with methanol. The secondary solution (50 mg/L) was made by diluting with distilled water. 0.01 M acetic acid – acetate buffer (pH 3.5–5) and 0.01 M phosphate buffer (pH 6–7.5) were applied to settle the pH of the solutions, when necessary.

3. Synthesis of iron magnetic nanoparticles in four stages

3.1. First stage – synthesis of iron oxide magnetic nanoparticles

Details of the synthesis of the iron oxide magnetic nanoparticles have been described elsewhere [42]. The preparation of iron oxide magnetic nanoparticles was made possible using chemical co-precipitation [42]. Firstly, into a three-necked flask containing 100 mL of distilled water were 2.5 g of FeCl₃.6H₂O and 4 g of FeCl₂.4H₂O were dissolved. A solution containing 8 mL ammonia in 100 mL distilled water was added to the solution, dropwise [42]. The solution was kept at a temperature of 80°C for 2 h coupled with strong stirring under nitrogen atmosphere. The solution in flask was washed with water and ethanol, and the resultant precipitate was decanted by external magnet and dried under vacuum at room temperature for 24 h [42].

3.2. Second stage – surface modification of iron magnetic nanoparticles by 3-mercaptotrimethoxysilane

For surface modification of iron magnetic nanoparticles, nanoparticles obtained from the first stage (3 g), 50 mL anhydrous toluene and 2.5 mL MTPMS were refluxed at 110°Cfor 48 h [43]. The resultant precipitate was decanted by external magnet and washed with 20 mL anhydrous toluene or acetone and dried at room temperature for usage in the next stage [43].

3.3. Third stage – polymer grafting by allylglycidylether and 2-dimethyl acrylamide

This stage involved the grafting of functionalized monomer onto the modified magnetic nanoparticles. The mixture of 10 mL AGE and 2 mL 2-dimethyl acrylamide as the monomers, 0.1 g AIBN as initiator, 30 mL ethanol as solvent and 3 g as the modified magnetic nanoparticles were

poured into a two-necked flask and refluxed at 65°C–70°C for 7 h in a water bath under nitrogen atmosphere [44]. The solution was washed in flask with distilled water and then with ethanol, and was decanted using an external magnet.

3.4. Fourth stage – coupling by 3-Hydroxytyraminium chloride

In the final stage, coupling of 3-hydroxytyraminium chloride onto the grafted and modified magnetic nanoparticles was carried out. 3-hydroxytyraminium chloride (1 g) was dissolved in 50 mL buffer solution (pH 5), containing 0.1 g NaCl salt, and polymer grafted magnetic nanoparticles were placed on an incubator shaker at 40°C for 48 h. The solution was decanted using an external magnet and washed with 50 mL buffer solution (pH 5) and then 50 mL distilled water, followed by drying at room temperature. In a schematic form, Fig. 1 shows the synthesis of iron magnetic nanoparticles in four stages.

4. Adsorption studies of deltamethrin

4.1. Batch method

The adsorption tests of deltamethrin by PCH-MNP were studied in aquatic media. In general, 0.05 g of PCH-MNP adsorbent was taken into a beaker and mixed with 10 mL of working solution for 45 min at pH 7. The magnetic nanoad-sorbents were removed using a magnetic field, and the supernatant was filtered. The concentration of deltamethrin in the solution was measured at a maximum wavelength of deltamethrin (250 nm), using UV/Vis spectrophotometer or HPLC. The volume of adsorbed deltamethrin onto adsorbent was calculated with the following equation (Eq. (1)):

$$q_{e} = (C_{0} - C_{e}) V/W$$
(1)

where C_0 and C_e (mg/L) are initial and equilibrium concentrations of deltamethrin; V (L) is the amount of the deltamethrin solution and W (g) is the mass of PCH-MNP used.

5. Results and discussion

5.1. The characterization of modified magnetic nanoparticles

Different techniques including FT-IR, CHNS, TGA, TEM, SEM, and BET were used to characterize the PCH-MNP, all of which confirmed the synthesis and modification of the nanoadsorbent.



