

Sorption kinetics of zinc and nickel on modified chitosan

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Abstract This study was conducted to evaluate the effect of equilibration time on adsorption of zinc [Zn(II)] and nickel [Ni(II)] on pure and modified chitosan beads. The initial adsorption of Zn(II) was high on molybdenum (Mo)-impregnated chitosan beads (MoCB) during the initial 60 min. However, after 240 min, Zn(II) adsorption occurred

more on single super phosphate chitosan beads (SSPCB), followed by monocalcium phosphate chitosan beads (MCPCB), untreated pure chitosan beads (UCB), and MoCB. Similarly, Ni(II) adsorption was greatest on MoCB during the initial 60 min. At the conclusion of the experiment (at 240 min), the greatest adsorption was occurred on MCPCB, followed by MoCB, UCB, and SSPCB. Chemical sorption and intra-particle diffusion were probably the dominant processes responsible for Zn(II) and Ni(II) sorption onto chitosan beads. The results demonstrated that modified chitosan beads were effective in adsorbing Zn and Ni and hence, could be used for the removal of these toxic metals from soil.

Capsule abstract

Pure and modified chitosan beads were studied for equilibration time on Zn and Ni adsorption. Modified beads had higher potential for metal removal as seen with the models tested.

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Introduction

Trace elements (often referred to as “heavy metals”) occur naturally in soil; some are essential for plant growth at low levels (also referred to as “micronutrients”). Zinc (Zn) not only enhances crop productivity but also improves the quality of crop produce (Kumar et al. 2011; Srivastava and Srivastava 2008; Srivastava et al. 2008). However, at elevated levels, Zn may become toxic and pose acute and chronic risks to human health and ecological receptors through plant uptake and leaching into

groundwater. Exposure to high concentrations of Zn may cause serious health problems such as stomach and skin irritations, respiratory disorders, and disturbance of protein metabolism (Nriagu 2007). Zinc and its salts pose acute and chronic toxicity to aquatic life in polluted waters and cytological disorders in plants (Rout and Das 2003). Similarly, an exposure to higher concentrations of nickel (Ni) may result into several human (e.g., lung, nose, larynx, and prostate cancers; birth defects; asthma and chronic bronchitis; heart disorders; and allergic skin reactions) and plant disorders such as iron (Fe) uptake and metabolism (Denkhaus and Salnikow 2002). Mining activities and rapid industrialization are major sources of elevated concentrations of these contaminants in soil and water. Since trace elements are not biodegradable, they tend to accumulate as metallo-organic complexes in living organisms (Trgo et al. 2006). However, Zinc and Ni are essential trace elements for human health and plants.

Heavy metal removal has been attempted through conventional methods such as physical, chemical, and various biological processes, involving sedimentation, settling, filtration, adsorption, precipitation, coprecipitation into insoluble compounds, and biological and phytoremediation techniques (Sheoran and Sheoran 2006). Although these methods are adequate for the treatment of medium to high concentration solutions, using natural materials for the removal of heavy metals can be both cost effective and environmentally friendly. A large number of biosorbents such as algae, polysaccharides, fungi, bacteria, and waste biomass from food industries have been investigated for removal of heavy metal(loid)s from contaminated soils. However, selection of biosorbents from readily available and inexpensive biomaterials has been a challenge (Wang and Chen 2009). Chitin and chitosan are the biosorbents that are abundantly available and could potentially fill this gap.

Chitin is isolated from the exoskeletons of crustaceans and chitosan is prepared from the deacetylation of chitin. It is the world's second most abundant naturally occurring polysaccharide (Abdou et al. 2008; Shahidi et al. 1999). Chitosan has been studied with some chemical modifications for retention of metals. Chitosan consists of amino and hydroxyl groups that can act as binding sites for metal ion complexation. It is a powerful chelating agent possessing high adsorption capacity for a variety of heavy metals including Zn, copper (Cu), and mercury (Hg) (Burke et al. 2002; Chu 2002; Dhakal

et al. 2005; Guibal et al. 1998; Ravi Kumar 2000). Chen et al. (2007) modified chitosan beads with molybdenum (Mo) and Fe. The very strong affinity for molybdate and Fe resulted in an improved adsorption of metals and organic contaminants to the Mo- and Fe-impregnated chitosan beads. Based on earlier studies (Chen et al. 2007; Guibal et al. 1998) on heavy metal removal from water using modified chitosan, we selected molybdenum, single super phosphate, and monocalcium phosphate for modifying chitosan. It was hypothesized that these modification materials can also serve as slow-release nutrients in nutrient-deficient soils.

Adsorption and desorption of heavy metals is affected by several rate-limiting processes, such as kinetic sorption and release reactions (Zhao and Selim 2010; Rezaei et al. 2014). Kinetics is a generic term elucidating time-dependent phenomena (e.g., surface diffusion and chemical kinetics) necessary to understanding the mechanisms for metal sorption and the fate of metals in soils (Sparks 1990). Moreover, the study of kinetics is imperative for describing the fate of applied chemicals and pollutants in soils over time and to improve nutrient availability and groundwater quality (Sparks 1989).

This study was conducted to assess the efficacy of pure chitosan and modified chitosan beads in removal of Zn and Ni. In this study, chitosan was modified with molybdenum (MoCB), single super phosphate (SSPCB) and monocalcium phosphate (MCPCB) chitosan beads. The study also investigates various kinetic models to explain Zn and Ni sorption on pure and modified chitosan beads.

Material and methods

Preparation of pure and modified chitosan beads

Chitosan was sourced from Qingdao Yuanrun Chemical Co., China and used without further purification. The average molecular weight (MW_w) of chitosan was 200 kDa and the degree of deacetylation was approximately 88 %. A sample (2 g) of chitosan was dissolved in 50 mL of 5 % (v/v) acetic acid solution and left overnight to form a yellow viscous chitosan acetate solution. Pure chitosan beads (untreated pure chitosan beads, (UCB)) were prepared through phase inversion of chitosan acetate solution using 0.5 M NaOH (Chen et al. 2009). For bead preparation,

chitosan solution was dropped into NaOH bath using a peristaltic pump. In phase inversion of chitosan, the positively charged amino groups were coupled with negatively charged acetic acid (Duarte et al. 2010; Fu 2006). The wet chitosan gel beads were rinsed thoroughly with deionized water to remove excess NaOH and subsequently dried at 60 °C.

Three types of modified chitosan beads were prepared by impregnating molybdenum (Mo), single super phosphate (SSP), and monocalcium phosphate (MCP). Molybdenum-impregnated chitosan beads (MoCB) were prepared by immersing wet chitosan beads (prepared with 50 mL of chitosan solution) in 5 g MoL⁻¹ solution of ammonium hepta-molybdate [(NH₄)₆Mo₇O₂₄·4H₂O] at pH 6 and stirred on a magnetic stirrer for 24 h at 200 rpm (Dambies et al. 2001). Molybdenum concentration in the chitosan beads was obtained by mass balance between the wet and dried beads, and was reported as a function of dry mass of chitosan. The SSPCB was prepared by inversing a mixture of 2.5 g SSP, 2.0 g chitosan, and 50 mL of 5 % acetic acid. Similarly, MCPCB were prepared using a mixture of 2.0 g of MCP, 3.5 g of chitosan powder in 50 mL of 5 % acetic acid (v/v). All mixtures were dripped into 3 M NaOH solution through a tube with 2-mm internal diameter to form the beads. All chitosan gel beads were oven dried at 60 °C to obtain their dry mass. Pure and modified chitosan beads were characterized for cation exchange capacity (CEC) (Gillman and Sumpter 1986) and Brunauer Emmett Teller (BET) surface area (Brunauer et al. 1938).

