



King Saud University  
Journal of Saudi Chemical Society

www.ksu.edu.sa  
www.sciencedirect.com



## ORIGINAL ARTICLE

# Removal of permethrin pesticide from water by chitosan–zinc oxide nanoparticles composite as an adsorbent



Shahram Moradi Dehaghi <sup>a</sup>, Bahar Rahmanifar <sup>b,\*</sup>, Ali Mashinchian Moradi <sup>b</sup>, Parviz Aberoomand Azar <sup>c</sup>

<sup>a</sup> Faculty of Chemistry, Tehran North Branch, Islamic Azad University, Tehran, Iran

<sup>b</sup> Department of Marine Chemistry, Faculty of Marine Science and Technology, Science and Research Branch, Islamic Azad University, Tehran, Iran

<sup>c</sup> Department of Chemistry, Faculty of Science, Science and Research Branch, Islamic Azad University, Tehran, Iran

Available online 5 February 2014

## KEYWORDS

ZnO nanoparticles;  
Chitosan;  
Permethrin;  
Adsorption;  
Nanocomposite

**Abstract** Synthesis of chitosan–ZnO nanoparticles (CS–ZnONPs) composite beads was performed by a polymer-based method. The resulting bionanocomposite was characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD) spectroscopy and infrared spectroscopy (FT-IR). Adsorption applications for removal of pesticide pollutants were conducted. The optimum conditions, including adsorbent dose, agitating time, initial concentration of pesticide and pH on the adsorption of pesticide by chitosan loaded with zinc oxide nanoparticles beads were investigated. Results showed that 0.5 g of the bionanocomposite, in room temperature and pH 7, could remove 99% of the pesticide from permethrin solution (25 ml, 0.1 mg L<sup>-1</sup>), using UV spectrophotometer at 272 nm. Then, the application of the adsorbent for pesticide removal was studied in the on-line column. The column was regenerated with NaOH solution (0.1 M) completely, and then reused for adsorption application. The CS–ZnONPs composite beads appear to be the new promising material in water treatment application with 56% regeneration after 3 cycles.

© 2014 King Saud University. Production and hosting by Elsevier B.V.  
Open access under [CC BY-NC-ND license](#).

## 1. Introduction

Nowadays, existing commercial sorbents including, activated carbon, zeolites, activated alumina, and silica gels play important roles in adsorptive separation and purification. However, innovative technological developments are needed in the new economy and under the stringent environmental regulations. Despite of very promising features of the newly developed nanostructured sorbent materials, basically exploring and

\* Corresponding author. Tel.: +98 9352525402.

E-mail address: [arsniyas@yahoo.com](mailto:arsniyas@yahoo.com) (B. Rahmanifar).

Peer review under responsibility of King Saud University.



Production and hosting by Elsevier

systematic investigations are needed on both synthesis methods and adsorption characteristic studies [1].

Chitosan, poly[ $\beta$ -(1 $\rightarrow$ 4)-2-amino-2-deoxy-*D*-glucopyranose], is a natural cationic, cellulose biopolymer of high molecular weight obtained commercially from deacetylation of chitin by thermochemical reaction. As a natural polymer, it is in abundance and has many qualities such as non-toxicity, non-allergenic, biodegradability, biocompatibility, inexpensiveness and hydrophilicity, with ability of the biological activity and fiber and film formation [2–8].

Chitosan contains high units of two functional groups, hydroxyl (–OH) and amino (–NH<sub>2</sub>), which are responsible for the reactivity of this polymer as an excellent natural adsorbent and give chitosan its powerful adsorptive capacity [9–11]. Due to the highly reactive amino groups and carboxyl groups, chitosan has been regarded as a useful material for various purposes such as treatment of wastewater, ion-exchanger and functional matrixes [2]. Because of its multi-functionality, in the field of water and wastewater treatment applications, chitosan has been used as an absorbent as well as primary coagulant or flocculent [12–14].

The goal of nanotechnology is to make nanostructures or nanoarrays with special properties, which do not exist in their bulk or single particle types. Oxide nanoparticles can present unique physical and chemical properties, because of their limited size and a high density in their corner or edge surface sites [15,16].

In recent years, chitosan based metal particles composites have been studied increasingly as an alternative adsorbent in water treatment, such as using metals [17], metal oxides [18], and bimetals [19]. Saifuddin et al. [20] have embedded silver nanoparticles in chitosan by using microwave irradiation for the removal of pesticides from water. The main goal of our last study was to develop an adsorbent with chitosan–silver oxide nanoparticles composite. It was demonstrated that the AgO nanoparticles-chitosan beads could be used for the adsorption of permethrin as the model pesticide [21].

In this paper, the application of chitosan beads modified with ZnO nanoparticles to remove Permethrin (Fig. 1), (3-phenoxyphenyl)-methyl(+)cistrans-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate, a neurotoxin widely used in agriculture [22], has been proposed. The main goal of this study is to develop an on-line filter, by using a column of CS–ZnONPs beads and also its application in pesticide adsorption in 3 cycles.