Fig. 1. Schematic presentation of four stages of iron magnetic nanoparticles synthesis.

5.1.1. FT-IR spectrum

The FT-IR spectrums of magnetic nanoparticles, before and after modification, were compared. The peaks at 3,157.86 cm⁻¹ (O-H) and 567.93 cm⁻¹ (Fe-O) are for synthesis of iron oxide magnetic nanoparticles. There exist an additional band for the modification of iron magnetic nanoparticles by MTPMS, which is shown by the peaks at 2,922.74 cm⁻¹ (C-H) and 1,099.33 cm⁻¹ (SiO). Additional bands in the stage of polymer grafting by AGE and 2-dimethyl acrylamide, with peaks at 2,928.23 cm⁻¹ (aliphatic C-H), 1,669.21 cm⁻¹ (C=O), 1,454.28 cm⁻¹ (CH₂) and 1,097.68 cm⁻¹ (SiO and CO) are shown in this stage. The additional peaks at 3,212.93 cm⁻¹ (aromatic C-H), 2,930.71 cm⁻¹ (aliphatic C-H) and 1,095.26 cm⁻¹ (SiO and CO) were related for coupling by 3-hydroxytyraminium chloride and confirmed the success of the synthesis.

5.1.2. Thermal gravimetric analysis

The TGA of PCH-MNP displayed two-step weight loss of up to 600°C. The weight loss of up to 120°C was due to the adsorbed water molecules on the PCH-MNP. The major weight loss from 200°C to 550°C was as a result of the decomposition and desorption of the grafted polymer moiety. These results confirmed the successful polymeric modification of magnetic nanoparticles.

5.1.3. Elemental analysis

The modification was also confirmed by elemental analysis. The CHNS analysis was used to determine the mass percentages of carbon, hydrogen, nitrogen and sulfur of the molecular weights of PCH-MNP. The following results were found C, 15.43%; H, 2.76%; S, 1.33%; N, 4.31%, which confirmed the formation of the polymer.

5.1.4. Scanning electron microscopy and transmission electron microscopy

The morphology of PCH-MNP were analyzed by TEM and SEM. Figs. 2(a) and (b) displays spherical agglomerated parti-

cles with an average diameter fewer than 100 nm (30–80 nm) and the surface of PCH-MNP, which was not smooth.

5.1.5. Surface area determination

The BET equation is applicable for surface area analysis of nonporous materials. Accurate measurement of surface area and porosity of nanoadsorbents was done by analysis of nitrogen adsorption and desorption. The total surface area of the PCH-MNP was measured by the BET method with a resultant calculated value for the specific surface area of about 239 m^2/g .

5.2. Adsorption quality of modified magnetic nanoparticles for deltamethrin

5.2.1. Effect of pH

The pH of solutions has a significant effect on the progress of adsorption. In this study, the range of pH investigated was between 3.5 and 7.5. As shown in Fig. 3, the highest adsorption capacity was obtained at pH 7. Optimal pH value at 7 indicated that a neutral pH was ideal for the adsorption. Fortunately, the agricultural wastewater was used as a real sample and had a pH around 7, and this demonstrated that the optimum pH suitable for increased adsorption was operative in the aquatic environment. This can be demonstrated by the various solubility of deltamethrin at different pH values. A pH level below 3 and above 8 was not expected as a result of the capability for decomposing and dissolving modified magnetic nanoparticles, respectively. Regardless of the type of adsorbate and modification, the highest adsorption of deltamethrin by OSA was achieved at pH 3 [29].

5.2.2. Effect of contact time

Adsorption as a function of contact time for the deltamethrin is shown in Fig. 4. It can be seen that an increase in exposure time resulted in an increase in the amount of deltamethrin adsorption. Less than 5 min shaking was required for 40% sorption; short contact time was ideal for the removal



Fig. 2. (a) TEM and (b) SEM images of PCH-MNP.



B. Ghafari et al. / Desalination and Water Treatment 59 (2017) 304-311

Fig. 3. Effect of pH on uptake of deltamethrin (20 mg/L) by PCH-MNP (0.05 g) at 20°C (results are represented as mean \pm SD; n = 4).



