### Heliyon 6 (2020) e03684

Contents lists available at ScienceDirect

### Heliyon

journal homepage: www.cell.com/heliyon

**Research article** 

**Cell**Press

# Adsorptive removal of Co(II) in aqueous solutions using clearing nut seed powder

Check for

Kavitha H. Ranaweera<sup>a</sup>, Pahan I. Godakumbura<sup>a</sup>, B. Asiri Perera<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka

#### ARTICLE INFO

Keywords: Analytical chemistry Inorganic chemistry Adsorption Isotherms Kinetics Clearing nut seed powder Cobalt (II)

### ABSTRACT

The present study assessed the potential use of clearing nut seed powder (*Strychnos potatorum*) as an adsorbent for the removal of Co(II) ions from aqueous solutions. Based on FTIR analysis, the adsorbent possesses hydroxyl, C-N, and C-O functional groups and SEM analysis indicated the presence of uneven porous surface structure, which is important for adsorption. Batch adsorption studies were performed to investigate the effect of contact time, initial pH, initial Co(II) concentration, adsorbent dosage, and temperature on adsorption. The Langmuir isotherm model provided the best explanation to experimental data with the highest correlation coefficient and the maximum monolayer adsorption capacity obtained was 4.245 mg/g. The pseudo-second-order kinetic model fitted well with the adsorption kinetic data. Sorption thermodynamic data showed that the adsorption process is spontaneous and exothermic in nature. The clearing nut seed powder obtained after surface modification by acid treatment showed a higher adsorption capacity.

### 1. Introduction

It is common knowledge that rapid industrialization has accelerated the release of toxic heavy metals to natural water bodies. As a result, contamination of water by toxic heavy metals has become a worldwide environmental problem [1]. Cobalt containing compounds are widely used in hard metal, electroplating, paint, pigment and electronic industries [2, 3, 4]. High levels of cobalt in water have been reported from several countries including Bangladesh [5] and Nigeria [6] increasing the risk of exposing to high cobalt levels. With Cobalt exposure health problems such as diarrhea, paralysis, low blood pressure, lung irradiation and bone defects may arise [7].

Many treatment methods are employed for the removal of heavy metals including electrocoagulation [8], membrane filtration [9], chemical precipitation [10], coagulation-flocculation [11], ion exchange [12] and electrodialytic method [13]. As adsorption is a simple, cleaner, rapid and cheap method, it is considered as one of the most effective pollution control technology for the removal of heavy metal ions from aquatic systems [14, 15].

Studies have been carried out to remove Co(II) ions from aqueous solutions utilizing adsorbents including Saudi activated bentonite [2], Cross-Linked Calcium Alginate Beads [16], banana peels [17], mont-morillonite [18] and Kaolinite [19].

Clearing nut is a member of the kingdom Plantae belonging to the order of Gentianales of the Loganiaceae family. This plant species is found in India, Burma, and Sri Lanka and it is commonly known as "Igini" in Sri Lanka [20]. The seeds of this plant are quite popular among the rural community as a natural water purifier and these seeds are widely used in Ayurvedic and traditional medicine as well [21]. Clearing nut seeds have the ability to remove turbidity from aqueous solutions due to the presence of polyelectrolytes, proteins, lipids, carbohydrates, and alkaloids [22]. Recently studies have been done to investigate the capacity of this seed powder to bind metal ions [14, 23]. However, the potential of clearing nut seed powder for the removal of Co(II) ions has not yet been investigated.

Herein, we explore the potential of clearing nut seed powder for the removal of Co(II) ions from aqueous solutions, the isotherms, thermodynamics and kinetics of the adsorption process, and the influence of biomass, pH, initial metal concentration, contact time and temperature in Co(II) ions adsorption.

### 2. Materials and methods

### 2.1. Preparation of clearing nut seed powder

The clearing nut seeds (*Strychnos potatorum*) were collected from the Embilipitiya district, Sri Lanka and washed with distilled water to

E-mail address: basirip@sjp.ac.lk (B.A. Perera).

https://doi.org/10.1016/j.heliyon.2020.e03684

Received 5 November 2019; Received in revised form 2 March 2020; Accepted 24 March 2020



<sup>\*</sup> Corresponding author.