Adsorption experiments

Aqueous solutions of metal ions (Zn and Ni) (1000 mg L⁻¹) were prepared from ZnSO₄·7H₂O and NiSO₄·7H₂O, with initial pH 5.67 and 6.35, respectively, and ionic strength of approximately 0.0111 for Zn and 0.0115 for Ni solutions. The batch adsorption isotherm studies with three replicates were carried out with initial Zn and Ni ion concentration of 1000 mg L⁻¹ each. Aliquots of 2.5 g of each pure and modified chitosan beads were placed in 500-mL beakers containing 250 mL of metal ion solution with known initial concentrations (1000 mg L⁻¹). The suspensions were agitated at a speed of 200 rpm using a magnetic stirrer at 25 °C

for 4 h. At 30-min intervals, 10 mL aliquots of each suspension were collected. The equilibrium solution was analyzed with ICP-OES to quantify the amount of Zn(II) and Ni(II) adsorbed onto the chitosan beads. Zinc and Ni adsorption was calculated using Eq. (1):

$$Q_t = (C_0 - C_t) \times V / m_s \tag{1}$$

where Q_t is the absorbed concentration in milligrams per gram at time t . C_0 and C_t are the initial metal concentration and the metal concentration at time t , respectively. V is the volume of solution, and m_s is the weight of chitosan bead in grams.

Adsorption kinetics

In order to explain the mechanism controlling the adsorption processes of Zn(II) and Ni(II) on chitosan beads, different kinetic models (pseudo first-order, pseudo second-order, Elovich, and intra-particle diffusion) were tested (Chien and Clayton 1980; Ho et al. 2000; Lagergren 1898; Sparks 1986; Weber and Morris 1963). To identify the rate-controlling mechanisms during the adsorption of Zn and Ni, three main steps were considered: (1) mass transfer of the metallic ions from the bulk solution to the chitosan surface, (2) adsorption of the metallic ions onto sites, and (3) internal diffusion of metallic ions onto chitosan. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients. A relatively high regression coefficient value indicates that the model closely describes the kinetics of Zn(II) and Ni(II) adsorption.

Pseudo first-order kinetics

A pseudo first-order equation (Lagergren 1898) is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2}$$

where, q_e and q_t represent the adsorption capacity (mg g⁻¹) of chitosan at equilibrium and at time t , respectively. k_1 is the rate constant (L min⁻¹) of pseudo first-order adsorption.

After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Eq. 2 becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

The values of $\log(q_e - q_t)$ are linearly correlated with t . The plot of $\log(q_e - q_t)$ vs. t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

Pseudo second-order kinetics

The pseudo second-order adsorption kinetic rate equation (Ho et al. 2000) is generally expressed as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

Where k_2 is the rate constant ($\text{g mg}^{-1} \text{min}^{-1}$) of the pseudo second-order adsorption.

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Eq. 4 becomes

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (5)$$

which is the integrated rate law for a pseudo second-order reaction. Eq. 5 can be rearranged to obtain Eq. 6, which has a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (6)$$

if the initial adsorption rate, h ($\text{g mg}^{-1} \text{min}^{-1}$) is:

$$h = k_2 q_e^2 \quad (7)$$

then Eqs. 6 and 7 become:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_t} t \quad (8)$$

The plot of (t/q_t) and t of Eq. 6 should give a linear relationship and q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

The Elovich model

The Elovich model equation (Chien and Clayton 1980; Sparks 1986) is generally expressed as:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (9)$$

Where α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is the desorption constant (mg g^{-1}). During any one experiment, to simplify the Elovich equation, Chien and Clayton (1980) assumed $\alpha \beta t \gg t$. By applying the boundary conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq. (9) becomes;

$$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t \quad (10)$$

If metal adsorption fits the Elovich model, a plot of q_t vs. $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha \beta)$.

The intra-particle diffusion model

The intra-particle diffusion model (Srivastava et al. 1989; Weber and Morris 1963) is expressed as:

$$R = (t)R = k_{id}(t)^a \quad (11)$$

A linearized form of the equation is expressed as:

$$\log R = \log k_{id} + a \log(t) \quad (12)$$

where R is the percent metal adsorbed, t is time (h), a is the gradient of linear plots, and k_{id} is the intra-particle diffusion rate constant (h^{-1}). While a depicts the adsorption mechanism and k_{id} may be regarded as a rate factor, i.e., percent metal adsorbed per unit time.

Results and discussion

Physical characteristics of chitosan beads

The physical characteristics of chitosan beads are described in Table 1. Modified chitosan beads had a larger CEC than pure chitosan beads. The order of increase in CEC was UCB ($21.01 \pm 0.12 \text{ cmol kg}^{-1}$) < SSPCB

Table 1 Physical characteristics of chitosan beads

Samples	CEC (cmol kg ⁻¹)	BET surface area (m ² g ⁻¹)	Pore size (Å)
UCB	21.01 ± 0.12	0.186 ± 0.001	8.34 ± 0.02
MoCB	34.02 ± 0.07	6.63 ± 0.01	17.94 ± 0.01
SSPCB	24.03 ± 0.02	4.67 ± 0.01	17.38 ± 0.03
MCPCB	32.63 ± 0.04	2.0 ± 0.1	16.59 ± 0.02

(24.03 ± 0.02 cmol kg⁻¹) < MCPCB (32.63 ± 0.04 cmol kg⁻¹) < MoCB (34.02 ± 0.07 cmol kg⁻¹). Similarly, the BET surface area of modified chitosan beads was larger than pure chitosan beads. The higher surface area and therefore, the higher CEC of modified beads could be attributable to the swelling and crosslinking, if any, of chitosan with modification materials (Hastuti et al. 2016). The largest surface area was measured on MoCB (6.63 m² g⁻¹), followed by SSPCB (4.67 m² g⁻¹), MCPCB (2.0 m² g⁻¹), and UCB (0.186 m² g⁻¹). Pore size was greatest for MoCB (17.94 Å), followed by SSPCB (17.38 Å), MCPCB (16.59 Å), and UCB (8.34 Å). The trend suggested modification of chitosan beads with Mo and P resulted in higher CEC, surface area, and pore size. However, Mo was more effective than P in enhancing these physical characteristics of chitosan beads. Similar observations have been reported in the literature where physical modifications, such as conversion into gel or bead form (Benavente 2008) and chemical modifications, such as insertion of functional groups (Benavente 2008; Rinaudo 2006), have led to changes in the physical characteristics of chitosan.

Adsorption kinetics

Adsorption of Zn and Ni ions increased with time (Fig. 1), but the adsorption rate slowed down to varying degrees. The suspension pH increased from 4.93 to around 6.00 after 150 min, and then plateaued at pH 6.06. Initial adsorption of Zn was greatest on MoCB for up to 30 min, but was subsequently overtaken by other chitosan beads. After 150 min, maximum Zn was adsorbed on MCPCB and SSPCB, followed by UCB and MoCB. However, UCB showed maximum Zn adsorption at the conclusion of the experiment after 240 min. In the case of Ni, the suspension pH increased with time from 4.94 after 30 min to 6.00 after 150 min, and then plateaued at 6.05. MoCB had the highest Ni adsorption for the first 90 min, but was subsequently

overtaken by MCPCB. At the conclusion of the experiment, after 240 min, maximum Ni adsorption was observed on MCPCB, followed by MoCB, UCB, and SSPCB.