## 2. Experimental

### 2.1. Chemicals and reagents

Chitosan with medium molecular weight was purchased from Sigma Chemical Company. Zinc Oxide was purchased from

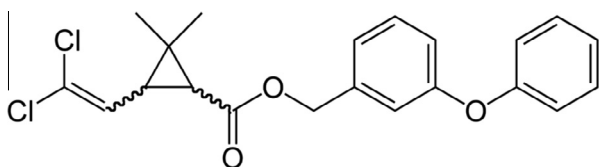


Figure 1 Structure of permethrin.

Merck. Permethrin (25%, Moshkam Fars) was used in order to prepare the stock solution of pesticide. Other chemicals were chemical grade from Merck.

### 2.2. Preparation of CS–ZnONPs composite

Typically, 0.75 g of ZnO powder was dissolved in 100 ml of 1% acetic acid by adding 10 ml of 65% Nitric acid. Then, 1 g of chitosan was added to this solution. After that, sonication process was performed for 30 min. This step was followed by adding drop by drop NaOH solution until the pH reached about 10. The solution was kept in water bath at 60 °C for about 3 h. The mixture was filtered and washed with deionized water a few times; then it was dried in an oven at 50 °C for 1 h. The preparation procedure employed has been reported elsewhere with some modification [23].

### 2.3. Dissolution and swelling study

A solubility study was performed on both the chitosan and CS–ZnONPs beads. The beads were tested with regard to their solubility in each of 5% (v/v) acetic acid, distilled water and 0.1 M NaOH solution. A value of 1.0 g of each of the beads, using analytical balance, was weighted accurately. The samples were kept in each solution for about 24 h at room temperature under stirring using mechanical stirrer (100 rpm). After that, the mixture was filtered, washed with distilled water and dried for 24 h at room temperature. Then, the dried samples were weighted using the analytical balance.

The swelling study of chitosan and CS–ZnONPs beads was carried out in distilled water at room temperature for about 24 h. Then, the swollen beads were removed from water, dried and weighed as soon as possible. The swelling percent ( $S\%$ ) of beads was calculated from the following equation [20]:

$$S(\%) = \frac{W_s - W}{W} \times 100\% \quad (1)$$

where,  $W_s$  and  $W$  represent the weight (g) of swollen beads and dry beads, respectively.

### 2.4. Characterization methods

Fourier transform infrared spectroscopy (FT-IR) of nanocomposite samples was recorded on a Thermo Nicolet FTIR spectrometer (America) using KBr powder. Surface morphology was studied by scanning electron microscope (EM3200, KYKY) at a voltage of 25.0 kV. The surfaces of sample were gold coated before the analysis. The crystallinity of nanocomposite in powder form was studied by the X-ray diffraction method (*STOE Stadi P*), using Cu K $\alpha$  radiation generated at 40 kV and 30 mA in the region of  $2\theta$  from 10 to 90.

### 2.5. Adsorption experiments

To obtain a preliminary assessment of the performance of the sorbent materials, batch experiments were carried out by using a mechanical shaker at a speed of 150 rpm and 25 °C for 45 min with specified amount of adsorbents (the dosage varied from 0.01 to 1.5 g) in contact with 25 ml of synthetically prepared Permethrin solution (0.1 ppm). The pH of the adsorbate solution was adjusted to around 7 at the beginning of the

experiment. To estimate the evaporation losses of the pesticide, a control blank sample was simultaneously placed in the same shaker. Similar results between control and treated samples indicated no losses due to evaporation.

After 45 min with different dosages of adsorbents ranging from 0.01 to 1.5 g, the removal percentage of pesticide from water solution was determined by measuring the difference in absorbance at 272 nm using T60 UV-Vis Spectrophotometer. The adsorbed concentration of permethrin into sorbents was calculated by the difference in the detector response absorbance before and after shaking. The removal efficiency or sorption percent of permethrin and distribution coefficient ( $R_d$ ) may be evaluated by using the following equations:

$$\text{Removal of pesticide (\%)} = \frac{\text{Abs}_i - \text{Abs}_t}{\text{Abs}_i} \times 100\% \quad (2)$$

$$R_d \text{ (ml g}^{-1}\text{)} = \frac{\text{Amount of Permethrin onto sorbent}}{\text{Residual amount of Permethrin in solution at equilibrium}} \times \frac{\text{Volume of solution } V \text{ (ml)}}{\text{Amount of sorbent } W \text{ (g}^{-1}\text{)}} \quad (3)$$

$$Q_t = \left( \frac{C_0 - C_t}{m} \right) v \quad (4)$$

where  $Q_t$  is the amount of adsorbed analyte at any time  $t$ ,  $C_0$  and  $C_t$  are the initial and liquid-phase concentrations of permethrin, respectively,  $v$  is the pesticide solution volume (ml) and  $m$  is the adsorbent mass (g). All experiments were carried out at least in triplicate at pH 7 and 25 °C. The results were the mean of three independent measurements.