Fig. 4. Effect of contact time on the uptake of deltamethrin (20 mg/L) by PCH-MNP (0.05 g) at pH 7 and 20°C (results are represented as mean \pm SD; n = 4).

of deltamethrin from aquatic environment. Adsorption of deltamethrin from solution by PCH-MNP in 45 min was sufficient and optimum. At an exposure time beyond 45 min, no significant changes were seen in the amount of deltamethrin adsorption. This may be due to the filling of adsorbent pores or difficult access of deltamethrin molecules to active sites on the surface of the adsorbent. However, quick adsorption of deltamethrin in early exposure times may be due to the large surface area of the PCH-MNP adsorbent, which can apply numerous active sites to deltamethrin molecules. The profile of deltamethrin uptake on this sorbent was considered as available good active sites in the nanosorbent.

5.2.3. Effect of temperature

The adsorption tests were done at six different temperatures (15°C, 20°C, 25°C, 30°C, 35°C and 40°C) under optimized conditions settled by prior tests, and the conclusions of these tests are shown in Fig. 5. An increase in temperature resulted in a decrease in the adsorption capacity due to the high mobility of the sorbate molecule, deltamethrin. Good adsorption was recorded at temperatures below 30°C. The optimum temperature was estimated at 20°C, and this



Fig. 5. Effect of temperature on the uptake of deltamethrin (20 mg/L) by PCH-MNP (0.05 g) at pH 7 (results are represented as mean \pm SD; n = 4).

is advantageous as a result of the reaction involving the removal of the deltamethrin by PCH-MNP, which can be performed at room temperature. In some countries, in different seasons of one year, temperature varies from 15°C to 40°C. The mean bulk removal for one year is about 97% and is very suitable for one adsorbent that can adsorb pesticides with this high efficiency, for this range of temperature variation.

5.2.4. Effect of agitation speed

The effect of different agitator speeds on adsorption of deltamethrin with PCH-MNP is studied. It is clear that the rate of adsorption increases as the agitator speed increases. This effect can be explained by the increased turbulence and the decrease in boundary layer thickness around the nanoadsorbent particles, as a result of an increase in the degree of mixing. It has been discovered that an increase in the mixing rate increased the adsorption capacity until a mixing rate of 300 rpm was reached. Beyond this mixing rate, there was a decrease in adsorption, which implies an inefficiency in energy consumption.

5.2.5. Stability and reusability of the nanosorbent

Deltamethrin was sorbed and desorbed on 0.1 g of PCH-MNP several times. It was discovered that the sorption capacity of nanosorbent after 13 cycles of its equilibration with deltamethrin experienced less than 17% change from 100% to 83%. The result of reusability nanosorbent is studied. Consequently, repeated use of the nanosorbent is possible, and there was no significant difference between the usage times. The nanosorbent after loading with samples can be quickly and easily regenerated with methanol. The sorption capacity of the nanosorbent stored for more than one year under ambient conditions has been provided to be practically unchanged.

5.3. Adsorption isotherms

The equilibrium data were correlated by Langmuir, Freundlich and Temkin equations for deltamethrin adsorption on PCH-MNP and were used to define and describe adsorption data.

308

Langmuir is a broadly applied adsorption isotherm. This adsorption isotherm has been applied to estimate the capacity of a nanosorbent, by discovering the volume of deltamethrin adsorbed by a gram of PCH-MNP. The Langmuir equation is as follows (Eq. (2)) [45]:

$$C_{e}/q_{e} = (C_{e}/q_{\max}) + (1/q_{\max}K_{L})$$
(2)

