Efficient adsorption of heavy metals and pesticides onto chitosan nanoparticles and chitosan-zinc oxide nanocomposite

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ABSTRACT
Nanotechnology-derived products that reduce the concentrations of toxic compounds in water and wastewater to sub-ppb levels can assist in the attainment of water quality standards and health advisories. The potential of chitosan nanoparticles (CSNPs) to remove Cu (II) and Zn (II) and chitosan-ZnO nanocomposites (CS-ZnONCs) to remove λ-cyhalothrin from simulated water has been investigated. The proposed nanomaterials were prepared by ionic gelation and polymer-based methods and characterized using Transmission and Scanning Electron Microscopy (TEM& SEM), X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy. The adsorption capacity of nanomaterials was optimized with amount of sorbent, agitation time, initial concentration of pollutant and pH parameters using batch wise experiments. Under optimum conditions, at adsorbent dose of 2g/L, CSNPs showed a highly-efficient adsorption capacity for low concentrations of Cu (II) and Zn (II), reaching 96.7% for Cu (II) within 180 min at pH 5.0 and 98.2% for Zn (II) at pH 7.0 within 60 min at room temperature. The kinetic data for the sorbent were fitted relatively better to pseudo second-order kinetic model than the pseudofirst-order model. Nanoparticles adsorption features were characterized using Langmuir and Freundlich isotherm models. The Langmuir adsorption isotherm was found to have the best fit to the experimental equilibrium adsorption data, suggesting monolayer coverage of the surface of CSNPs by Cu (II) and Zn (II). On the other hand, removal efficiency of λ-cyhalothrin as a model pesticide (50 ml, 0.2 ppm) onto CS-ZnONCs was found to be pH-sensitive and time/adsorbent dose-dependent. Maximum removal efficiency (97.7%) was achieved at adsorbent dose of 0.7 g within 60 min at room temperature and pH 7. The results of this study show that the synthesized nanomaterials proved high capacity as adsorbents and can serve as biocompatible and environmentally benign synthetic strategy for heavy metals and pesticide removal with a good potential for developing bio-adsorbent filters towards several environmental pollutants.

Key words: Nanoparticles, chitosan, ZnO, heavy metals, pesticides, water.

INTRODUCTION
Contamination of water resources via hazardous materials such as heavy metals and pesticides represents a serious global threat to the surrounding environment affecting all living creatures, household, recreation, fishing, transportation and other commercial activities. Modern agriculture consumes huge amounts of fertilizers, pesticides and many other agrochemicals, which can enter the aquatic ecosystem through direct agricultural runoff,
leaching and improper disposal of empty containers (Shannon et al., 2008). Among all water contaminants, lead, mercury, nickel, chromium, thallium, zinc, copper, cobalt, selenium, arsenic and cadmium are the heavy metals known for their toxicity and persistency (Kaushal and Singh, 2017). Unlike organic pollutants, they are mostly non-biodegradable. They find their way into water bodies through refineries, sludge disposal, mining operations, industries, such as paints, electronic and electrical devices, batteries, fertilizers and pesticides. Their presence above the prescribed limits in the body can cause several damage to vital organs of the body, such as kidney, liver, brain, reproductive and nervous system. They may also pose mutagenic and carcinogenic threats (Goel, 2006).

In Egypt, λ-cyhalothrin (a pyrethroid insecticide) represents one of the most commonly used insecticides to control chewing and sucking insects in fields, beside its wide use in public health (Dikshit et al., 2000). Residues of λ-cyhalothrin were detected in several vegetables (Ahmed et al., 2014), among pesticides with high frequency in fruit samples and was the most abundant (12.9%) (Gad Alla et al., 2015) and in cotton products recording 0.056 and 0.090 mg/kg in raw cotton samples (Attallah and Abdelwahed, 2017). Chronic exposure to λ-cyhalothrin; as a pyrethroid insecticide, can cause endocrine disrupting effects, liver function impairment and respiratory problems. Oxidative stress, lipid peroxidation and allergy may be some underlying mechanisms of toxicity (Abou El-Magd et al., 2011). Thus, the removal of such toxic materials from water and wastewater is becoming a crucial issue.