## 2.6. Competitive experiment

Besides CS-ZnONPs beads, pure chitosan beads are another adsorbent, which were used for comparison. Pure chitosan beads (without zinc oxide nanoparticles) were prepared as reported elsewhere with some modification [20,24–27]. Typically, 3.0 g chitosan dissolved in 100 ml, 1% (v/v) acetic acid. Then,

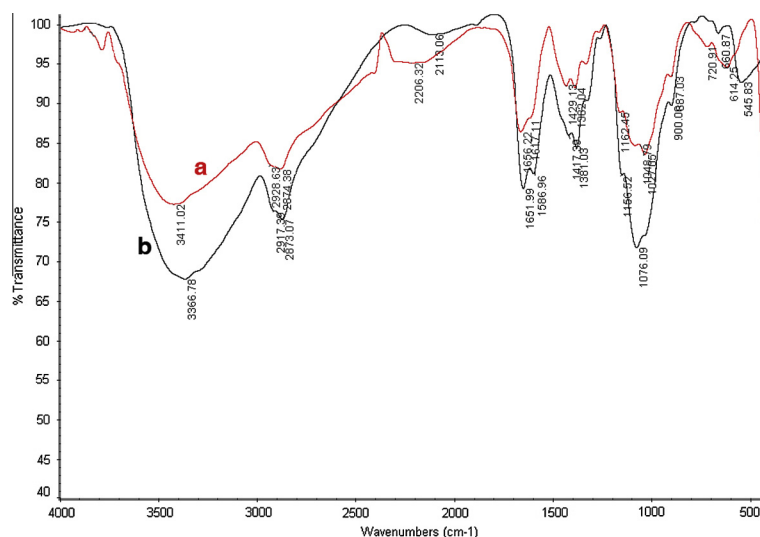
drop by drop, the NaOH solution (1 M) was added to this solution and chitosan beads formed instantaneously. The chitosan beads were stored in the NaOH solution for 24 h and then rinsed with distilled water until final pH of the solution reached the neutral pH. The beads were filtered and stored in distilled water. Percent removal was determined by calculating the difference in the absorbance at any amount of the sorbent (g).

## 2.7. Column study

Column flow studies are performed in a plastic column of 9 cm length and 2.2 cm diameter (i.d.). The CS-ZnONPs composite beads (3 g) were stored in 25 ml water for about 24 h. The column was filled up with this mixture without gaps and the level of the beads' height reached 1.5 cm. To ensure the absence of chemicals in the column, the column was washed with deionized water. The pesticide solution (0.1 ppm, 25 ml) was allowed to pass through the column, flow rate of the column was 3.1 ml min<sup>-1</sup>. The effluent solution was collected in constant time intervals and the concentrations of the pesticide solution were determined by measuring absorbance at 272 nm using UV-Vis spectrophotometer [20].

## 2.8. Desorption study

After using the column for the first time, desorption study was carried out by 0.1 M NaOH solution as an eluent [20]. The eluent was poured into the column at a flow rate of 1 ml min<sup>-1</sup> at the constant conditions. The concentration of effluent samples at different time intervals was determined by measuring the absorbance at 272 nm using a UV-Vis spectrophotometer. When the concentration of outlet solution reached almost zero, the column would be supposed to regenerate. After that, to remove NaOH from the column, the adsorbent column was washed with distilled water before the next adsorption-desorption cycles. The adsorption-desorption cycles were repeated three times using the same condition to check the sustainability of the column for repeated use.



**Figure 2** FT-IR spectra for pure chitosan (a) and CS-ZnONPs composite (b).

### 3. Results and discussion

#### 3.1. Dissolution and swelling study

It is well known that usually chitosan is needed to improve its chemical stability in acid media. Because of primary amine groups, the chitosan beads or raw chitosan has high hydrophilicity. Hence, chitosan beads are easily soluble in dilute acetic or formic acid solutions and can produce a hydrogel in water [20,28,29].

Chitosan beads exhibited an extremely high degree of swelling attributing to the high water affinity brought by the introduced carboxyl groups. However, the high solubility of chitosan in acidic solution limits its usage as a sorbent [20,27]. By loading the metal oxide nanoparticles, this shortcoming can be overcome to some extent. The swelling behavior of ZnO nanoparticles loaded chitosan beads improved greatly. The swelling of CS–ZnONPs composite and chitosan beads was 13.7% and 35.2% in distilled water, respectively.

#### 3.2. Characterization of adsorbent

The infrared spectra of chitosan and CS–ZnONPs are shown in Fig. 2. The FTIR spectra of pure chitosan (a spectrum) exhibit bands at  $3411\text{ cm}^{-1}$  due to the stretching vibration mode of OH and  $\text{NH}_2$  groups. The peaks at  $2928$  and  $2874\text{ cm}^{-1}$  are typical of C–H stretch vibration, while the band at  $1656\text{ cm}^{-1}$  is due to the amide I group (C–O stretching along with N–H deformation mode),  $1617\text{ cm}^{-1}$  peak is attributed to the  $\text{NH}_2$  group due to N–H deformation,  $1429\text{ cm}^{-1}$  peak is due to C–N axial deformation (amine group band),  $1382\text{ cm}^{-1}$  peak is due to the COO– group in carboxylic acid salt,  $1162\text{ cm}^{-1}$  is assigned to the special broad peak of  $\beta$  (1–4) glucosidic band in polysaccharide unit,  $1048\text{ cm}^{-1}$  is attributed to the stretching vibration mode of the hydroxyl group,  $1027\text{ cm}^{-1}$  stretching vibration of C–O–C in glucose circle and  $1080$ – $1020\text{ cm}^{-1}$  bands correspond to CH–OH in cyclic compounds [30].