In Langmuir equation, C_e (mg/L) is the equilibrium concentration of deltamethrin; q_e (mg/g) is the concentration of deltamethrin on the adsorbent; K_L (L/mg) is the Langmuir constant for adsorption capacity and energy and q_{max} (mg/g) is the maximum adsorption capacity, corresponding to the complete coverage on the surface. Respectively, the data appropriated well in the Langmuir equation as shown by the regression coefficient values (Table 2). The level of desirability or undesirability of adsorption is studied in the Langmuir equation by calculation of another quantity. The important characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_i , defined as Eq. (3) [45]:

$$R_{L} = 1/(1+K_{L}C_{0}) \tag{3}$$

where C_0 is the initial deltamethrin concentration (mg/L) and K_L is the energy of interaction at the surface. If $R_L > 1$ is undesirable adsorption, $R_L = 1$ is linear adsorption; $0 < R_L < 1$ is desirable adsorption and $R_L = 0$ is irreversible adsorption. Thus, the R_L value of 0.27 calculated at optimum pH lies between 0 and 1, indicating a highly favorable and desirable adsorption (Table 2).

The Freundlich adsorption was also related to the adsorption of deltamethrin by PCH-MNP and is given as follows (Eq. (4)) [46]:

$$\ln q_e = \ln K_f + 1/n \ln C_e \tag{4}$$

In the Freundlich equation, q_e (mg/g) is the amount of deltamethrin adsorbed per unit weight of the adsorbent; C_e (mg/L) is the equilibrium concentration; K_f is the Freundlich constant (mg/g) (L/mg)^{1/n} and 1/n is the factor of heterogeneity. The Freundlich equation predicts that the deltamethrin concentration on the adsorbent will increase while there is an increase in the deltamethrin concentration of the liquid.

The Temkin equation implies a linear decrease of sorption energy as the grade of completion of the sorption

Table 2

Isotherm parameters obtained using the linear method

Langmuir isotherm model			
$q_{\rm max} ({\rm mg/g})$	K_L (L/mg)	R^2	R_{L}
27.5	0.26	0.9947	0.27
Freundlich isotherm model			
$K_f (mg/g) (L/mg)^{1/n}$	п	R^2	
4.90	1.33	0.9806	
Temkin isotherm model			
A (L/g)	В	b (J/mol)	R^2
5.5	4.5006	550.49	0.9503

centers of an adsorbent is increased. The Temkin is usually related in the following Eq. (5) [46]:

$$q_e = B \ln A + B \ln C_e \tag{5}$$

In the Temkin equation, B = RT/b and b (J/mol) is the Temkin constant related to the heat of sorption; R (8.314 J/mol.K) is the gas constant; A (L/g) is the Temkin isotherm equilibrium constant of binding and T (293 K) is temperature.

It was observed that the operative of determination of Langmuir is higher than the other isotherms. According to the Langmuir isotherm, maximum adsorption capacity at 20°C is equal to 27.5 mg/g. The conclusion states that the Langmuir isotherm presents the most suitable equilibrium data for the adsorption of deltamethrin on PCH-MNP.

5.4. Comparison with other methods

Comparison between bare magnetic nanoparticles and modified magnetic nanoparticles was also examined. Our results show that the bare and modified magnetic nanoparticles can sorb deltamethrin about 20% and 80%, respectively. As a result, the modification has in fact improved the sorption of deltamethrin by magnetic nanosorbent.

Various methods were used to study comparative information from researchers on the adsorption of deltamethrin. The sorption capacity of the present sorbent (PCH-MNP) is superior with a high capacity of 27.5 mg/g, in comparison with other methods like OSA (10.74 mg/g) [29] and ATOSA (11.4 mg/g) [30]. This newly developed method has been successfully applied in the adsorption of deltamethrin in wastewater samples.

5.5. Application of method

PCH-MNP was applied to determine deltamethrin pesticide in agricultural wastewater from Damavand agricultural farm, Tehran state, Iran. The pH level of the water sample was similar to the optimum pH. Adsorption with PCH-MNP with HPLC was used to determine deltamethrin in the agricultural wastewater sample. The results indicated the applicability of the procedure for deltamethrin determination with good removal (63%) in a sample. Experiments indicated that the method can be successfully used for determination, adsorption and removal of deltamethrin pesticide in samples of wastewater and water from the environment.