The adsorption of metal ions on cellulosic materials could be attributed to intrinsic adsorption and coulombic interactions resulting from the electrostatic energy generated in the interaction between adsorbent and adsorbate (Gang and Weixing 1998). Surface area of the materials determines the extent of intrinsic adsorption onto them (Igwe et al. 2008). Ghosh and Yuan (1987) proposed the transfer of a proton to the hydroxyl groups on the surface of adsorbent as a reason of interaction.

Increased Zn sorption on both phosphate-impregnated chitosan beads (MCPCB and SSPCB) and Ni sorption on MCPCB were clearly manifested in this study. Reduction in Zn desorption could be attributable to the presence of P, which tends to increase the specific sorption sites for Zn (Selim 2012; Zhao and Selim 2010). High levels of Zn in soil tend to occupy most of the newly formed adsorption sites due to phosphate addition or consume phosphate through precipitation (Lambert et al. 2007).

Low adsorption of Zn on MoCB, despite favorable physical characteristics (large surface area, CEC and pore size), was surprising. However, Ni was adsorbed to MoCB in reasonable amounts; greater than on pure chitosan beads. Enhanced uptake of Zn was expected on MoCB due to high surface area and CEC, particularly as a strong interaction was reported between Mo and Zn (Rodriguez and Kuhn 1995). Basak et al. (1982) reported adsorption of Zn on Mo applied to soil. Similarly, oxides of Mo are observed to react strongly with phosphates of Zn (Martin et al. 2000).

The adsorption kinetics of Zn and Ni onto chitosan beads explained a faster initial stage of metal ion uptake followed by slower adsorption. The adsorption of Zn and Ni increased rapidly from 30 to 150 min. Thereafter, adsorption slowed down. Zinc adsorption on UCB, MoCB, and SSPCB plateaued after 180 min of

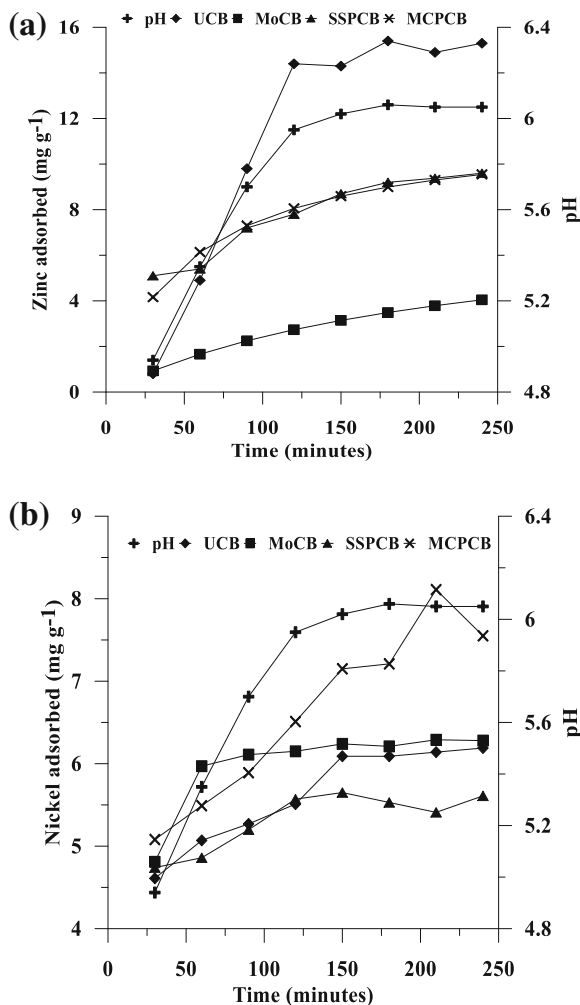


Fig. 1 Zinc and nickel adsorption on unmodified and modified chitosan beads as a function of time; *cross* pH curve; *diamond* unmodified chitosan beads (UCB); *square* molybdenum-modified chitosan beads (MoCB); *triangle* single superphosphate-modified chitosan beads (SSPCB); and *asterisk* monocalcium phosphate-modified chitosan beads (MCPCB)

equilibration, whereas MCPCB continued to adsorb Zn even after 240 min. Similarly, Ni adsorption on UCB, MoCB, and SSPCB plateaued after 120 min, whereas MCPCB continued to adsorb Ni even after 240 min, albeit at a reduced rate.

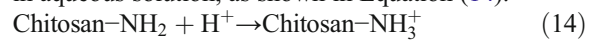
Chitosan is characterized by a high percentage of nitrogen, present in the form of amine groups. Amine sites are the main reactive groups for metal ions, though hydroxyl groups, especially in the C-3 position, bind metal ions through chelation mechanisms (Ravi Kumar 2000; Varma et al. 2004). The unprotonated amino groups of chitosan mainly regulate the adsorption of transition metal

ions on to it (Monteiro and Airoidi 1999; Onsoyen and Skaugrud 1990).

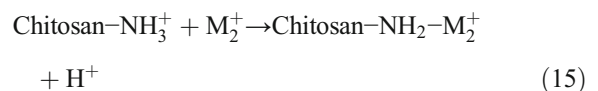
Increase in pH of the equilibrium solution was observed as adsorption progressed with time. This may be attributed to rupture of internal hydrogen bonds and protonation of amino groups of chitosan after reaction with water (Agulló et al. 2004), given no pH control was used in the experiment. The mechanism can be understood through Equation (13).



In addition, chitosan acts as a weak base. At low pH, amino groups of chitosan receive the protons available in aqueous solution, as shown in Equation (14).



This reduces the concentration of H^+ ions and raises the pH of the solution. Ngah et al. (2004, 2011) ascribed the low adsorption capacity in acidic solution to competition between protons and metallic ions for available amino adsorption sites. According to Jeon and Höll (2003), high electrostatic repulsion may result in low adsorption capacity in acidic solution. The following relationship (Eq. 15) shows the influence of pH on the uptake of metallic ions:



However, as the adsorption process progresses, the pH of the solution increases. At higher pH, the improved adsorption performance is achieved due to the reduced competition for binding sites and decreased electrostatic repulsion (Benavente 2008).

Factors regulating metal adsorption on chitosan beads

Cation exchange capacity

Greater CEC of the modified chitosan beads compared to UCB was potentially due to impregnation of anions (molybdate and phosphate) into the chitosan bead structure leading to greater negative charge. Cation exchange is an important sorption mechanism for many clay minerals (Ikhsan et al. 2005; Kraepiel et al. 1999; Srivastava

et al. 2005). Chitosan beads, having high CEC, provide more available exchange sites and are responsible for cation uptake at low pH (Stathi et al. 2010). Cation exchange capacity indicates the improved biomass surface and hence the sorption of cationic species in solution (Popuri et al. 2009).