In comparison with chitosan, the broader and stronger peak shifted considerably to lower wavenumber at  $3366\text{ cm}^{-1}$ , which indicates strong attachment of ZnO to the amide groups of chitosan molecules. The absorption peaks at

$2917$ ,  $2873\text{ cm}^{-1}$  are due to asymmetric stretching of  $\text{CH}_3$  and  $\text{CH}_2$  of chitosan polymer. The absorption peaks at  $1651$  and  $1076\text{ cm}^{-1}$  are attributed to bending vibration of the  $-\text{NH}_2$  group and the C–O stretching group. A new broad absorption band at the range of  $580$ – $400\text{ cm}^{-1}$  was found in the FTIR spectra of CS–ZnONPs composite, which were ascribed to the vibration of O–Zn–O groups. Similar phenomena were observed with the peaks of C=O,  $-\text{NH}_2$ ,  $3'$ -OH, and  $5'$ -OH groups. The reason of the above phenomena was the formation of hydrogen bonds between ZnO and chitosan [31–36].

Scanning electron microscopy (SEM) was used to investigate the surface morphology of CS–ZnONPs composite. SEM studies (Fig. 3) reveal the globular porous morphology of CS–ZnONPs indicating the formation of CS–ZnONPs composite, that the ZnO nanoparticles can be observed with a size of 58 nm. The particles in nanocomposite were found with almost spherical morphology. However, some of the agglomeration of nanoparticles were also found, possibly due to the presence of the capping agent. It is significant that the nanoparticles in chitosan matrix disperse non-uniformly.

Fig. 4 shows the XRD pattern of the CS–ZnONPs composite. There are mainly two strong peaks at about  $10$  and  $20$  degree for the pure chitosan due to the high degree of crystallinity. These peaks are very weak in the spectrum of the CS–ZnONPs composite, which indicates low crystallinity. The weak peaks reflect great disarray in chain alignment of chitosan with production of new peaks identifying Zinc oxide. The main peaks of ZnO nanoparticles were at  $2\theta = 31.74^\circ$ ,  $34.44^\circ$ ,  $36.24^\circ$ ,  $47.47^\circ$ ,  $56.54^\circ$ ,  $62.72^\circ$ ,  $66.38^\circ$ ,  $67.90^\circ$  and  $68.97^\circ$ , which were corresponding to the (100), (002), (101), (102), (110), (103), (200), (112) and (201) crystal planes of pure ZnO, respectively. These peaks are consistent with the database in Joint Committee on Powder Diffraction Standards (JCPDS file, PDF No. 36-1451) [34]. At the same time, it can be seen that the strong characteristic diffraction peaks ((100), (002), and (102)) could be found in the pattern of CS–ZnONPs composite. According to the Debye–Scherrer equation, the ZnO nanoparticles in CS–ZnONPs composite had an average diameter of 60 nm, which was in accordance with the scanning electron microscopy result. This result indicated that the CS–ZnONPs composite has been prepared successfully without damaging the crystal structure of ZnO core [27].

#### 3.3. Effect of the amount of adsorbent

Effect of sorbent amount (0.01–1.5 g) on permethrin removal percentage was investigated by using CS–ZnONPs composite, while keeping other parameters constantly. The amount of adsorbent is an important parameter, which affects the capacity of a sorbent for a given initial concentration of sorbate [20,37]. Fig. 5 shows the removal percentage of pesticide (25 ml, 0.1 ppm) after 45 min with different amounts of the composite. The experiments were performed by different concentrations of adsorbent, which showed that the removal efficiency increased with an increase in adsorbent concentration up to 0.5 g in 25 ml solution. After a very slow increase in removal percentage, it was found that the increase in adsorbent of more than 0.5 g dose did not affect the removal percentage significantly. 96% removal of pesticide was found in the dosage range of 0.5–1.5 g.

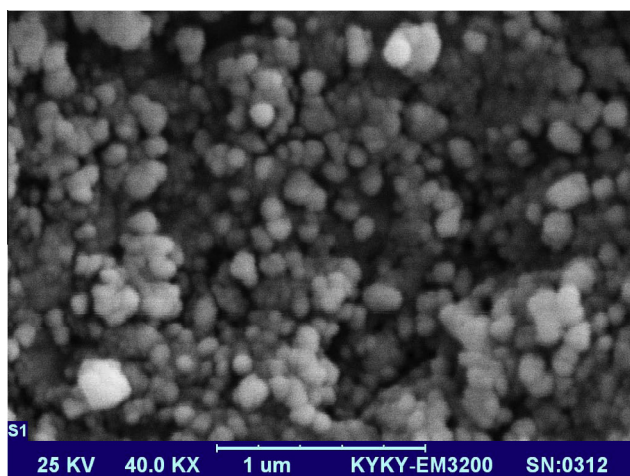


Figure 3 SEM of CS–ZnONPs composite.