<sup>2405-8440/© 2020</sup> Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

remove dust particles and impurities. After drying the wet plant material under the sunlight, it was ground to reduce the particle size and sieved to obtain 250–500  $\mu$ m size fraction (average particle size 375  $\mu$ m) [24]. The obtained clearing nut seed powder (CNSP) was stored in sealed plastic bags to avoid the effects of moisture. It is important to keep the sample away from moisture to prevent the errors that may occur during weighing a constant amount of adsorbent material for batch adsorption studies.

### 2.2. Preparation of Co(II) solutions

The 500 ppm Co(II) stock solutions were prepared in 500.00 cm<sup>3</sup> volumetric flask by dissolving 1.247 g of  $Co(NO_3)_2.6H_2O$  in distilled water and the stock solutions were diluted to prepare the desired concentrations. The aqueous phase pH was adjusted using 0.1 M HCl and 0.1 M NaOH solutions.

### 2.3. Characterization studies

IR spectrum of CNSP was obtained using Thermo Fisher SCIENTIFIC NICOLET iSIO IR spectrometer with spectral range 4000–400 cm<sup>-1</sup> and the SEM analysis was carried out with ZEISS EVO LS 15 microscope with an acceleration voltage of 10.00 kV to observe the surface morphology of the CNSP before and after interaction with metal ions. Before examination, the samples were coated with gold to prevent charge buildup on the samples. The surface area and the average pore radius of CNSP were determined using automated gas sorption analyser according to the BET multipoint technique (Model: Anton Parr Quanta Tech (AUTOSORB IQ-MP (1 STAT) VITON).

The residual metal ion concentrations were analysed with Flame Atomic Absorption Spectrophotometer (FAAS) Thermo scientific iCE 3000 series. Thermo Scientific SOLAAR software allowed quick and easy optimization of the method.

The standard solutions were prepared by diluting the standard 1000 ppm Co(II) stock solution. The instrument was calibrated within the linear range of analysis and a correlation coefficient ( $R^2$ ) of 0.99–1.000 was obtained for the calibration curve.

### 2.4. Batch adsorption tests

The effect of adsorbent dose, initial metal ion concentration, temperature, contact time and pH on adsorption of Co(II) ions on to CNSP was determined by conducting batch adsorption studies. These experiments were carried out in 250 ml stoppered conical flasks by adding the required quantity of CNSP in 100 ml of the adsorbate of the desired concentration and desired solution pH. The samples were equilibrated by shaking at 200 strokes per minute in a temperature-controlled shaker. Then at a pre-determined time, 20 ml of metal solution was pipetted out, centrifuged for 10 min and the supernatant was collected into clean sample bottles. The Air-acetylene flame of the atomic absorption spectrophotometer was used to analyse the remaining residual metal ion concentration. Eq. (1) was used to express the results as % removal.

$$\% \text{ removal} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \tag{1}$$

where  $C_o$  and  $C_t$  are the initial and final metal ion concentrations in ppm. The amount of metal ions adsorbed by the adsorbent was calculated using Eq. (2).

$$q = \left[\frac{(C_0 - C_e)V}{W}\right]$$
(2)

where q is the adsorption capacity (mg g<sup>-1</sup>),  $C_e$  is the equilibrium concentration of the metal ions in ppm, V is the volume of metal ions in the solution in dm<sup>3</sup> and W is the mass of adsorbent added in grams.

A blank analysis was conducted to measure the adsorption of Co(II) on walls of glass stoppered conical flasks. For the blank analysis, 100 ml of the 20 ppm metal ion solution and all other reagents used in adsorption study were added except CNSP. This was agitated for 180 min at 30  $^{\circ}$ C with the shaking speed of 200 strokes per minute and the concentration of the solution was analysed by using atomic absorption spectrophotometer.

### 2.5. Comparison of surface modified clearing nut seed powder with the surface unmodified clearing nut seed power

The seeds were washed with distilled water to remove the dust particles, dried under the sunlight and made into powder. The obtained powdered material was treated in a 2:1 ratio (acid: seed powder) with concentrated sulphuric acid for about 24 h. Then the excess acid present in the system was removed by washing the material with distilled water until the pH of the supernatant reaches the pH value of 7. The wet solid material was dried at 105 °C for 3 h. The dried material was grounded, sieved to obtain a 250–500  $\mu$ m size fractions and stored in sealed plastic bags [23, 25].