Adsorption is a conventional efficient technique to remove heavy metals and/or organics from aqueous solutions using different adsorbents (Parmar and Thakur, 2013). In most cases, these adsorbents are highly porous materials, providing adequate surface area for adsorption. Nowadays advances in nanoscale science suggest that many of the current drawbacks involving water quality could be resolved or greatly ameliorated using nanosorbents, nanocatalysts and bioactive nanoparticles. Nanocomposites based on metallic nanoparticles have also witnessed an exponential growth as powerful alternatives for extended periods. Permethrin was also removed using chitosan–ZnO nanocomposite (Dehaghi et al., 2014), where batch studies showed that the adsorbent capacity toward atrazine was 0.5 mg g⁻¹ within 65 min and on-line filter using a column of nanocomposite beads was used for pesticide removal for extended periods. Permethrin was also removed using chitosan–ZnO nanocomposite (Dehaghi et al., 2014), where 0.5 g of the adsorbent, at room temperature and pH 7, removed 99% of permethrin (25 ml, 0.1 mg L⁻¹) and on-line column of such nanocomposite beads for pesticide removal with 56% regeneration after 3 cycles. Gold nanoparticles embedded in chitosan, was successfully used for efficient removal of methyl-parathion (Dwivedi et al., 2014) at 58 mmol g⁻¹ of the nanocomposite from waste water. Diazinon was also efficiently removed at various dosages of polyethylene glycol magnetite nanoparticles at an optimum dose of adsorbent of 1 mg (Naeimi and Saeidi, 2016) accompanied with increasing temperature from 15 to 45°C through an endothermic process. Recently, carbon nanoparticle synthesized from Pomegranate Peel was used
for the removal of trifuralin, glyphosate and 2,4D (0.5 g) so that the removal efficiency was equal to 97, 98.8 and 98.4%, respectively within 20 min (Yousefi, 2017).

The current study presents chitosan nanoparticles and chitosan-ZnO nanocomposite as recent proposed biocompatible and eco-friendly materials for removal of heavy metal (Cu and Zn) and λ-cyhalothrin (as a pesticide model), respectively from simulated water.

MATERIALS AND METHODS

Chitosan with moderate molecular weight (Deacetylation> 85%), Tripolyphosphate, and Zinc Nitrate hexahydrate (ZnNO₃.6H₂O) were purchased from Sigma Aldrich. Acetic acid, Hydrochloric acid, Nitric acid and Sodium Hydroxide were all of chemical grade. Lambda cyhalothrin (10%, El-Nasr Co. for pesticides) was used to prepare the stock solution of pesticide. Double-distilled water was used for the preparation of all solutions throughout the study.

Preparation of chitosan nanoparticle (CSNPs)

CSNPs were synthesized by the ionotropic gelation of chitosan with TPP according the method of Pourdounighi et al. (2010). CSNPs were formed by adding TPP solution (50 mg of TPP in 50 ml of double distilled water) to the chitosan solution (375 mg in 125 ml of 2% acetic acid) drop wise under magnetic stirring (600 rpm, 1 hour) at room temperature until an opalescent suspension is formed. The nanoparticles were separated by centrifugation at 16,000 rpm at room temperature for 30 min and CSNPs were washed several times with distilled water and lyophilized till use.

Preparation of chitosan-ZnO nanocomposite (CS-ZnONCs)

Typically, 0.75 g of ZnO powder was dissolved in 100 ml of 1% acetic acid with stirring until it was completely dissolved. Then 1 g of chitosan was added to this solution gradually. The solution was sonicated for 30 min. After it has completely dissolved, NaOH solution (1M) was added dropwise until the pH reached 10. The solution was kept in water bath at 60°C for 3h and the mixture was filtered, washed 3 times with deionized water and then finally dried in an oven at 60°C for 1 h (Dehaghi et al., 2014).

Characterization of the prepared nanomaterials

Transmission and scanning electron microscopy (JEOL-TEM 100 CX, and JEOL, JSM-6360 LA-Japan) were used to determine the shape, topography and particle size of the nanoparticles. The crystalline structure of CSNPs and CS-ZnONCs was studied using X-ray diffraction (Shimadzu, XRD-700, X-ray diffractometer, Japan). Fourier transforms infrared (IR) characterization of CSNPs and CS-ZnONCs were performed with FTIR spectrophotometer (Shimadzu, FTIR-8400S, Japan) with a frequency range of 400-4000 cm⁻¹.