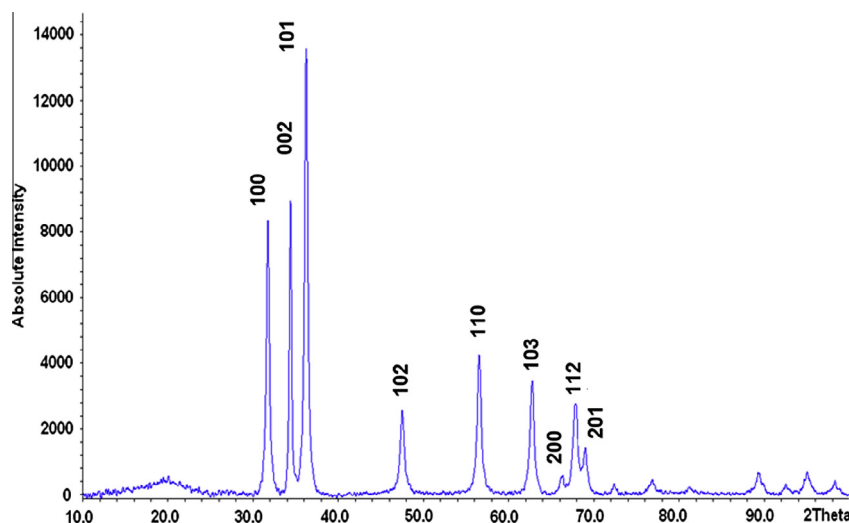


Figure 4 XRD pattern of CS-ZnONPs composite.

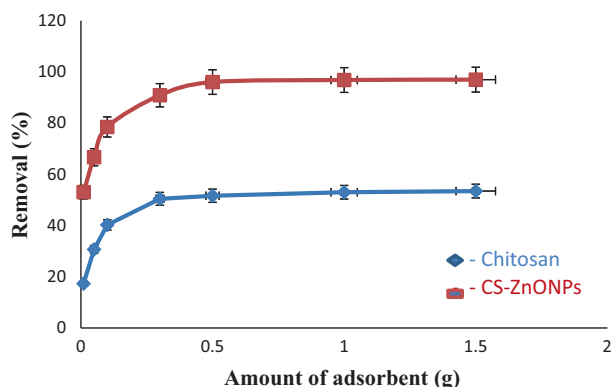


Figure 5 Influence of the amount of sorbent on removal percentage.

This may be presumed that the availability of active sites on the nanocomposite is decreasing at higher doses of sorbents ( $> 0.5$  g). The total active surface area increases by increasing composite dosage. At the same time, due to increasing amount of sorbent, the sorbent-sorbent interactions are more dominating than sorbate-sorbent interactions [37,38]. Since the most effective removal of permethrin was observed with 0.5 g of CS-ZnONPs composite, the other experiments were performed in this concentration.

#### 3.4. Effect of agitation time

The influence of agitation time (10–150 min) on 0.5 g CS-ZnONPs composite in 25 ml of 0.1 ppm pesticide concentration was monitored. Fig. 6 shows the effect of agitation time on the pesticide adsorption on the prepared nanocomposite at 25 °C, 150 rpm shaker speed and  $\text{pH} \approx 7$ . The plot shows that the adsorption of permethrin increases with time and then reaches a constant value beyond which no more pesticide would be further removed from the solutions. The initial fast rate is probably due to the abundant available binding sites on the surface of the adsorbent. The percent sorption increased

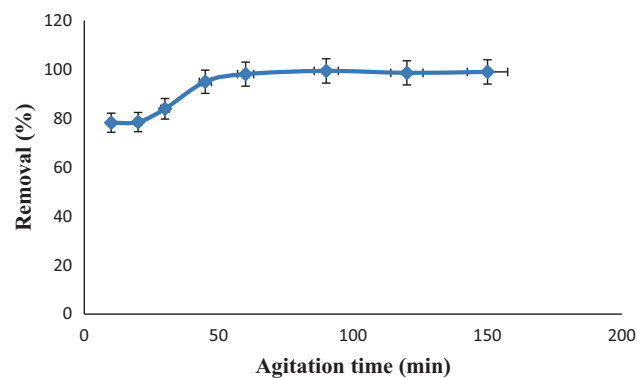


Figure 6 Effect of agitation time on removal percentage.

from 78% to 99% with an increase in agitation time (10–90 min), and became almost constant after 90 min. The results revealed that the pesticide adsorption was fast at initial stages of the contact period, and then slowed down near the equilibrium. This phenomenon was due to the availability of many vacant surface sites for adsorption during the initial stage, and after that, other vacant surface sites were difficult to be absorbed due to repulsive forces between the adsorbate molecules

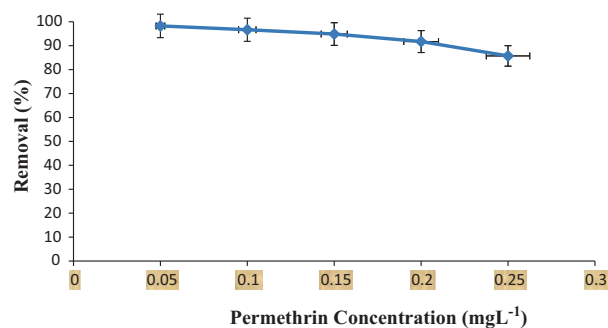


Figure 7 Effect of initial pesticide concentration on removal percentage.

on the adsorbent [39]. The equilibration time of 90 min was selected for further studies.