An increase in surface charge with specific adsorption of anions and cations can be explained both by double-layer theory, as well as by empirical reaction equations. By using empirical equations, White (1980) demonstrated in the case of HPO_4^{2-} -impregnated chitosan, that the charge conveyed to the surface was large when the HPO_4^{2-} -displaced water molecules coordinated with the surface, and small when it displaced the OH^- . In the first reaction, which involves the displacement of water molecules, the charge on the HPO_4^{2-} is balanced by changes in the electrolyte ions associated with the surface, either with an increased concentration of cations, or a decreased concentration of anions. In the second reaction, the charge balance is by displacement of OH^- . The surface always receives some negative charge, which is always less than the charge on the anion (Bowden et al. 1980; Hingston 1970; Naidu et al. 1990). Similarly, the output of Bowden's variable charge model shows the charge added to the surface, per unit molecule of HPO_4^{2-} adsorbed (ξ), is always less than two (Bowden et al. 1980). The negative charge added to the surface by adsorption of HPO_4^{2-} increases with the ionic strength of the background electrolyte (Atkinson et al. 1967; Hingston et al. 1972; Ryden and Syers 1975).

By using double-layer theory, Davies et al. (1978) explained that in electrolyte solutions, the surface charge is dominated by reactions of ionizable surface sites and electrolyte ions. Oxonium (R_3O^+)/hydronium (H_3O^+) ions and hydroxide (OH^-) ions are the principal determining ions. Bivalent cations often influence the surface charge (Breeuwsma and Lyklema 1973). Bolan et al. (1993) reported that the specific adsorption of calcium ions on oxide surfaces increases positive charge on the surface. They also observed that the formation of calcium surface groups can help in the specific adsorption of calcium ions by the release of hydronium ions (H_3O^+). Chakrabarty et al. (2010) observed in a cadmium adsorption study on chitosan that nitrogen and oxygen atoms were responsible for metal binding due to the presence of lone pair of electron in their atoms, which help in binding the positively charged ion via electron pair sharing. The easy release of a lone pair from the

nitrogen atom makes it the main binding site and forms stable metal complexes.

Surface area and pore volume of chitosan beads

The greater surface area of MoCB, SSPCB, and MCPCB compared to UCB could be ascribed to the intercalation of the chitosan structure by their respective anions (molybdate, phosphate, or hydrogen phosphate) (Kamari et al. 2009; Sapalidis et al. 2011). These anion-intercalates may have minimized close contact between adjacent chitosans. Low surface area of UCB was possibly due to the formation of extensive hydrogen bonds between chitosan structures.

Greater adsorption of Zn and Ni (Fig. 1) on modified chitosan beads may be attributed to high BET surface area of modified chitosan beads as contrasted with the pure chitosan beads, with the exception of Zn adsorption on MoCB. Slow adsorption rate after an initial rapid adsorption can be attributed to the intra-particle diffusion of solutes into the porous matrix of chitosan materials. When the external surface area of the particles is smaller than that of their pores, the adsorption capacity may be independent of particle size (Shen and Duvnjak 2005), because there is no big gain in the total surface area accessible to metal ions with a decrease in the size of its particles. For chitosan beads, which have comparatively smaller sorbent radius, particle size does not influence equilibrium, while for chitosan flakes, increasing sorbent radius results in decreased uptake of metals (Guibal et al. 1998). Wu et al. (2000) also reported high adsorption of heavy metals from fishery waste on chitosan beads, in contrast to chitosan flakes. The reason for greater adsorption was attributed to the high surface area of the chitosan beads.

Kinetic models

The pseudo first-order, pseudo second-order, Elovich equation, and intra-particle diffusion models are presented in Figs. 2 and 3, and the results of the parameters and correlation coefficients (R^2) are listed in Table 2.

Pseudo first- and second-order kinetics

The R^2 values suggested the adsorption of Zn on MoCB was well described by both pseudo first- (Fig. 2a) and second-order (Fig. 2b) kinetics, but Zn adsorption on UCB, MCPCB, and SSPCB did not fit well with pseudo

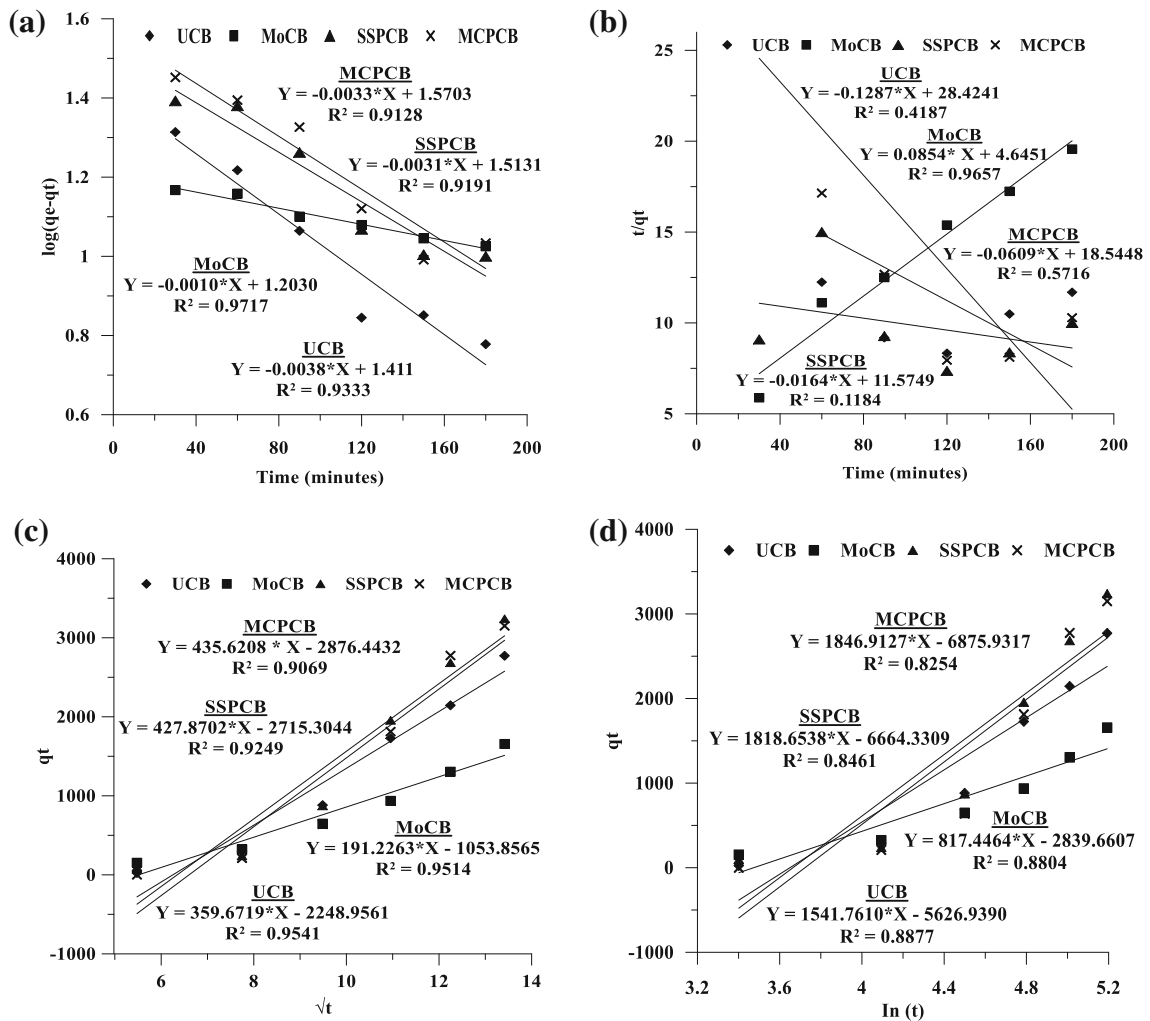


Fig. 2 Zinc adsorption data fitted with different kinetics models **a** pseudo first-order, **b** pseudo second-order, **c** diffusion model, and **d** Elovich equation. *Diamond* unmodified chitosan beads (UCB); *square* molybdenum-modified chitosan beads (MoCB); *triangle*