The magnetic separation process of PCH-MNP after deltamethrin adsorption shows a representative separation process of PCH-MNP from an aqueous solution of deltamethrin. It indicated that the dispersion showed fast movement and assembled after 5 min to the applied magnetic field, suggesting that the PCH-MNP possessed excellent magnetic responsivity, which was an advantage to their practical applications.

6. Conclusion

In this research, the ability of PCH-MNP to adsorb deltamethrin was studied. PCH-MNP was successfully synthesized and used as adsorbent for the removal of deltamethrin. It showed good capability in practical cases and

309

was useful in the treatment of agricultural wastewater. The adsorption of deltamethrin took 45 min and was found at pH 7, 20°C, and at a concentration using 0.05 g of PCH-MNP. Good-fitted data were obtained for the Langmuir, Freundlich and Temkin adsorption isotherm models. Best fitting was gained by the Langmuir model, with an estimated adsorption capacity of 27.5 mg/g. The favorability of the progress was investigated using a separation factor ($0 < R_L < 1$). Consequently, this type of PCH-MNP can be presented as simple, high adsorption capacity, good reusability, high chemical stability and effective adsorbent for deltamethrin adsorption from aqueous solutions.

References

- E. Maillard, S. Payraudeau, E. Faivre, C. Gregoire, S. Gangloff, G. Imfeld, Removal of pesticide mixtures in a storm water wetland collecting runoff from a vineyard catchment, Sci. Total Environ., 409 (2011) 2317–2324.
- [2] M.P. Ormad, N. Miguel, A. Claver, J.L. Ovelleiro, Pesticides removal in the process of drinking water production, Chemosphere, 71 (2008) 97–106.
- [3] M.L. Feo, E. Eljarrat, D. Barcelo, Determination of pyrethroid insecticides in environmental samples by GC-MS and GC-MS-MS, TrAC, Trends Anal. Chem., 29 (2010) 692-705.
- MS-MS, TrAC, Trends Anal. Chem., 29 (2010) 692–705.
 [4] G. Shenguang, Z. Congcong, Y. Feng, Y. Mei, Y. Jinghua, Layer-by-layer self-assembly CdTe quantum dots and molecularly imprinted polymers modified chemiluminescence sensor for deltamethrin detection, Sens. Actuators, B, 156 (2011) 222–227.
- [5] M.L. Feo, A. Ginebreda, E. Eljarrat, D. Barceló, Presence of pyrethroid pesticides in water and sediments of Ebro River Delta, J. Hydrol., 393 (2010) 156–162.
- [6] A.S. Pawar, G.V. Mali, H.V. Deshmukh, Biodegradation of deltamethrin by using indigenous bacteria isolated from contaminated soil, Int. J. Curr. Microbiol. Appl. Sci., 5 (2016) 258–265.
- [7] J. Haverinen, M. Vornanen, Deltamethrin is toxic to the fish (crucian carp, Carassius carassius) heart, Pestic. Biochem. Physiol., 129 (2016) 36–42.
- [8] H. Karimi, A. Rahimpour, M.R. Shirzad Kebria, Pesticides removal from water using modified piperazine-based nanofiltration (NF) membranes, Desal. Wat. Treat., 57 (2016) 24844– 24854. doi: 10.1080/19443994.2016.1156580
- [9] J.S. Van Dyk, B. Pletschke, Review on the use of enzymes for the detection of organochlorine, organophosphate and carbamate pesticides in the environment, Chemosphere, 82 (2011) 291–307.
- [10] W.K. Lafi, Z. Al-Qodah, Combined advanced oxidation and biological treatment processes for the removal of pesticides from aqueous solutions, J. Hazard. Mater., 137 (2006) 489–497.
- [11] W. Zheng, M. Guo, T. Chow, N. Rajagopalan, Sorption properties of green waste biochar for two triazine pesticides, J. Hazard. Mater., 181 (2010) 121–126.
- [12] D. Barceló, Trace Determination of Pesticides and Their Degradation Products in Water, (BOOK REPRINT). Vol. 19. Elsevier, 1997.
- [13] D. Marino, A. Ronco, Cypermethrin and chlorpyrifos concentration levels in surface water bodies of the Pampa Ondulada, Argentina, Bull. Environ. Contam. Toxicol., 75 (2005) 820–826.
- [14] A. Mittal, Adsorption kinetics of removal of a toxic dye, Malachite Green, from wastewater by using hen feathers, J. Hazard. Mater., 133 (2006) 196–202.
- [15] A. Mittal, Use of hen feathers as potential adsorbent for the removal of a hazardous dye, Brilliant Blue FCF, from wastewater, J. Hazard. Mater., 128 (2006) 233–239.
- [16] J. Mittal, V. Thakur, A. Mittal, Batch removal of hazardous azo dye Bismark Brown R using waste material hen feather, Ecol. Eng., 60 (2013) 249–253.