### 3.5. Effect of permethrin initial concentration

The influence of initial concentration of permethrin solution over a range of 0.05–0.25 ppm on its adsorption by 0.5 g CS–ZnONPs composite is illustrated in Fig. 7. The removal percentage was decreased by increased initial concentration of the pesticide. When the initial concentration increases, more organic substances are adsorbed on the surface of the sorbent, thus, the distribution coefficient ( $R_d$ ) decreases, which suggests limiting number of sorption sites available for sorption at higher concentration of the sorbate molecules. Also, this effect could be explained by the fact that at low sorbate/sorbent ratios, the sorbate sorption involves the higher energy sites. Further, as the concentration of a pesticide solution increases, the higher energy sites are saturated and lower energy sites will be used for sorption, and so the removal percentage will reduce [20,27,37].

### 3.6. Effect of initial pH

The influence of pH of the aqueous solution on removal percentage of permethrin by CS–ZnONPs composite is shown in Fig. 8. The pH was monitored in the range of 3–11 using 0.1 M HCl and NaOH solutions at 0.5 g of sorbent dose during 90 min agitation time and all remaining parameters were kept same as before. The results indicated that the removal percentage of permethrin increased with increasing pH up to 8, and then decreased. The effect of pH on the adsorption performance can be explained by interaction between the sorbent surface and the sorbate. The values of pH affect the surface properties of the sorbent i.e. surface charge of the cells present in the sorbent. Therefore, pH plays an important role in the sorption onto these surfaces. The potential binding sites in the chitosan are amine and hydroxyl groups. At different pH values, these functional groups may be dissociated as their dissociation constants, and therefore, could take part in the surface complexation [37].

In acidic media, the decrease in the amount of permethrin adsorbent on the sorbent was due to the phenomenon of partial dissolution. In the pH range of 6–8, the surface of the sorbent might be affected by the excessive hydronium ions, which would increase the sorbate interaction with functional groups of the sorbents by greater attractive forces, and thereby,

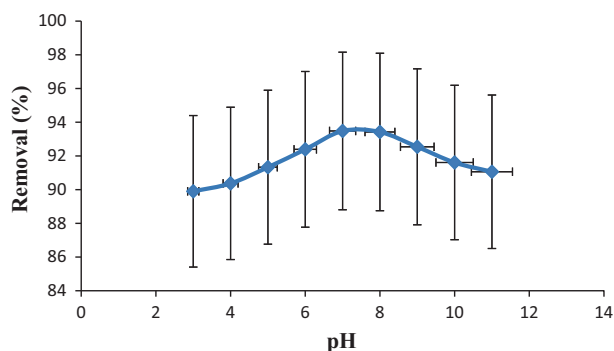


Figure 8 Effect of pH on removal percentage.

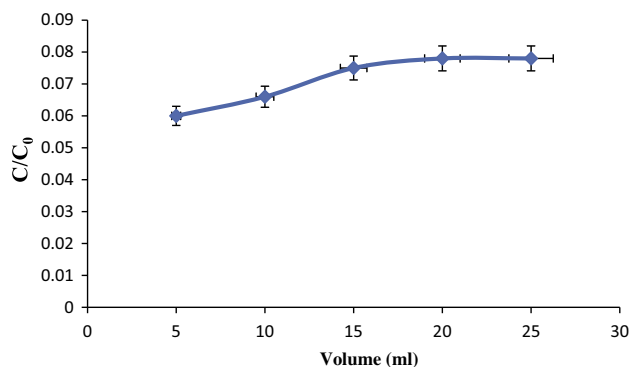


Figure 9 Removal curve for Permethrin for CS–ZnONPs composite beads column.

improve its adsorption on polar sorbent [40]. This may result in increased electrostatic attraction between negatively charged pesticide anions and positively charged surface of the sorbent. Above pH 8, the reduction of adsorption capacity of the nanocomposite can originate from competition of hydroxyl ions of the sorbent with pesticide anions [41].

### 3.7. Column study

At the end of batch experiments and complete removal of the pesticide, we have investigated the application of this method for water treatment system to remove pesticides from water. The experimental results, including the volume versus  $C/C_0$  (ratio of effluent concentration to initial concentration) curve are shown in Fig. 9. A column system was made as described earlier using about 3 g of the chitosan beads impregnated with zinc oxide nanoparticles. A volume of 25 ml of 0.1 ppm pesticide solution was used as input solution with flow rate of  $3.1 \text{ ml min}^{-1}$ . The data were calculated by determining pesticide concentrations at different time intervals. This demonstrated that after passing the 20 ml of permethrin solution, the total adsorption capacity has been reached. After that, the efficiency of column was decreased. When the effluent reached to this level, it is time for regeneration of the adsorbent.

### 3.8. Desorption study

After the column is emptied, the column should be regenerated. In this study, the regeneration was performed by 0.1 M of NaOH solution, which was known to be efficient in recovery process [20]. The column was regenerated with 50 ml of NaOH solution completely and then reused for adsorption application. The results demonstrated that the adsorption and desorption percentage decreases from the first cycle to the next and after the third cycle, the adsorption capacity decreased to 56%.

## 4. Conclusions

The chitosan/zinc oxide nanocomposite beads were prepared by a polymer-based method. The removal ability of nanocomposite beads was examined, and batch studies were performed. It was demonstrated that the CS/ZnONPs beads had an excellent adsorption performance. In comparison with chitosan

beads, the removal efficiency of CS/ZnONPs beads was increased from 49% to 99% for 25 ml of permethrin solution ( $0.1 \text{ mg L}^{-1}$ ). The adsorption and regeneration studies of permethrin demonstrated that the CS/ZnONPs beads could be re-used effectively with 56% regeneration after 3 cycles in on-line column. In conclusion, the CS-ZnONPs beads have high capacity as an adsorbent, which could explore a new biocompatible and eco-friendly strategy for pesticide removal, and could be used in water treatment process.