single superphosphate-modified chitosan beads (SSPCB); and *asterisk* monocalcium phosphate-modified chitosan beads (MCPCB)

first-order kinetics. The pseudo second-order kinetics equation has been used to explain adsorption of Zn on chitosan derivates (Li et al. 2007). The first-order kinetic process is mainly used for reversible reaction with an equilibrium being established between liquid and solid phases, albeit does not fit well to the initial stages of the adsorption process (Ding et al. 2006; Low et al. 2000).

As per the R^2 values, the kinetics of Ni adsorption on both modified and pure chitosan beads fitted well with pseudo second-order kinetics (Fig. 3a). The pseudo second-order kinetics equation (Fig. 3b) fitted best with the data on Ni adsorption on all types of chitosan

beads—both pure and modified, suggested that Ni adsorption on chitosan probably followed a chemisorption mechanism (Gerente et al. 2007; Vijaya et al. 2008).

Intra-particle diffusion model

Zinc adsorption on UCB and MoCB was observed to follow the intra-particle diffusion mechanism as described by its best fit in the Webber-Morris model ($R^2 = 0.95$ for both UCB and MoCB) (Fig. 2c). Zinc adsorption on SSPCB and MCPCB was also described adequately by intra-particle diffusion models ($R^2 = 0.93$

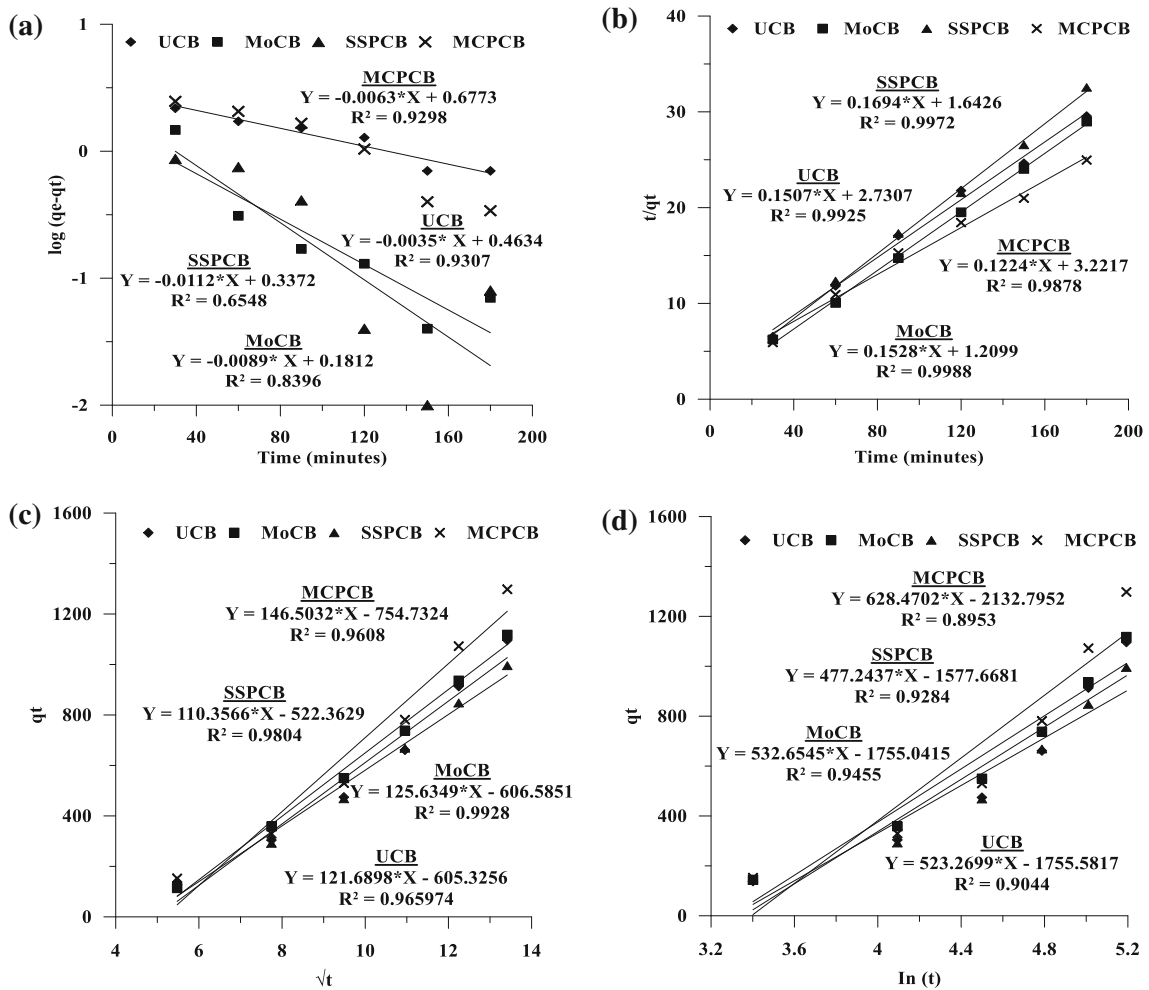


Fig. 3 Nickel adsorption data fitted with different kinetics models **a** pseudo first-order, **b** pseudo second-order, **c** intra-particle diffusion model, and **d** Elovich equation. *Diamond* unmodified chitosan beads (UCB); *Square* molybdenum-modified chitosan beads

(MoCB); *triangle* single superphosphate-modified chitosan beads (SSPCB); and *asterisk* monocalcium phosphate-modified chitosan beads (MCPCB)

Table 2 Comparison between kinetic models for Zn and Ni adsorption on different chitosan beads

Metal	Sorbent	Pseudo first-order			Pseudo second-order			Elovich equation			Intra-particle diffusion	
		R^2	K_1	q_e	R^2	K_2	q_e	R^2	α	β	R^2	k_i
Zinc	UCB	0.9334	25.79	0.0087	0.42	0.00057	7.82	0.89	40.1	0.00064	0.95	359.67
	MoCB	0.9717	15.96	0.0023	0.96	0.00063	11.71	0.88	25.34	0.00122	0.95	135.21
	SSPCB	0.9192	32.6	0.0071	0.12	0.00015	60.98	0.85	46.60	0.00055	0.92	427.87
	MCPCB	0.9129	37.19	0.0076	0.57	0.0002	16.42	0.82	44.63	0.00054	0.91	435.62
Nickel	UCB	0.9308	2.91	0.0081	0.99	0.0054	7.12	0.90	18.27	0.001911	0.97	121.69
	MoCB	0.8396	1.52	0.0205	0.99	0.0193	6.54	0.94	19.75	0.001877	0.99	125.63
	SSPCB	0.6549	2.17	0.0260	0.99	0.0175	5.9	0.93	17.5	0.002095	0.98	110.36
	MCPCB	0.9298	4.76	0.0145	0.99	0.00466	8.16	0.89	21.11	0.001591	0.96	146.5

and 0.91, respectively). It can be assumed that intra-particle diffusion is negligible, as Zn concentration at the sorbent surface tends to be zero during the initial stage, (McKay et al. 1986).