### 3. Results and discussion

### 3.1. Characterization

The responsible functional groups for the metal ion adsorption can be identified performing FTIR spectral analysis.

According to Figure 1, the broad and strong band observed around 3339 cm<sup>-1</sup> can be assigned to O-H stretching vibration. The peaks observed around 2930 cm<sup>-1</sup> can be attributed to C-H stretching vibration by alkyl groups. The peak at 1634 cm<sup>-1</sup> occurs due to the bending vibration mode of water. The presence of C-N stretching vibration is indicated by the peak around 1121 cm<sup>-1</sup>. CH<sub>2</sub> bending vibration is indicated by the peaks around 1344 cm<sup>-1</sup>. The presence of C-O-C stretching vibrations and C-O stretching vibrations of alcohol indicated by the peak at 1033.54 cm<sup>-1</sup> [26].

Figure 2 shows the changes in FTIR spectra before and after the metal ion binding process into CNSP. It can be observed that there is a reduction in peak intensities after metal ion binding process. This peak intensity reductions are especially visible around 3340 cm<sup>-1</sup>, 1121 cm<sup>-1</sup> and 1033 cm<sup>-1</sup> which suggest the participation hydroxyl, C-N and C-O functional groups in the adsorption of Co(II) ions by the adsorbent [27].

The SEM analysis was performed to observe the surface morphology of CNSP before and after adsorption of metal ions and the representative images are shown in Figure 3 (a, b) and Figure 3 (c, d) respectively.



Figure 1. FTIR spectrum of clearing nut seed powder at 30 °C.



Figure 2. FTIR spectrum of (a) clearing nut seed powder before adsorption (b) after adsorption at 30 °C.

According to Figure 3 (c, d), the surface morphology of the adsorbent has changed after the interaction with Co(II) ions. Figure 3 (a, b) show that CNSP possesses irregular and porous surface structure. This structure reveals the possibility of metal ions penetration into these pores which leads to enhancement of adsorption [28]. The porosity of the seed powder surface has been greatly reduced after adsorption of Co(II) ions









which may have occurred due to the bond formation with the functional groups present on the adsorbent. Based on the results, it can be suggested that adsorbent morphology favours metal ion adsorption.

The surface area of the CNSP is 10.214  $m^2/g$  and the average pore radius is 1.53353e+00 nm.

### 3.2. Effect of contact time and adsorption kinetics studies

The adsorption of Co(II) ions onto the surface of glass conical flasks is negligible according to the blank analysis.

The impact of agitation period on the Co(II) ions adsorption process is shown in Figure 4. As can be seen, the adsorption process occurs quite rapidly at initial stages. Thereafter percentage removal values tend to increase at a very slow rate finally reaching equilibrium around 120 min of contact time.

When consider the general trend of adsorption, at the initial stages the adsorption process occurs rapidly due to the abundant availability of accessible binding sites on the surface of the adsorbent [29, 30]. With time, due to the generation of repulsive forces between the metal ions on the adsorbent and aqueous solution, it becomes difficult to occupy the remaining vacant sites on the adsorbent leading system to equilibrium [31].

The rate and the rate of controlling step of the Co(II) ions adsorption process on to the CNSP can be explained with the aid of the kinetic models. The pseudo-first-order model [32], pseudo-second-order model [33], intraparticle diffusion model [34], and liquid film diffusion model [35] are widely used to investigate the adsorption mechanism and











**Figure 4.** The effect of contact time on adsorption of Co(II) into surface unmodified clearing nut seed powder at various initial Co(II) concentrations, 30 °C, adsorbent dosage 0.300 g/100 ml and particle size  $250-500 \mu m$ . The error bars represent the standard deviation for three separate sample runs.

behavior. The pseudo-first-order model and pseudo-second-order model are given by Equation 3 and Equation 4 respectively.

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$
 (4)

where  $k_1$  (min<sup>-1</sup>) is the equilibrium rate constant of pseudo-first-order adsorption,  $k_2$  is the rate constant for pseudo-second-order adsorption (g mg<sup>-1</sup> min<sup>-1</sup>),  $q_t$  denotes the amount of solute adsorbed onto adsorbent surface at time *t* (mg g<sup>-1</sup>),  $q_e$  is the amount adsorbed onto adsorbent surface at equilibrium (mg g<sup>-1</sup>) and *t* is the time (min).