Assessment of the adsorption behavior of CSNPs

Through a batch procedure, adsorption of Cu (II) and Zn (II) ions by CSNPs was carried out at different pH ranges (3- 9) at room temperature. Dried CSNPs (0.1 g) were added to 50 mL solution of Cu (II) or Zn (II) at different initial concentrations (10, 30, 50, 80 and 100 mg/L). Effect of contact time on the adsorption process was studied using time range(0- 300 min) at a stirring speed of 200 rpm. CSNPs adsorbents were separated by centrifugation and the removal percent/adsorbed amount of Cu (II) and Zn (II) were determined by atomic absorption spectrophotometric (AAS) (Shimadzu 6800) before and after removal process. Also the effects of adsorbent dose of nanoparticles on the Cu (II) and Zn (II) removal were studied.

Adsorption kinetics

For kinetic study, 0.1 g of dried CSNPs was added to a 50 mL solution of Cu (II) or Zn (II) at different initial concentrations (10, 30, 50, 80 and 100 mg/L). The effect of contact time on the adsorption process was studied in time range (0- 300 min). Samples of 5 mL were withdrawn at fixed time intervals. CSNPs, centrifuged at 12,000 x g for 10 min and concentrations of Cu (II) or Zn (II) in supernatant were determined by AAS.

The adsorption capacity (q, mg/g) was calculated according to the following equation:

\[ q = \frac{C_0 - C_t}{m} V \]  

Where \(q\) is the adsorption capacity (mg/g), \(C_0\) and \(C_t\) are the initial and equilibrium concentrations (mg/L), \(m\) is the mass of the adsorbent (g), and \(V\) is the volume of solution (L).

The removal efficiency (\(\eta\)%) was calculated according to the following equation:

\[ \text{Removal efficiency (\(\eta\)%)} = \frac{C_0 - C_t}{C_0} \times 100 \]  

The kinetics of the adsorption process either following pseudo first order (PFO) or pseudo second order (PSO)
were tested. The conformity between experimental data and the model predicted values was expressed by the correlation coefficient (R² values; close or equal to 1). A relatively high R² value indicated that the model successfully describes the adsorption kinetics (Ho and McKay, 1998).

**Pseudofirst-order kinetic model**

The PFO model describes the rate of adsorption to be proportionally related to the number of unoccupied sites of the solute and can be expressed by Lagergren equation:

\[ \log(q_e - q_t) = \log q_e - k_1 t \]

(3)

Where \( q_e \) and \( q_t \) (mg/g) are the amount of metal ions adsorbed at equilibrium and at time \( t \), respectively. \( k_1 \) (min⁻¹) is the rate constant of the pseudo-first-order adsorption (Lagergren, 1898; Cheng et al., 2010).

**Pseudosecond-order kinetic model**

The PSO model was expressed by the equation of Ho and McKay:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]

(4)

Where \( k_2 \) (g mg⁻¹ min⁻¹) is the rate constant of the pseudo-second order adsorption.

**Adsorption Isotherms**

**Langmuir isotherm:** The generalized form of the Langmuir isotherm is represented by the following equation:

\[ \frac{c_e}{q_e} = \frac{1}{q_m k_l} + \frac{c_e}{q_m} \]

(5)

Where \( q_e \) (mg/g) is the equilibrium metal ion concentration on the adsorbent, \( C_e \) (mg/L) is the equilibrium metal ion concentration in solution, \( q_m \) (mg/g) is the monolayer capacity of the adsorbent and \( k_l \) (L/mg) is the Langmuir adsorption constant.

The essential characteristic of the Langmuir isotherm can be evidenced by the dimensionless constant called equilibrium parameter, \( R_L \) from the following equation:

\[ R_L = \frac{1}{1 + K_l C_o} \]

(6)

Where \( K_l \) (L/mg) is the Langmuir constant related to the energy of adsorption and \( C_o \) (mg/L) is the lowest initial concentration. The value of \( R_L \) could indicate the shape of isotherm to be either unfavorable \((R_L > 1)\) or linear \((R_L = 1)\) or favorable \((0 < R_L < 1)\) or irreversible \((R_L = 0)\) (Liu, 2006). The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the equilibrium parameter \( R_L \) that is defined by the following equation:

\[ R_L = \frac{1}{(1 + K_l C_o)} \]

(7)

Where, \( K_l \) is Langmuir adsorption constant and \( C_o \) is the initial concentration. The value of \( R_L \) is calculated from the above expression. The nature of the adsorption process is either unfavorable \((R_L > 1)\), linear \((R_L = 1)\), favorable \((0 < R_L < 1)\) or irreversible \((R_L = 0)\).