The kinetics of Ni adsorption on pure and all the modified chitosan beads was reasonably described by Webber-Morris equations (R^2 ranging from 0.90 to 0.95) (Fig. 3c), suggesting an intra-particle diffusion mechanism for Ni sorption onto chitosan beads. Guibal et al. (1998) observed intra-particle diffusion mechanism controlling the sorption kinetics of metals on chitosan beads. They proposed chitosan gel bead formation allowed an expansion of the polymer network that improved access to the internal sorption sites by reducing steric hindrance due to metal ions, enhancing diffusion.

This suggests Ni adsorption follows chemisorption mechanisms. Rudzinski and Plazinski (2009) suggested both pseudo second-order and Elovich equations were similar when certain conditions were fulfilled.

Zinc and Ni adsorption data fitted to different kinetics equations indicated no single mechanism operating and controlling the adsorption phenomenon and probably suggests several mechanisms are involved. This assumption is affirmed by Guibal et al. (1998) stating that no single controlling-mechanism can be applied to accurately describe the sorption mass transfer for chitosan flakes. No single equation best describes all the sorption studies and conformity of data to a particular equation does not necessarily indicate the equation to be the best one (Sparks 1989). Eddy and Odoemelam (2009) reported Zn adsorption on tiger nut shell followed the Webber-Morris model. It was observed that the adsorption plots of Zn and Ni did not show the stage corresponding to the diffusion of metallic ions through the external film, while these describe intra-particle diffusion mechanism as the rate-limiting step. These findings conform to the observation of Bhattacharyya and Sharma (2004); the plot of uptake vs. the square root of time should be linear when intra-particle diffusion is involved in the adsorption process and if these lines pass through the origin then intra-particle diffusion is the rate-controlling step. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control, suggesting other kinetic models control the rate of adsorption, all of which may be operating simultaneously (Ozcan et al. 2005). Several models operating simultaneously have also been observed in Cu(II) adsorption on chitosans (Ngah et al. 2008).

Elovich model

Zinc adsorption on pure and modified chitosan beads did not show a good fit with the Elovich kinetic model ($R^2 = 0.83$ to 0.89) (Fig. 2d). Similarly, Ni adsorption on all chitosan beads did not fit well with the Elovich model (Fig. 3d).

Conclusions

Modified chitosan beads had higher adsorption capacity for Zn and Ni, in contrast to pure chitosan, evincing their great potential for metal removal in a wide range of environmentally friendly applications. Modified chitosan beads showed improved physical characteristics in terms of their CEC, BET surface area and pore size, in contrast with pure chitosan bead, with MoCB the most promising. However, phosphate-impregnated chitosan beads (both SSPCB and MCPCB) adsorbed greater quantities of Zn than UCB and MoCB. Nickel adsorption was greatest on MCPCB followed by MoCB, UCB, and SSPCB.

Zn sorption on pure and modified chitosan beads mostly followed pseudo first-order and particle diffusion processes, except for Zn sorption on MoCB, which also displayed pseudo second-order kinetic modeling. However, among all kinetic models, the particle diffusion model best described Zn sorption on chitosan. Nickel sorption followed pseudo second-order, Elovich, and intra-particle diffusion models, with the pseudo second-order giving a better fit, followed by Elovich and intra-particle diffusion mechanisms.

These observations suggest that the adsorption of Zn and Ni on pure and modified chitosan beads follows chemical adsorption and intra-particle diffusion, but several other adsorption mechanisms may also occur simultaneously. However, the kinetic models can only attempt to theoretically describe the adsorption process, and are never confirmatory. Therefore, further study to confirm the mechanisms that explain metal adsorption on chitosan is recommended.