The liquid film diffusion model (Equation 5) and the intraparticle diffusion model (Equation 6) can be used to further evaluate the rate-controlling step.

$$ln(1-F) = -k_{fd}t \tag{5}$$

$$q_t = k_{id} t^{\frac{1}{2}} + C \tag{6}$$

where *F* is the fractional attainment of equilibrium  $(q_t/q_e)$ ,  $k_{fd}$  is the film diffusion adsorption rate constant (min<sup>-1</sup>), *C* is the intercept of the intraparticle diffusion model (mg g<sup>-1</sup>) related to the mass transfer across the boundary layer and  $k_{id}$  is the intraparticle diffusion rate constant (mg g<sup>-1</sup> min<sup>-1/2</sup>).

Effect of agitation period data was fitted to the pseudo-first-order model, pseudo-second-order model, intraparticle diffusion model, and liquid film diffusion model to study the adsorption kinetics. The obtained results are summarized in Table 1 and Table 2.

According to the results, the-pseudo-second-order model has given correlation coefficient  $(R^2)$  values almost equal to unity and a better

consistence can be observed between the calculated equilibrium adsorption capacity values and experimental adsorption capacity values when compared to the other kinetic models. This model is based on the assumption that chemisorption is the rate-limiting step [36]. It is applicable to predict the behavior over a whole range of adsorption and use to describe the chemisorption involving valency forces through the sharing or exchange of electrons between the adsorbent and adsorbate as covalent forces and ion exchange [37]. Therefore it can be suggested, the adsorption of Co(II) ions on to the CNSP obeys the pseudo-second-order model suggesting rate-limiting step could be chemisorption. The generated kinetics curves are given in Figure 5.

### 3.3. Effect of initial metal ion concentration and adsorption isothermal studies

The influence of initial metal ion concentration on the removal of metal ions was investigated in the range of 10 ppm–60 ppm and the acquired results are given in Figure 6. An increasing trend was observed in the percentage removal with the increment of adsorbate concentration as a limited number of Co(II) ions compete for the available active sites present on CNSP reaching the maximum removal at around 20 ppm. Further enhancement of initial metal ion concentration resulted in a reduction of percentage removal. The ratio of metal ions to active sites was high at higher metal ion concentrations hence the percentage removal was observed to decrease with increasing metal ion concentration and also the repulsive forces among adsorbate molecules increase the dispersion, minimizing the adsorption in to the interior surface of the adsorbent leading to low percentage removal values [14, 38].

The isotherm models explain the distribution of Co(II) ions between the CNSP (solid phase) and the liquid phase at a constant temperature (30 °C) at equilibrium. In the present study, the batch adsorption data obtained from the effect of initial metal ion concentration was fitted to Langmuir [39], Freundlich [40], and Dubinin-Radushkevich (D-R) models [41] which are represented by Eqs. (7), (8), and (9) respectively and the results are summarized in Table 3.

$$\frac{C_e}{q_e} = \frac{1}{bX_m} + \frac{C_e}{X_m}$$
(7)

$$qe = K C e^{\frac{1}{n}}$$
(8)

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{9}$$

where  $q_e$  denotes the amount of solute adsorbed per unit mass of adsorbent at equilibrium (mg g<sup>-1</sup>),  $X_m$  is the amount of solute required to form a complete monolayer (mg g<sup>-1</sup>),  $C_e$  is the residual liquid phase concentration at equilibrium (mg dm<sup>-3</sup>) and b is the adsorption coefficient or Langmuir constant, 1/n and K are Freundlich constants,  $q_m$  is the theoretical isotherm saturation capacity (mg g<sup>-1</sup>),  $\beta$  is a constant related to the mean free energy of adsorption (mol<sup>2</sup> J<sup>-2</sup>).