**Freundlich isotherm:** Freundlich isotherm can be expressed by the equation:

\[ \log q_e = \log k_f + \frac{1}{n} \log c_e \]

(8)

Where \( q_e \) (µg/g) is the equilibrium metal ion concentration on the adsorbent, and \( C_e \) (µg/L) is the equilibrium metal ion concentration in solution. \( k_f \) (L/µg) and \( n \) are the Freundlich constants that can be related to the adsorption capacity and the adsorption intensity, respectively (Quiñones and Guiochon, 1996).

**Assessment of pesticide removal using CS-ZnONCs**

For removal of λ-cyhalothrin (10%) from the polluted water using CS-ZnONCs, a batch experiment was
performed. Stock solution of 0.2 ppm of the pesticide was prepared. The effect of pH on adsorption process was studied at pH range (3-9) for aliquots of pesticide solution (0.2 ppm / 50 mL) with 0.5 g adsorbent for 24 h. Furthermore, different doses of adsorbent (0.3-1.0 gm) were added to each 50 ml of pesticide solution (0.2 ppm) under stirring conditions (100 rpm for 2 hours). Effect of contact time (0-120 min) on removal efficiency was tested via withdrawal of 3 ml every 10 min for analysis. Finally, influence of different initial pesticide concentrations (0.1-0.4 ppm) on the removal efficiency of adsorbent was studied under optimum pH, adsorbent dose and contact time.

High performance liquid chromatography (HPLC)

Concentrations of λ-cyhalothrin were measured using HPLC system (Agilent technologies 1200 series) according the method of Bissacot and Vassilieff (1997). The analytical column was eclipse XDB, C-18, 5 µm, 4.6x150 mm and injection volume was 20 µl, while the flow rate was 1.0 ml/min. The analytical column was operated at ambient temperature. The UV spectra were scanned from 200 to 350 nm and quantification was carried out at 250 nm. The mobile phase was a mixture of acetonitrile/water (80:20). Quantification of pesticides in samples was accomplished by comparing the peak area response with the standards. Data were gathered using Chemstation software.

RESULTS

Characterization of nanoparticles

The prepared nanomaterials (CSNPs and CS-ZnONCs) were characterized using Transmission Electron Microscope (TEM), Scanning Electron Microscope (SEM), X-Ray diffraction (XRD) and Fourier Transformer Infrared Spectroscopy (FTIR).

Transmission electron microscope (TEM)

The size and shape of CSNPs and CS-ZnONCs were determined by TEM. Micrographs of CSNPs revealed spherical morphology with average diameter of 40 and 56 nm for CSNPs and CS-ZnONCs, respectively. Figure 1 shows that CS-ZnONCs were in nanoscale with particle size range of 40-70 nm, with an average size 55 nm.

Scanning electron microscopy (SEM)

SEM micrographs of CSNPs and CS-ZnONCs biopolymers are shown in Figure 2. Spherical porous morphology with average diameter of 40 and 56 nm for CSNPs and CS-ZnONCs, respectively was observed.

X-ray diffraction

Figure 3 shows the XRD pattern of the CSNPs and CS-ZnONCs, respectively. There are mainly two strong peaks at about 10.67 and 20 degrees for the pure chitosan due to high degree of crystallinity. These peaks are very weak in the spectrum of the CS-ZnONPs composite indicating low crystallinity. Seven characteristic diffraction peaks of ZnO are shown in the XRD pattern of CS-ZnONPs at 2θ = 31.74°, 34.44°, 36.24°, 47.47°, 56.54°, 62.72°, 67.90°and 68.90° and they correspond to the (100), (102), (101), (102), (110), (103) and (112) crystal planes of pure ZnO, respectively.
Fourier-transform Infrared Spectroscopy:

Figure 4 shows the FTIR spectrum of chitosan nanoparticles. The stretching vibration mode of OH and NH$_2$ groups are centered at 3446 cm$^{-1}$, the peaks at 2916 and 2886 cm$^{-1}$ are typical of C-H stretch vibration. Amide I band corresponding to C=O vibration appears at 1650 cm$^{-1}$ of acetyl groups in chitosan, the peak at 1591 cm$^{-1}$ is attributed to the NH$_2$ group due to N-H deformation. The band of Amide III appears at 1332 cm$^{-1}$, due to combination of NH deformation. The CN stretching vibration and the band at 1089 cm$^{-1}$ correspond to CH-OH in cyclic compound (Kumirska et al., 2010).