- [17] J. Mittal, A. Mittal, Green Chemistry for Dyes Removal from Wastewater, Hen Feather: A Remarkable Adsorbent for Dye Removal, Scrivener Publishing LLC, USA, 2015, pp. 409–457.
- [18] H. Daraei, A. Mittal, M. Noorisepehr, J. Mittal, Separation of chromium from water samples using eggshell powder as a low-cost sorbent: kinetic and thermodynamic studies, Desal. Wat. Treat., 53 (2015) 214–220.
- [19] H. Daraei, A. Mittal, J. Mittal, H. Kamali, Optimization of Cr(VI) removal onto bio sorbent eggshell membrane: experimental & theoretical approaches, Desal. Wat. Treat., 52 (2014) 1307–1315.
- [20] A. Mittal, L. Kurup, Column operations for the removal and recovery of a hazardous dye 'acid red - 27' from aqueous solutions, using waste materials'- bottom ash and de-oiled soya, Ecol. Environ. Cons., 12 (2006) 181–186.
- [21] J. Mittal, D. Jhare, H. Vardhan, A. Mittal, Utilization of bottom ash as a low-cost sorbent for the removal and recovery of a toxic halogen containing dye eosin yellow, Desal. Wat. Treat., 52 (2014) 4508–4519.
- [22] M. Asif Hanif, H. Nawaz Bhatti, Remediation of heavy metals using easily cultivable, fast growing, and highly accumulating white rot fungi from hazardous aqueous streams, Desal. Wat. Treat., 53 (2015) 238–248.
- [23] A. Rashid, H. Nawaz Bhatti, M. Iqbal, S. Noreen, Fungal biomass composite with bentonite efficiency for nickel and zinc adsorption: a mechanistic study, Ecol. Eng., 91 (2016) 459–471.
- [24] G. Sharma, M. Naushad, D. Pathania, A. Mittal, G.E. El-desoky, Modification of *Hibiscus cannabinus* fiber by graft copolymerization: application for dye removal, Desal. Wat. Treat., 54 (2015) 3114–3121.
- [25] R. Hudson, Y. Feng, R. Varma, A. Moores, Bare magnetic nanoparticles: sustainable synthesis and applications in catalytic organic transformations, Green Chem., 16 (2014) 4493–4505.
- [26] P. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, S. Hu, M.H. Zhao, Use of iron oxide nanomaterials in wastewater treatment: a review, Sci. Total Environ., 424 (2012) 1–10.
- [27] J. Wang, K. Zhang, Z. Peng, Q. Chen, Magnetic properties improvement in Fe₃O₄ nanoparticles grown under magnetic fields, J. Cryst. Growth, 266 (2004) 500–504.
- [28] A. Mittal, R. Ahmad, I. Hasan, Iron oxide-impregnated dextrin nanocomposite: synthesis and its application for the biosorption of Cr(VI) ions from aqueous solution, Desal. Wat. Treat., 57 (2016) 15133–15145.
- [29] Z. Al-Qodaha, A.T. Shawaqfeh, W.K. Lafi, Adsorption of pesticides from aqueous solutions using oil shale ash, Desalination, 208 (2007) 294–305.
- [30] Z. Al-Qodaha, A.T. Shawaqfeh, W.K. Lafi, Two-resistance mass transfer model for the adsorption of the pesticide deltamethrin using acid treated oil shale ash, Adsorption, 13 (2007) 73–82.
- [31] K.V. Plakas, A.J. Karabelas, Removal of pesticides from water by NF and RO membranes – a review, Desalination, 287 (2011) 255–265.
- [32] K.M. Agbekodo, B. Legube, S. Dard, Atrazine and simazine removal mechanism by nanofiltration: influence of natural organic matter concentration, Water Res., 30 (1996) 2535–2542.
- [33] K.Y. Foo, B.H. Hameed, Detoxification of pesticide waste via activated carbon adsorption process, J. Hazard. Mater., 175 (2009) 1–11.
- [34] A. Colume, S. Cardenas, M. Gallego, M. Valcarcel, Semiautomatic multiresidue gas chromatographic method for the screening of vegetables for 25 organochlorine and pyrethroid pesticides, Anal. Chim. Acta, 436 (2001) 153–162.
- [35] I. Mahmood, C. Guo, Y. Guan, H. Liu, Adsorption and magnetic removal of neutral red dye from aqueous solution using Fe₃O₄ hollow nanospheres, J. Hazard. Mater., 181 (2010) 1039–1050.
- [36] J. Gómez-Pastora, E. Bringas, I. Ortiz, Recent progress and future challenges on the use of high performance magnetic nano-adsorbents in environmental applications, Chem. Eng. J., 256 (2014) 187–204.