The D-R constant, is given by;

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{10}$$

Concentration (mg dm <sup>-3</sup> )	Pseudo first order			Pseudo second order			Experimental qe (mg g <sup>-1</sup> )
	$K_1$ (min <sup>-1</sup> )	Qe (mg $g^{-1}$ )	$\mathbb{R}^2$	$K_2 (g mg^{-1} min^{-1})$	Qe (mg $g^{-1}$ )	R <sup>2</sup>	
20.00	-0.016	0.508	0.5346	0.171	1.866	0.9987	1.862
30.00	-0.059	1.387	0.8365	0.152	2.522	0.9999	2.477
40.00	-0.018	0.720	0.5999	0.130	2.707	0.9992	2.724
60.00	-0.044	1.323	0.4195	0.116	3.299	0.9998	3.250

Table 1. Kinetic model parameters for adsorption of Co(II) into clearing nut seed powder at 30 °C for pseudo-first- order and pseudo-second-order models.

Concentration (mg dm <sup>-3</sup> )	g dm <sup>-3</sup> ) Intra-particle diffusion model		Liquid film diffusion model	
	$K_{id} (mg g^{-1} min^{-1/2})$	R <sup>2</sup>	$K_{\rm fd} ({\rm min}^{-1})$	R <sup>2</sup>
20.00	0.012	0.6549	0.016	0.5350
30.00	0.032	0.7712	0.059	0.8362
40.00	0.027	0.7557	0.018	0.6000
60.00	0.036	0.7181	0.044	0.4194



**Figure 5.** Pseudo-second order plot for Co(II) adsorption by clearing nut seed powder at 30  $^{\circ}$ C, dosage 0.300 g/100 ml and particle size 250–500  $\mu$ m. The error bars represent the standard deviation for three separate sample runs.



**Figure 6.** The effect of initial metal ion concentration on adsorption of Co(II) into clearing nut seed powder at 30 °C, adsorbent dosage 0.300 g/100 ml and particle size 250–500  $\mu$ m for 180 min contact time. The error bars represent the standard deviation for three separate sample runs.

where *R* is the universal gas constant (J  $K^{-1}$  mol<sup>-1</sup>) and *T* is the absolute temperature (K) at equilibrium.

Based on the results, the best explanation to experimental data was provided by the Langmuir adsorption isotherm model within the considered concentration range with a correlation coefficient ( $R^2$ ) of 0.9944 (Figure 7). The calculated maximum adsorption capacity for the adsorption was 4.245 mg g<sup>-1</sup> and the calculated Langmuir constant was 0.060 dm<sup>3</sup> mg<sup>-1</sup> at 30 °C. This model is based on the assumption that metal ions adsorb onto localized active sites, no interaction between adsorbed molecules and the adsorption sites present on the adsorbent are energetically equivalent having the same affinity for adsorption of a layer of single molecules [42].

However, the formation of a multilayer on the CNSP also seems to be possible as the adsorption data fitted well with the Freundlich isotherm model as well. According to the results, the adsorption process is more likely to undergo monolayer formation along with multilayer coverage.

### 3.4. Effect of temperature and sorption thermodynamics

The effect of temperature on adsorption of Co(II) ions on to CNSP was investigated at 30, 40, 50 and 60 °C as shown in Figure 8. As can be seen, the percentage removal values tend to decrease as the temperature increases from 30 °C to 60 °C indicating that the adsorption process is indicates the particular reaction is spontaneous exothermic. The bonds



Figure 7. Langmuir isotherm plot for Co(II) adsorption by clearing nut seed powder at 30 °C, 0.300 g/100 ml adsorbent dosage and particle size 250–500  $\mu$ m. The error bars represent the standard deviation for three separate sample runs.

Table 3. Parameters obtained for Co(II) adsorption on to clearing nut seed powder from Langmuir, Freundlich and D-R isotherms at 30 °C.

Langmuir isotherm			Freundlich isotherm			D-R isotherm		
b (dm <sup>3</sup> mg <sup>-1</sup> )	$X_m (mg g^{-1})$	R <sup>2</sup>	K	1/n	R <sup>2</sup>	qm (mg g <sup>-1</sup> )	$\beta \text{ (mol}^2 \text{ J}^{-2}\text{)}$	$\mathbb{R}^2$
0.060	4.245	0.9944	1.359	0.38	0.987	3.152	-1.639×10 <sup>-5</sup>	0.9186

formed between the metal ions and the binding sites rupture at high temperatures, thus decreasing the percentage removal [43].