In comparison with chitosan- ZnO nanocomposite, the broader and stronger peak shifted considerably to lower wave number at 3363 cm$^{-1}$, indicating strong attachment of ZnO to the amide groups of chitosan molecules. The absorption peak at 2873 cm$^{-1}$ is due to asymmetric stretching of CH3 and CH2 of chitosan polymer. The absorption peaks at 1642 and 1063 cm$^{-1}$ are attributed to the bending vibration of the -NH2 group and the C-O stretching group. A new broad absorption band at the range of 600–400 cm$^{-1}$ was found which were ascribed to the vibration of O-Zn-O groups. Similar phenomena were observed with the peaks of C=O, -NH2, 3'-OH, and 5'-OH groups. The reason for the above phenomena was the formation of hydrogen bonds between ZnO and chitosan (Li et al., 2010; Salehi et al., 2010).

Removal of heavy metals from water using CSNPs

The prepared CSNPs were tested as adsorbent matrices for Cu (II) and Zn (II) from simulated polluted water using batch technique. The potential parameters affecting the adsorption process were monitored.
Effect of pH

The effect of different pH values (3-9) on Cu (II) and Zn (II) adsorption using CSNPs was studied. As shown in Figure 5, the removal efficiency increased with increasing pH until it reached maximum (96.7%) at pH=5 for Cu (II) and 98.2% at pH=7 for Zn(II).

Effect of adsorbent dose

The effect of adsorbent dose on the removal of Cu (II) and Zn(II) was carried out by varying the amount of CSNPs from 50 to 200 mg/50 ml of Cu (II) or Zn(II) solutions (50 ppm) initial concentration and pH 5 & 7, respectively at room temperature. It was observed that the removal percentage improved with the increasing adsorbent dose until 100 mg, after which the removal percentage remains constant (Figure 6). In the present study, 0.1 g/50 ml (50g/L) of CSNPs was considered as the optimum dose.

Effect of contact time and initial concentration

The effect of both contact time and different initial concentrations for Cu(II) and Zn(II) were studied by
plotting the adsorbed metal capacity ($q_t$) versus the time ($t$) and the removal efficiency with time as shown in Figures 7 and 8, respectively. The adsorption reached equilibrium within 180 min for Cu(II) and 60 min for Zn(II) and the total amount of adsorbed metals increased as the initial concentrations increased. For Cu(II), about 97% adsorption was observed for the initial concentrations (10, 30 and 50 mg/l) and 93.5 and 92% for initial concentrations of 80 and 100 mg/L, respectively within 180 min. On the other hand, about 99% adsorption of Zn (II) was observed for the initial concentrations (10 and 30 mg/l) within 60 min while 98.2 % adsorption was achieved for initial concentration of 50 mg/l within 60 min. For initial concentrations of 80 and 100 mg/l, the adsorption percentage reached about 93.5 and 92%, respectively within 60 min. The decreasing removal efficiency with increasing Cu (II) and Zn(II) concentrations could be attributed to the tendency of absorbent to
become saturated.

**Adsorption kinetics**

The linear plots of ln \((q_e - q_t)\) versus \(t\), \(t/q_t\) versus \(t\) and \(q_t\) versus \(t^{1/2}\) are shown in Figures 9 and 10 for adsorption of Cu (II) and Zn (II) by CSNPs, respectively. Values of \(k_1\), \(k_2\) and \(q_e\) calculated from the slopes and intercepts of the lines are listed in Table 1.

**Isotherm adsorption study**

Figure 11 shows the fitting of Langmuir and Freundlich isotherm models for Cu (II) adsorption by CSNPs, respectively. Figure 12 showed the fitting of Langmuir and Freundlich isotherm models for Zn (II) adsorption by CSNPs, respectively. The model parameters and statistical fits of the sorption data of Cu (II) and Zn (II) are given in Table 1.

**Removal of pesticide using CS-ZnONCs**

**Effect of pH**

The adsorption of the \(\lambda\)-cyhalothrin pesticide onto CS-ZnONCs at pH range (3-9) was investigated and the data are plotted in Figure 13. Results indicated that the removal percentage of \(\lambda\)-cyhalothrin from water increased with increasing pH up to 7, recording about 96%, and then began to decrease.