## References

- [1] S. Deng, Sorbent technology, Encyclopedia Chem. Process (2006), <http://dx.doi.org/10.1081/E-ECHP-120007963>, 2825-2845.
- [2] G. Crini, Studies on adsorption of dyes on beta-cyclodextrin polymer, Bioresour. Technol. 90 (2003) 193–198.
- [3] G. Crini, Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, Prog. Polym. Sci. 30 (2005) 3870.
- [4] G. Crini, P.M. Badot, Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: a review of recent literature Prog. Polym. Sci. 33 (2008) 399–447.
- [5] S. Hansan, A. Krishnaiah, T.K. Ghosh, Adsorption of chromium(VI) on chitosan coated perlite Sep, Sci. Technol. 38 (2003) 3775–3793.
- [6] B.J. Liu, D.F. Wang, Y. Xu, G.Q. Huang, Adsorption properties of Cd(II)-imprinted chitosan resin J, Mater. Sci. 46 (2011) 1535–1541.
- [7] R.A.A. Muzzarelli and C. Muzzarelli, Polysaccharides 1: Structure, Characterization and Use, In: T. Heinze, (ED), 2005, Springer, 151–209.
- [8] E.Y. Ozmen, M. Sezgin, A. Yilmaz, M. Yilmaz, Synthesis of  $\beta$ -cyclodextrin and starch based polymers for sorption of azo dyes from aqueous solutions, Bioresour. Technol. 99 (2008) 526–531.
- [9] K.M. Gregorio-Jauregui, M.G. Pineda, J.E. Rivera-Salinas, G. Hurtado, H. Saade, J.L. Martinez, A. Ilyina, R.G. Lopez, One-step method for preparation of magnetic nanoparticles coated with chitosan, J. Nanomater. 2012 (2012) 1–8.
- [10] W.S. Wan, Ngah and S. Fatinathan, Pb(II) biosorption using chitosan and chitosan derivatives beads: equilibrium, ion exchange and mechanism studies, J. Environ. Sci. 22 (3) (2010) 338–346.
- [11] L. Fan, Y. Zhang, C. Luo, H. Qiu, M. Sun, Synthesis and characterization of magnetic  $\beta$ -cyclodextrin–chitosan nanoparticles as nano-adsorbents for removal of methyl blue, Int. J. Biol. Macromol. 50 (2012) 444–450.
- [12] E. Assaad, A. Azzouz, D. Nistor, A.V. Ursu, T. Sajin, D.N. Miron, F. Monette, P. Niquette, R. Hausler, Metal removal through synergic coagulation–flocculation using an optimized chitosan–montmorillonite system, Appl. Clay Sci. 37 (2007) 258–274.
- [13] A.R. Cestari, E.F.S. Vieira, A.M.G. Tavares, R.E. Bruns, The removal of the indigo carmine dye from aqueous solutions using cross-linked chitosan-evaluation of adsorption thermodynamics using a full factorial design, J. Hazard. Mater. 153 (2008) 566–574.
- [14] W.P. Cheng, F.H. Chi, R.F. Yu, Y.C. Lee, Using chitosan as a coagulant in recovery of organic matters from the mash and lauter wastewater of brewery, J. Polym. Environ. 13 (4) (2005) 383–388.
- [15] C.R. Bhattacharjee, D.D. Purkayastha, S. Bhattacharjee, A. Nath, Homogeneous chemical precipitation route to ZnO nanosphericals, Assam Univ. J. Sci. Technol. Phys. Sci. Technol. 7 (2) (2011) 122–127.
- [16] M. Fernández-García, J.A. Rodriguez, Metal Oxide Nanoparticles, Encyclopedia of Inorganic Chemistry. (2009), <http://dx.doi.org/10.1002/0470862106.ia377>.
- [17] A. Gupta, V.S. Chauhan, A. Gupta, N. Sankaramakrishnan, Preparation and evaluation of iron–chitosan composites for removal of As(III) and As(V) from arsenic contaminated real life groundwater, Water Res. 43 (2009) 3862–3870.
- [18] Z. Zainal, L.K. Hui, M.Z. Hussein, A.H. Abdullah, I.R. Hamadneh, Characterization of  $\text{TiO}_2$ -chitosan/glass photocatalyst for the removal of a monoazo dye via photodegradation–adsorption process, J. Hazard. Mater. 164 (2009) 138–145.
- [19] D. Thakre, S. Jagtap, N. Sakhare, N. Labhsetwar, S. Meshram, S. Rayalu, Chitosan based mesoporous Ti–Al binary metal oxide supported beads for defluoridation of water, Chem. Eng. J. 158 (2010) 315–324.
- [20] N. Saifuddin, C.Y. Nian, L.W. Zhan, K.X. Ning, Chitosan–silver nanoparticles composite as point-of-use drinking water filtration system for household to remove pesticides in water, Asian J. Biochem. (2011), <http://dx.doi.org/10.3923/ajb.2011>.
- [21] B. Rahmanifar, S. Moradi, Dehaghi, Removal of organochlorine pesticides by chitosan loaded with silver oxide nanoparticles from water, Clean Technol. Environ. Policy (2013), <http://dx.doi.org/10.1007/s10098-013-0692-5>.
- [22] M.S. Arayne, N. Sultana, F. Hussain, Validated RP-HPLC method for determination of permethrin in bulk and topical preparations using UV–vis detector, J. Chromatogr. Sci. 49 (2011) 287–291.
- [23] M.M. AbdElhady, Preparation and characterization of chitosan/zinc oxide nanoparticles for imparting antimicrobial and UV protection to cotton fabric, Int. J. Carbohydr. Chem. 2012 (2012) 1–6.
- [24] T. Chandy, C.P. Sharma, Chitosan matrix for oral sustained delivery of ampicillin, Biomaterials 14 (1993) 939–944.
- [25] T.Y. Guo, Y.Q. Xia, G.J. Hao, M.D. Song, B.H. Zhang, Adsorption separation of hemoglobin by molecularly imprinted chitosan beads, Biomaterial 25 (2004) 5905–5912.
- [26] X.Z. Shu, K.J. Zhu, Chitosan/gelatin microspheres prepared by modified emulsification and ionotropic gelation, J. Microencapsul. 18 (2001) 237–245.
- [27] R. Sivaraj, C. Namasivayam, K. Kadirvelu, Orange peel as an adsorbent in the removal of acid violet 17 (acid dye) from aqueous solutions, Waste Manage. (Oxford) 21 (2001) 105–110.
- [28] N. Saifuddin, S. Dinara, Immobilization of *Saccharomyces Cerevisiae* onto cross-linked chitosan coated with magnetic nanoparticles for adsorption of uranium(VI) ions, Adv. Nat. Appl. Sci. 6 (2) (2012) 249–267.
- [29] N. Saifuddin, Y.A.A. Nur, S.F. Abdullah, Microwave enhanced synthesis of chitosan-graft-polyacrylamide molecular imprinting polymer for selective removal of  $17\beta$ -estradiol at trace concentration, Asian J. Biochem. 6 (2011) 38–54.
- [30] J. Kumirska, M. Czerwicka, Z. Kaczynski, A. Bychowska, K. Brzozowski, J. Thoming, P. Stepnowski, Application of spectroscopic methods for structural analysis of chitin and chitosan, Mar. Drugs 8 (2010) 1567–1636.
- [31] M. Andres-Verges, C.J. Serna, Morphological characterization of ZnO powders by X-ray and IR spectroscopy, J. Mater. Sci. Lett. 7 (1988) 970–972.
- [32] J. Brugnerotto, J. Lizardi, F.M. Goycoolea, W. Arguelles-Monal, J. Desbrieres, M. Rinaudo, An infrared investigation in relation with chitin and chitosan characterization, Polymer 42 (2001) 3569–3580.
- [33] Z.F. Dong, Y.M. Du, L.H. Fan, Y. Wen, H. Liu, X.H. Wang, Preparation and properties of chitosan/gelatin/nano- $\text{TiO}_2$  ternary composite films, J. Funct. Polym. 17 (2004) 61–66.
- [34] L.-H. Li, J.-C. Deng, H.-R. Deng, Z.-L. Liu, L. Xin, Synthesis and characterization of chitosan/ZnO nanoparticle composite membranes, Carbohydr. Res. 345 (2010) 994–998.