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References

- Abdou, E. S., Nagy, K. S. A., & Elsabee, M. Z. (2008). Extraction and characterization of chitin and chitosan from local sources. *Bioresource Technology*, *99*, 1359–1367.
- Aguiló, E., Mato, R., Tapia, C., Heras, A., Román, J.S., Argüelles, W., Goycoolea, F., Mayorga, A., Nakamatsu, J., Pastor A (2004) Quitina y Quitosano: Obtención, Caracterización y Aplicaciones, Pontificia Universidad Católica del Perú, Fondo Editorial, 244–245.
- Atkinson, R. J., Posner, A. M., & Quirk, J. P. (1967). Adsorption of potential determining ions at the ferric oxide aqueous electrolyte interface. *Journal of Physical Chemistry*, *71*, 550–558.
- Basak, A., Mandal, L. N., & Haldar, M. (1982). Interaction of phosphorus and molybdenum and the availability of zinc, copper, manganese, molybdenum and phosphorus in water-logged rice soil. *Plant and Soil*, *68*, 271–278.
- Benavente, M. (2008). Adsorption of Metallic Ions onto Chitosan: Equilibrium and Kinetic Studies. Licentiate Thesis. TRITA CHE Report 2008:44. ISBN 978–91–7178–986–0. Link: www.diva-portal.org/smash/get/diva2:13755/FULLTEXT01.pdf; Accessed on 1st August 2016.
- Bhattacharyya, K. G., & Sharma, A. (2004). *Azadirachta indica* leaf powder as an effective biosorbent for dyes: a case study with aqueous Congo red solutions. *Journal of Environmental Management*, *71*, 217–229.
- Bolan, N. S., Syers, J. K., & Sumner, M. E. (1993). Calcium-induced sulphate adsorption by soils. *Soil Science Society of America Proceedings*, *57*, 691–696.
- Bowden, J. W., Nagarajah, S., Barrow, N. J., Posner, A. M., & Quirk, J. P. (1980). Describing the adsorption of phosphate, citrate and selenite on a variable charge mineral surface. *Australian Journal of Soil Research*, *18*, 49–60.
- Breuwisma, A., & Lyklema, J. (1973). Physical and chemical adsorption of ions in the electrical double layer on hematite ($\alpha\text{-Fe}_2\text{O}_3$). *Journal of Colloid Interface Science*, *43*, 437–442.
- Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, *60*, 309–319.
- Burke, A., Yilmaz, E., & Hasirci, N. (2002). Iron (III) ion removal from solution through adsorption on chitosan. *Journal of Applied Polymer Science*, *84*, 1185–1192.
- Chakrabarty, T., Kumar, M. & Shahi, V. K. (2010). Chitosan based membranes for separation, pervaporation and fuel cell applications: Recent Developments. Biopolymers, Magdy Elnashar (Ed.), ISBN: 978-953-307-109-1, InTech, Available from: <http://www.intechopen.com/books/biopolymers/chitosan-based-membranes->; Accessed on 25th July 2016.
- Chen, C., Li, X., Zhao, D., Tan, X., & Wang, X. (2007). Adsorption kinetic, thermodynamic and desorption studies of Th(IV) on oxidized multi-wall carbon nanotubes. *Colloids and surfaces a: physicochemical and engineering aspects*, *302*, 449–454.
- Chen, A. H., Yang, C. Y., Chen, C. Y., & Chen, C. W. (2009). The chemically crosslinked metal-complexed chitosans for comparative adsorptions of Cu(II), Zn(II), Ni(II) and Pb(II) ions in aqueous medium. *Journal of Hazardous Materials*, *163*, 1068.
- Chien, S. H., & Clayton, W. R. (1980). Application of Elovich equation to the kinetics of phosphate release and sorption in soils. *Soil Science Society of America Journal*, *44*, 265–268.
- Chu, K. H. (2002). Removal of copper from aqueous solution by chitosan in prawn shell: adsorption equilibrium and kinetics. *Journal of Hazardous Materials*, *90*, 77–95.
- Dambies, L., Vincent, T., Domard, A., & Guibal, E. (2001). Preparation of chitosan gel beads by ionotropic molybdate gelation. *Biomacromolecules*, *2*, 1198–1205.
- Davies, J. A., James, R. O., & Leckie, J. O. (1978). Surface ionization and complexation at the oxide/water interface. *Journal of Colloid Interface Science*, *63*, 480–499.
- Denkhaus, E., & Salnikow, K. (2002). Nickel essentiality, toxicity, and carcinogenicity. *Critical Reviews in Oncology/Hematology*, *42*, 35–56.
- Dhokal, R. P., Ghimire, K. N., & Inoue, K. (2005). Adsorptive separation of heavy metal from an aquatic environment using orange waste. *Hydrometallurgy*, *79*, 182–190.
- Ding, P., Huang, K. L., Li, G. Y., Liu, Y. F., & Zeng, W. W. (2006). Kinetics of adsorption of Zn(II) ion on chitosan derivatives. *International Journal of Biological Macromolecules*, *39*, 222.
- Duarte, A. R. C., Mano, J. F., & Reis, R. J. (2010). Novel 3D scaffolds of chitosan–PLLA blends for tissue engineering applications: preparation and characterization. *The Journal of Supercritical Fluids*, *54*, 282–289.
- Eddy, N. O., & Odoemelam, S. A. (2009). Modelling of the adsorption of Zn^{2+} from aqueous solution by modified and pure tiger nut shell. *African Journal of Pure and Applied Chemistry*, *3*, 145–151.
- Fu, J., Ji, J., Fan, D. & Shen, J. (2006). Construction of antibacterial multilayer films containing nanosilver via layer-by-layer assembly of heparin and chitosan-silver ions complex. *Journal of Biomedical Materials Research, Part A* DOI 10.1002/jbm.a. Wiley Inter Science (www.interscience.wiley.com). DOI: 10.1002/jbm.a.30819.
- Gang, S., & Weixing, S. (1998). Sunflower stalk as adsorbents for the removal of metal ions from waste water. *Industrial & Engineering Chemistry Research*, *37*, 1324–1328.
- Gerente, C., Lee, V. K. C., Cloirec, P. L., & McKay, G. (2007). Application of chitosan for the removal of metals from wastewaters by adsorption—mechanisms and models review. *Critical Reviews in Environmental Science & Technology*, *37*, 41–127.
- Ghosh, M. M., & Yuan, J. R. (1987). Adsorption of inorganic arsenic and organo-arsenicals on hydrous oxide. *Environmental Progress*, *6*, 150–156.
- Gillman, G. P., & Sumpter, E. A. (1986). Modification to the compulsive exchange method for measuring exchange characteristics of soils. *Australian Journal of Soil Research*, *24*, 61–66. doi:10.1071/SR9860061.
- Guibal, E., Milot, C., & Tobin, J. M. (1998). Metal-anion sorption by chitosan beads: equilibrium and kinetic studies. *Industrial & Engineering Chemistry*, *37*, 1454–1463.
- Hastuti, B., Masykur, A. and Hadi, S. (2016). Modification of chitosan by swelling and crosslinking using epichlorohydrin as heavy metal Cr (VI) adsorbent in batik industry wastes. IOP Conf. Series: Materials Science and Engineering 107 (2016) 012020 doi:10.1088/1757-899X/107/1/012020. Available at <http://iopscience.iop.org/article/10.1088/1757-899X/107/1/012020/pdf> (accessed on 7th July 2016).
- Hingston, F.J. (1970). Specific adsorption of anions on goethite and gibbsite. Ph.D. Thesis, Univ. Western Australia.