**Effect of the amount of CS-ZnONCs**

Figure 14 shows the removal percentage of pesticide (0.2 ppm/25 mL) at pH 7 for 100 min with different amounts of the composite (0.3-1.0 g). Thus the removal efficiency increased with increase in adsorbent dose up to 0.7 g, recording 97.7% after which there no increase was observed in the removal percentage.

**Effect of contact time**

Figure 15 shows the effect of agitation time (10–100 min) of 0.7 g CS- ZnONCson adsorption of \(\lambda\)-cyhalothrin (0.2 ppm/50 mL) at pH 7. The plot showed that the adsorption of pesticide increased with time until it reached a constant value beyond which no more pesticide would be further removed from the solution. The removal efficiency increased from 81 to 97% with an increase in agitation time (10–60 min), and became almost constant after 60 min.

**Effect of \(\lambda\)-cyhalothrin initial concentration**

Figure 16 shows the effect of \(\lambda\)-cyhalothrin initial
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Figure 9: a-Pseudo first order for adsorption of Cu (II) by CSNPs. b- Pseudo second order for adsorption of Cu (II) by CSNPs (pH=5 and 50 mg/L initial concentration).

Table 1. Adsorption kinetics and isotherm constants for adsorption of Cu (II) and Zn(II) on CSNPs at pH 5 and 7, respectively and 25°C.

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<th>Zn(II)</th>
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concentration (0.1–0.4 ppm) on adsorption process onto 0.7 g CS-ZnONCs at pH 7 for 60 min agitating time. The removal percentage decreased from 98% at 0.1 ppm initial concentration to about 89% at 0.4 ppm initial concentration.

DISCUSSION

Nanotechnology has been identified as a technology that could play an important role in resolving many environmental problems involving water purification and
quality (Bottero et al., 2006) as efficient, cost-effective and environmental friendly alternatives to existing treatment materials, from the standpoints of both resource conservation and environmental remediation (Dastjerdi and Montazer, 2010).

Chitosan nanoparticles can be prepared using several methods such as ionic gelation, complex co-acervation, emulsion, cross-linking and spray drying (Agnihotri et al., 2004; Sinha et al., 2004). In the present study, ionic gelation method using TPP as a crosslinking agent was implemented. Formation of the nanospheres by the ionotropic gelation occurs immediately upon mixing the two phases through intermolecular and intramolecular linkage between negatively charged TPP (pH 8) and positively charged chitosan amino groups (pH 4) (Tsai et al., 2007). The advantage of this method is being a simple procedure achieved without applying harmful organic solvents, heat or vigorous agitation. Chitosan-ZnO nanocomposite was successfully prepared using a simple and cost effective chemical precipitation method (Dehaghi et al., 2014).

Characterization of prepared nanomaterials

Scanning and transmission electron microscope

By SEM, both CNPs and CS-ZnONCs were spherical in shape with a smooth surface. This result is in agreement with that previously reported by Tsai et al. (2007), where most...
of the prepared nanospheres had a smooth surface and were spherical in shape when examined by SEM.

TEM indicated that CSNPs are spherical porous with several caves on their surface. These caves greatly expanded the surface area of CSNPs and exposed much more NH2 which could chelate with metals. The particles size of CSNPs and CS-ZnONCs were 40 and 55 nm respectively and the size distribution between them was quite narrow. The same result was obtained in a study conducted by Da Silva et al. (2012), where nanoparticles appeared to be spherical to oval in shape and 200 nm in diameter.

**X-ray diffraction**

The change in crystal lattice arrangements of CSNPs and CS-ZnONCs structure was investigated by XRD. The X-ray diffraction patterns of CSNPs and CS-ZnONCs showed that typical peaks of chitosan appeared at 2θ value, 10.67° and 19.99°, while these peaks become weak in the XRD pattern of CS-ZnONCs (Figure 3). 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 2θ = 31.74°, 34.44°, 36.24°, 47.44°, 56.54°, 62.72°, 66.38°, 67.90° and 68.97°, which were

Figure 12: Langmuir and Freundlich adsorption isotherms for Zn (II) by CSNPs.

Figure 13: Removal efficiency of λ-cyhalothrin at different pHs by CS-ZnONCs.
corresponded to the (100), (002), (101), (102), (110), (103) and (112) 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) (Li et al., 2010). 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 (Li et al., 2010).