The spontaneity of an adsorption process can be explained by the free energy change ( $\Delta G^{\circ}$ ). If  $\Delta G^{\circ}$  is a negative value at a given temperature that indicates the particular reaction is spontaneous.  $\Delta G^{\circ}$  value can be calculated using Eq. (11) where,  $K_0$  is the equilibrium constant of the process at a certain temperature, R (J K<sup>-1</sup> mol<sup>-1</sup>) and T (K) are universal gas constant and absolute temperature respectively.

$$\Delta G^0 = -RT ln K_0 \tag{11}$$

According to literature, approximation of Langmuir equilibrium constant to the thermodynamic equilibrium constant is reasonable for a diluted solution with a charged adsorbate [44]. Langmuir isotherm plots were generated at 30, 40, 50 and 60 °C as given in Figure 9 to calculate the thermodynamic equilibrium constant at each temperature.

Table 4 summarises the obtained parameters from the plots, Gibbs free energy changes, and the calculated thermodynamic equilibrium constant values. According to the table, the calculated Gibbs free energy values are negative which indicates that the adsorption process is feasible and spontaneous in nature and the spontaneity decreases as the temperature increases from 30 °C to 60 °C suggesting physisorption mechanism is taking place during adsorption.

The enthalpy change ( $\Delta H^o$ ) and the entropy change ( $\Delta S^o$ ) for the adsorption process were calculated by plotting  $lnK_o$  against 1/T as shown in Figure 10, based on the relationship given by Equation 12 [45].

$$lnK_o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$
(12)

The negative ( $\Delta H^{\circ}$ ) value of -23.03 kJ mol<sup>-1</sup> indicates the exothermic nature of Co(II) ions adsorption on to CNSP and the ( $\Delta S^{\circ}$ ) value of -7.962 J mol<sup>-1</sup> K<sup>-1</sup> confirms that metal ions concentration at the solid-liquid interface is reduced during adsorption [46].

### 3.5. Effect of pH

The pH effect on the adsorption of metal ions was investigated varying the pH of the solution from two to seven for 20 ppm initial metal ion concentration as given in Figure 11. When the pH of the medium increases, the adsorbate may get precipitated as  $Co(OH)_2$  which can lead



**Figure 8.** The effect of temperature on percentage removal of Co(II) by clearing nut seed powder at 20, 30, 40 and 60 ppm initial Co(II) concentrations, 0.300 g/ 100 ml adsorbent dosage and particle size 250–500  $\mu$ m. The error bars represent the standard deviation for three separate sample runs.



**Figure 9.** The Langmuir isotherm plots for the adsorption of Co(II) on to clearing nut seed powder at different temperatures, 0.300 g/100 ml adsorbent dosage and particle size 250–500  $\mu$ m. The error bars represent the standard deviation for three separate sample runs.

to higher percentage removal values [2]. Due to that reason, the analysis was restricted to the pH value seven.

As shown in Figure 11, removal of metal ions tend to increase with increasing pH up to about pH 5 and thereafter change in percentage removal was low.

At low pH values, the abundant availability of  $\rm H_3O^+$  ions in the solution phase creates a competition between the adsorbate (Co(II) ions) and  $\rm H_3O^+$  ions for the binding sites on the CNSP leading to low percentage removal values. On the other hand, the functional groups present on the adsorbent get protonated at low pH values, generating repulsive forces between the adsorbent and adsorbate preventing the attraction of Co(II) ions onto the surface of adsorbent [47]. With the increment of pH, the adsorbent surface get deprotonated creating negative charges on the surface of CNSP, allowing the adsorption of positively charged metal ions and thereby increasing the percentage removal. Based on the above-discussed factors, the pH of the medium seems to have a considerable effect on the adsorption process.

### 3.6. Effect of adsorbent dosage

The adsorbent dosage was increased from 0.05 g to 0.4 g to investigate the adsorbent dosage effect on Co(II) ions adsorption on to CNSP while keeping all the other parameters constant (Figure 12). With the increment of adsorbent dosage, more metal ions got removed from the solution as more binding sites are available for the binding of Co(II) ions along with increased specific surface area [48]. Beyond 0.3 g further increment in CNSP dosage didn't show considerable effect on the percentage removal due to the overlapping of binding sites and the aggregate formation of the adsorbents at high adsorbent dosage levels [36, 49].