- [35] F.G. Pearson, R.H. Marchessault, C.Y. Liang, V. Chitin, Infrared spectra of crystalline polysaccharides, *J. Polym. Sci.* 43 (1960) 101–116.
- [36] R. Salehi, M. Arami, N.M. Mahmoodi, H. Bahrami, S. Khorramfar, Novel biocompatible composite (chitosan zinc oxide nanoparticle): preparation, characterization and dye adsorption properties, *Colloids Surf. B* 80 (1) (2010) 86–93.
- [37] M. Akhtar, S.M. Hasany, M.I. Bhanger, S. Iqbal, Low cost sorbents for the removal of methyl parathion pesticide from aqueous solution, *Chemosphere* 66 (2007) 1829–1838.
- [38] N. Daneshvar, S. Aber, M.S. Seyed Dorraji, A.R. Khataee, M.H. Rasoulifard, Photocatalytic degradation of the insecticide diazinon in the presence of prepared nanocrystalline ZnO powders under irradiation of UV-C light, *Sep. Sci. Technol.* 58 (2007) 91–98.
- [39] H.H. Sokkera, N.M. El-Sawy, M.A. Hassan, B.E. El-Anadouli, Adsorption of crude oil from aqueous solution by hydrogel of chitosan based polyacrylamide prepared by radiation induced graft polymerization, *J. Hazard. Mater.* 190 (2011) 359–365.
- [40] X.-Y. Huang, H.-T. Bu, G.-B. Jiang, M.-H. Zeng, Cross-linked succinyl chitosan as an adsorbent for the removal of Methylene Blue from aqueous solution, *Int. J. Biol. Macromol.* 49 (2011) 643–651.
- [41] S. Rengarag, S.H. Moon, R. Sivabalan, Agricultural solid waste for the removal of organics from water and waste water by palm seed coated activated carbon, *Waste Manage. (Oxford)* 22 (2002) 543–548.