**Fourier-transform infrared spectroscopy**

By comparing the FTIR spectra of CSNPs and of CS–ZnONCs, the same peaks were found with broader or stronger peak shifted due to the formation of hydrogen bonds between ZnO and chitosan, these results are in agreement with previous studies (Abdelhady, 2012; Dehaghi et al., 2014), indicating successful formation of CS–ZnONCs.

**Removal of heavy metals via CSNPs**

Batch experiment was conducted to measure the

![Figure 14](image.png)

**Figure 14:** Influence of CS-ZnONCs doses on the removal efficiency of λ-cyhalothrin.

![Figure 15](image.png)

**Figure 15:** Effect of contact time on removal efficiency of λ-cyhalothrin.
performance of nanomaterials in removing metal ions and pesticide from simulated water. The initial pH of solution plays an important role in the adsorption process and particularly on the adsorption capacity by controlling the surface charge of the adsorbent and the degree of ionization of the materials in the solution. As shown in Figure 5, the removal efficiency of Cu(II) increased from about 59 to 98% by changing the pH from 3.0 to 5.0 and then began to decrease. Also removal of Zn(II) increased from 42 to 98% when the pH increased from 3.0 to 7.0. The increase of Cu(II) and Zn(II) adsorption on CSNPs with increasing pH could be attributed to the hydrolysis of Cu(II) and Zn(II) ions and the surface properties of CSNPs. Similar results were obtained where chitosan nanoparticles prepared by deacetylation of chitin were used to remove Fe(II), Mn(II), Zn(II) and Cu(II) metal ions from water. Chitosan exhibited metal removal efficiencies of 99.94% for Fe(II), 80.85% for Mn(II), 90.49% for Zn(II) and 95.93% for Cu(II) ions (Abd-Elhakeem et al., 2015).

The Cu and Zn presents in the species of Cu^{2+}, Cu(OH)^{+}, Cu(OH)_2^{2+}, Cu(OH)_3^{3+}, Cu(OH)_4^{4-} and Zn^{2+}, Zn(OH)^{+}, Zn(OH)_2^{2+}, Zn(OH)_3^{3+}, Zn(OH)_4^{4-} at different pH values. At low pH, the predominant species was Cu^{2+} and Zn^{2+}. Therefore, the low Cu^{2+} and Zn^{2+} adsorption at low pH can be attributed partly to the competition between H^+ and Cu^{2+}, or H^+ and Zn^{2+} on the surface sites. Furthermore, the CSNPs surface will be positively charged, creating electrostatic repulsion between the positively charged surface of the CSNPs and the Cu (II) and Zn (II) ions. At higher pH, the number of positive charged sites was reduced and increased the number of negatively charged sites, which in-turn increased the electrostatic attractions between Cu (II) and Zn (II) ions and CSNPs surface. Similar phenomenon has been reported by Sheela et al. (2012).

The contact time between the adsorbate and the adsorbent plays a crucial role in adsorption of metals from a solution. As shown in Figures 7 and 8, the removal efficiency of Cu (II) and Zn (II) by CSNPs increased with increasing contact time and then became constant. Equilibrium was achieved within 210 and 60 min for Cu (II) and Zn (II), respectively. During initial adsorption stage, rapid adsorption occurred due to the availability of more active sites over the adsorbent surface, while during the second adsorption stage, slow rate of Cu(II) and Zn(II) adsorption occurred probably due to the less availability of active sites onto the surface of adsorbent, as well as the slow pore diffusion of the solute into the adsorbent. Similar results have been found (Zhang et al., 2011).

Initial concentration of metals is an important factor for practical application. At a constant CSNPs dose, the decrease in the adsorption efficiency is probably due to the saturation of the active binding sites on the CSNPs surface at higher Cu (II) and Zn (II) concentrations. On the other hand, by increasing the initial Cu (II) and Zn (II) concentrations, the actual amount of metals adsorbed per unit mass of the CSNPs increased. The higher initial Cu(II) and Zn(II) concentrations provides an important driving force to overcome the mass transfer resistance for Cu (II) and Zn(II) transfer between the solution and the surface of the CSNPs. Similar phenomenon has been reported by Wen-Li Du et al.(2005). The removal efficiency increased with increase in dose of the CSNPs and the maximum adsorption was observed at 100 mg for Cu (II) and Zn (II). This result is in line with the findings of Madrakian et al. (2012).