310

- [37] P. Berg, G. Hagmeyer, R. Gimbel, Removal of pesticides and other micro pollutants by nanofiltration, Desalination, 113 (1997) 205–208.
- [38] X. Liu, L. Li, Y. Liu, L. Mao, Ultrasensitive detection of deltamethrin by immune magnetic nanoparticles separation coupled with surface plasmon resonance sensor, Biosens. Bioelectron., 59 (2014) 328–334.
- [39] R. Bonansea, M. Amé, D. Wunderlin, Determination of priority pesticides in water samples combining SPE and SPME coupled to GC–MS. A case study: Suquía River basin (Argentina), Chemosphere, 90 (2013) 1860–1869.
- [40] A.T. O'Geen, R. Budd, J. Gan, J. Maynard, S. Parikh, R.A. Dahlgren, Mitigating nonpoint source pollution in agriculture with constructed and restored wetlands, Adv. Agron., 108 (2010) 1–76.
- [41] B. Bruggen, C. Vandecasteele, Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible application in the drinking water industry, Environ. Pollut., 122 (2003) 435–445.

- [42] H. Ahmad Panahi, E. Mottaghinejad, A.R. Badr, E. Moniri, Synthesis, characterization, and application of amberlite XAD-2-salicylic acid-iminodiacetic acid for lead removal from human plasma and environmental samples, J. Appl. Polym. Sci., 121 (2011) 1127–1136.
- [43] A.H. Lu, E.L. Salabas, F. Schüth, Magnetic nanoparticles: synthesis, protection, functionalization, and application, Angew. Chem. Int. Ed. Engl., 46 (2007) 1222–1244.
- [44] P. Wang, T. Yan, Q. Ma, D. Hu, L. Wang, Preparation of hydrazine-modified CMC/Fe₃O₄ hybrid magnetic particles for adsorption of Reactive Blue 21 from water, Desal. Wat. Treat., 57 (2016) 14986–14996.
- [45] C. Prince Jebadass Isaac, A. Sivakumar, Removal of lead and cadmium ions from water using Annona squamosa shell: kinetic and equilibrium studies, Desal. Wat. Treat., 51 (2013) 7700–7709.
- [46] M. Asif Tahir, H. Nawaz Bhatti, M. Iqbal, Solar Red and Brittle Blue direct dyes adsorption onto *Eucalyptus angophoroides* bark: equilibrium, kinetics and thermodynamic studies, J. Environ. Chem. Eng., 4 (2016) 2431–2439.