- Hingston, F. J., Posner, A. M., & Quirk, J. P. (1972). Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. *Journal of Soil Science*, 23, 177–192.
- Ho, Y. S., McKay, G., Wase, D. A. J., & Forster, C. F. (2000). Study of the sorption of divalent metal ions onto peat. *Adsorption Science Technology*, 18, 639–650.
- Igwe, J. C., Abia, A. A., & Ibeh, C. A. (2008). Adsorption kinetics and intra-particulate diffusivities of Hg, As and Pb ions on unmodified and thiolated coconut fiber. *International Journal of Environmental Science and Technology*, 5, 83–92.
- Ikhsan, J., Wells, J. D., Johnson, B. B., & Angove, M. J. (2005). Surface complexation modeling of the sorption of Zn(II) by montmorillonite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 252, 33–41.
- Jeon, C., & Höll, H. (2003). Chemical modification of chitosan and equilibrium study for mercury ion removal. *Water Research*, 37, 4770–4780.
- Kamari, A., Wan Ngah, W. S., & Liew, L. K. (2009). Chitosan and chemically modified chitosan beads for acid dyes sorption. *Journal of Environmental Sciences*, 21, 296–302.
- Kraepiel, A. M. L., Kellers, K., & Morel, F. M. M. (1999). A model for metal adsorption on montmorillonite. *Journal of Colloid Interface Science*, 210, 43–54.
- Kumar, D., Singh, R. R., Singh, S. P., Jha, S., & Srivastava, P. (2011). Selection of suitable extractant for predicting the response of chickpea to zinc application in vertisols. *Communications in Soil Science and Plant Analysis*, 42, 728–740.
- Lagergren, S. (1898). About the theory of so-called adsorption of soluble substances. *Kungliga Suensk Vetenskapsakademiens Handlingar*, 241, 1–39.
- Lambert, R., Grant, C. & Sauv e, S. (2007). Cadmium and zinc in soil solution extracts following the application of phosphate fertilizers. *Science of the Total Environment*, 378, 293–305.
- Li, Q., Zhai, J. P., Zhang, W. Y., Wang, M. M., & Zhou, J. (2007). Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk. *Journal of Hazardous Materials*, 141, 163–167.
- Low, K. S., Lee, C. K., & Liew, S. C. (2000). Sorption of cadmium and lead from aqueous solutions by spent grain. *Process Biochemistry*, 36, 59–64.
- Martin, J. M., Grossiord, C., Mogne, T. L., & Igarashi, J. (2000). Transfer films and friction under boundary lubrication. *Wear*, 245, 107–115.
- McKay, G., Blair, H. S., Findon, A. (1986). Sorption of metal ions by chitosan. In: H. Eccles, S. Hunt ZEds., Immobilization of ions by bio-sorption. Ellis Horwood, Chichester, UK 59–69
- Monteiro Jr., O. A. C., & Airoidi, C. (1999). Some thermodynamic data on copper–chitin and copper–chitosan biopolymer interactions. *Journal of Colloid Interface Science*, 212, 212–219.
- Naidu, R., Syers, J. K., Tillman, R. W., & Kirkman, J. H. (1990). Effect of liming on phosphate sorption by acid soils. *Journal of Soil Science*, 41, 165–175.
- Ngah, W. S., Kamari, A., & Koay, Y. J. (2004). Equilibrium kinetics studies of adsorption of copper (II) on chitosan and chitosan/PVA beads. *International Journal of Biological Macromolecules*, 34, 155–161.
- Ngah, W. S., Wan, T. L. C., & Fatinathan, S. (2008). Adsorption of Cu(II) ions in aqueous solution using chitosan beads, chitosan–GLA beads and chitosan–alginate beads. *Chemical Engineering Journal*, 143, 62–72.
- Ngah, W. S., Wan, T. L. C., & Hanafiah, M. A. K. M. (2011). Adsorption of dyes and heavy metal ions by chitosan composites: a review. *Carbohydrate Polymers*, 83, 1446–1456.
- Nriagu, J. (2007). Zinc toxicity in humans. Encyclopedia of environmental health, Elsevier: Michigan, USA, pp.801–807.
- Onsoyen, E., & Skaugrud, O. (1990). Metal recovery using chitosan. *Journal of Chemical Technology*, 49, 395–404.
- Ozcan, A., Ozcan, A. S., Tunali, S., Akar, T., & Khan, I. (2005). Determination of the equilibrium, kinetic and thermodynamic parameters of adsorption of copper(II) ions onto seeds of capsicum annum. *Journal of Hazardous Materials*, 124, 200–208.
- Popuri, S. R., Vijayaa, Y., Boddu, V. M., & Abburi, K. (2009). Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads. *Bioresource Technology*, 100, 194–199.
- Rezaei, R. M., Esfandbod, M., Adhami, E., & Srivastava, P. (2014). Cadmium desorption behavior in selected subtropical soils: effects of soil properties. *Journal of Geochemical Exploration*, 144, 230–236.
- Ravi Kumar, M. N. V. (2000). A review of chitin and chitosan applications. *Reactive and Functional Polymers*, 46, 1–27.
- Rinaudo, M. (2006). Chitin and Chitosan: Properties and Applications. *Progress in Polymer Science*, 31, 603–632.
- Rodriguez, J. A., & Kuhn, M. (1995). Co-adsorption of Zn and S on Mo(110): weakening of the Zn & Mo bond and Zn-promoted sulfidation of Mo. *Surface Science*, 336, 1–12.
- Rout, G. R., & Das, P. (2003). Effect of metal toxicity on plant growth and metabolism: I. Zinc. *Agronomie*, 23, 3–11.
- Rudzinski, W., & Plazinski, W. (2009). On the applicability of the pseudo-second order equation to represent the kinetics of adsorption at solid/solution interfaces: a theoretical analysis based on the statistical rate theory. *Adsorption*, 15, 181.
- Ryden, J. C., & Syers, J. K. (1975). Charge relationships of phosphate sorption. *Nature*, 255, 51–53.
- Sapalidis, A.A., Katsaros, F.K., Kanellopoulos, N.K. (2011). PVA/montmorillonite nanocomposites: development and properties. Nanocomposites and polymers with analytical methods. John Cuppoletti (Ed), ISBN 978–953–307–352-1, 404 pages, Publisher: InTech (http://cdn.intechopen.com/pdfs/17185/InTech-Pva_montmorillonite_nanocomposites_development_and_properties.pdf)
- Selim, H. M. (2012). Competitive Sorption and Transport of Trace Elements in Soils and Geological Media. CRC/Taylor and Francis, Boca Raton, FL (425 p).
- Shahidi, F., Arachchi, J. K. V., & Jeon, Y. J. (1999). Food applications of chitin and chitosans. *Trends in Food Science & Technology*, 10, 37–51.
- Shen, J., & Duvnjak, Z. (2005). Adsorption kinetics of cupric and cadmium ions on corn cob particles. *Process Biochemistry*, 40, 3446–3454.
- Sheoran, A. S., & Sheoran, V. (2006). Heavy metal removal mechanism of acid mine drainage in wetlands: a critical review. *Minerals Engineering*, 19, 105–116.
- Sparks, D. L. (1986). *Kinetics of reaction in pure and mixed systems in soil physical chemistry*. Boca Raton: CRC Press.
- Sparks, D. L. (1989). *Kinetics of soil chemical processes*. San Diego: Academic Press.
- Sparks, D. L. (1990). Kinetics of soil chemical processes: an overview. *Trans. Int. Congress of Soil Science*, 2, 4–9.

- Srivastava, P., Singh, B., & Angove, M. (2005). Competitive adsorption behavior of heavy metals on kaolinite. *Journal of Colloid and Interface Science*, 290, 28–38.
- Srivastava, P. C., & Srivastava, P. (2008). Integration of soil pH with soil-test values of zinc for prediction of yield response in rice grown in mollisols. *Communications in Soil Science and Plant Analysis*, 39, 2456–2468.
- Srivastava, P. C., Naresh, M., & Srivastava, P. (2008). Appraisal of some soil tests for zinc availability to late-sown wheat grown in mollisols. *Communications in Soil Science and Plant Analysis*, 39, 440–449.
- Srivastava, S. K., Tyagi, R., & Pant, N. (1989). Adsorption of heavy metals on carbonaceous material developed from the waste slurry generated in local fertilizer plants. *Water Research*, 23, 1161–1165.
- Stathi, P., Papadas, I. T., Tselepidou, A., & Deligiannakis, Y. (2010). Heavy metal uptake by a high cation-exchange capacity montmorillonite: the role of permanent charge sites. *Global NEST Journal*, 12, 248–255.
- Trgo, M., Peric, J., & Vukojević, M. N. (2006). A comparative study of ion exchange kinetics in zinc/lead-modified zeolite-clinoptilolite systems. *Journal of Hazardous Materials*, 136, 938–945.
- Varma, A. J., Deshpande, S. V., & Kennedy, J. F. (2004). Metal complexation by chitosan and its derivatives: a review. *Carbohydrate Polymers*, 55, 77–93.
- Vijaya, Y., Srinivasa, R. P., Veera, M. B., & Krishnaiah, A. (2008). Modified chitosan and calcium alginate biopolymer sorbents for removal of nickel (II) through adsorption. *Carbohydrate Polymers*, 72, 261–271.
- Wang, J., & Chen, C. (2009). Biosorbents for heavy metals removal and their future. *Biotechnology Advances*, 27, 195–226.
- Weber, W. J., & Morris, J. C. (1963). Kinetics of adsorption on carbon from solution. *Journal of Sanitation Engineering Division of American Society of Civil Engineering*, 89, 31–60.
- White, R.E. (1980). Retention and release of phosphate by soil and soil constituents. In: *Soils and Agriculture* (P. B. Tinker, Ed.). Critical Reports on Applied Chemistry Volume 2. Soc. Chem. Ind. Oxford. Blackwell Scientific Publications, 71–114.
- Wu, F. C., Tseng, R. L., & Juang, R. X. (2000). Comparative adsorption of metal and dye on flake- and bead-types of chitosans prepared from fishery wastes. *Journal of Hazardous Materials*, 73, 63–75.
- Zhao, K., & Selim, H. M. (2010). Adsorption-desorption kinetics of Zn in soils: influence of phosphate. *Soil Science*, 175, 145–153.