Furthermore, pseudo-first order and pseudo-second-order models were conducted to test the dynamical experimental data (Table 1). The comparison of correlation coefficients (R^2) of the linearized form of both equations indicates that the kinetic data for the sorbent fitted well to the pseudo second-order kinetic model. The best fit to the pseudo-second order kinetics indicates that the adsorption mechanism depends on the adsorbate and adsorbent.

Adsorption isotherm can provide the most important parameter for designing a desired adsorption system. In

Figure 16: Effect of initial concentration of pesticide on removal efficiency.
this study, the Langmuir and Freundlich isotherms were applied to describe the adsorption behaviors of Cu (II) and Zn (II) onto CSNPs. Table 1 shows the calculated values of the Freundlich and Langmuir model’s parameters. The comparison of correlation coefficients (R^2) of the linearized form of both equations indicates that the Langmuir model yields a better fit for the experimental equilibrium adsorption data than the Freundlich model. This suggests monolayer coverage of the surface of CSNPs by Cu (II) and Zn (II). All the R_L-values for the adsorption of Cu (II) and Zn (II) onto CSNPs were in the range of 0–1, indicating that the adsorption process is favorable.

All the 1/n values for the adsorption of Cu (II) and Zn (II) onto CSNPs were less than 1, indicating that the isotherm is convex and more adsorbate presence in the adsorbent enhance the free energies for further adsorption.

The exponent is an index of the diversity of free energies associated with the adsorption of the solute by multiple components of a heterogeneous adsorbent. When n = 1, the isotherm is linear and system has a constant free energy at all adsorbate concentrations. When 1/n > 1, the isotherm is concave and sorbates are bound with weaker free energies, finally, when 1/n < 1, the isotherm is convex and more adsorbate presence in the adsorbent enhance the free energies of further adsorption (Lim et al., 2008).

**Removal of pesticide using CS-ZnONCs**

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 (Akhtar et al., 2007).

In acidic media, the decrease in the amount of λ-cyhalothrin 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 could increase the sorbate interaction with functional groups of the sorbents by greater attractive forces, and thereby, improve its adsorption on polar sorbent (Huang et al., 2011). 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 (Rengarag et al., 2002).

The amount of adsorbent is an important parameter, which affects the capacity of a sorbent for a given initial concentration of sorbate (Daneshvar et al., 2007). It was found that the increase in adsorbent more than 0.7 g dose did not affect the removal percentage significantly. About 98% removal of pesticide was achieved in dosage range of 0.7–1.0 g of adsorbent.

This may be presumed that the availability of active sites on the nanocomposite is decreasing at higher doses of sorbents (>0.7 g). The total active surface area increases by increasing the composite dosage. At the same time, due to the increasing amount of sorbent, the sorbent–sorbent interactions are more dominating than sorbate–sorbent interactions (Akhtar et al., 2007; Daneshyar et al., 2007). Since the most effective removal of permethrin was observed with 0.7 g of CS-ZnONPs composite, the other experiments were performed using this concentration.

The effect of agitation time on the pesticide adsorption on the prepared nanocomposite was investigated. The initial fast rate is probably due to the abundant available binding sites on the surface of the adsorbent. The percent sorption increased from 81 to 97% with an increase in agitation time (10–60 min), and became almost constant after 60 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 on the adsorbent (Sokkera et al., 2011).

The removal percentage of the pesticide was decreased by increasing the initial concentration of the pesticide. As the initial concentration increased, more organic substances were adsorbed on the surface of the sorbent. Thus, the distribution coefficient (R_d) decreased which suggest limited 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 be reduced (Akhtar et al., 2007).

**CONCLUSION**

Selection of the best method and material for water treatment is a highly complex task, which should consider a number of factors, such as the quality standards to be met and the efficiency, as well as the cost. Both CSNPs and CS-ZnONCs were successfully prepared through simple and cost effective methods. Such synthesized nanomaterials proved high capacity as adsorbents with excellent adsorption performance for the removal of heavy metals and pesticides from water and wastewater. Therefore, they are highly recommended as potential candidates for developing bio-adsorbent filters towards several environmental pollutants through biocompatible and environmentally benign synthetic strategy.

**REFERENCES**

Abdelhady MM (2012). Preparation and characterization of chitosan/zinc oxide nanoparticles for imparting antimicrobial and UV protection to