## 3.7. Comparison of surface modified clearing nut seed powder with the surface unmodified clearing nut seed power

Research has been done to improve the adsorption capacity of adsorbents by chemically modifying them. In the present study the sulfuric acid surface modification method was used to chemically modify the adsorbent. The acid modification method increases the number of

-					
Temperature (°C)	1/X <sub>m</sub> (g/mg)	$1/X_{m}b$ (×10 <sup>-3</sup> ) (mol g/l mg)	R <sup>2</sup>	Equilibrium constant (K <sub>0</sub> ) ( $\times 10^3$ )	$\Delta G^{o}$ (kJ mol <sup>-1</sup> )
30	0.233	0.066	0.9962	3.530	-20.579
40	0.273	0.101	0.9831	2.703	-20.564
50	0.268	0.129	0.9798	2.078	-20.514
60	0.250	0.162	0.998	1.543	-20.326





**Figure 10.** Plot of  $\ln K_0$  versus 1/T for the estimation of thermodynamic parameters for Co(II) adsorption process.



**Figure 11.** The effect of pH on percentage removal of Co(II) by clearing nut seed powder at 20 ppm initial concentration, 30 °C, adsorbent dosage 0.300 g/ 100 ml and particle size 250–500  $\mu$ m for 180 min contact time. The error bars represent the standard deviation for three separate sample runs.

binding sites available on the adsorbent by enhancing the porosity of the adsorbent and by reducing the organic matter content [50]. The adsorption capacity of the surface modified adsorbent was found to be as 2.838 mg g<sup>-1</sup> for 20 ppm initial metal ion concentration, 0.3 g adsorbent dosage, 180 min contact time at 30 °C. Under the same conditions, the adsorption capacity of the surface unmodified CNSP was 1.825 mg g<sup>-1</sup>.



**Figure 12.** The effect of adsorbent dosage on percentage removal of Co(II) by surface unmodified clearing nut seed powder at 20 ppm initial concentration, 100 ml, 30  $^{\circ}$ C and particle size 250–500 µm for 180 min contact time. The error bars represent the standard deviation for three separate sample runs.

Therefore the surface modification has increased the adsorption capacity of the adsorbent.

### 3.8. Comparison of adsorption capacity of CNSP with other adsorbents

Table 5 compares the adsorption capacity of some other adsorbents for Co(II) ions adsorption with the CNSP.

### 4. Conclusion

The potential of the clearing nut seed powder for the removal of Co(II) ions from aqueous solutions was investigated in the present study. The major findings are summarized as follows. The optimum conditions for the maximum removal of Co(II) ions by the adsorbent were found to be: 0.3 g in 100 ml of the adsorbate solution at pH 5 for 120 min contact time at the temperature of 30 °C. The percentage removal of Co(II) ions reached to a maximum around 20 ppm initial metal ion concentration with an adsorption capacity of  $1.862 \text{ mg g}^{-1}$ . The adsorption equilibrium data fitted well to the Langmuir and Freundlich isotherm models suggesting the presence of monolayer and multilayer adsorption mechanisms for the Co(II) ions adsorption by the adsorbent. The best isotherm model could be considered as the Langmuir model based on the highest correlation coefficient value obtained. The maximum monolayer adsorption capacity of the clearing nut seed powder for the removal of Co(II) ions was found to be 4.245 mg  $g^{-1}$ . The adsorption kinetics revealed that the pseudo-second-order kinetic model fitted well to the adsorption of Co(II) ions by the adsorbent indicating that the adsorption process followed chemisorption. The thermodynamic studies indicated

Table 5. Adsorption capacities of reported adsorbents for Co(II) ions adsorption.

Adsorbent	Adsorption Capacity (mg/g)	References
South African coal fly ash	0.40	[51]
Ficus benghalensis leaf powder	5.65	[52]
Banana peel	2.55	[17]
Coal based Granular Activated Carbon	0.34	[53]
Orange peel	1.82	[17]
Ficus religiosa leaf powder	3.60	[54]
Cross-Linked Calcium Alginate Beads	1.38	[16]
Kaolinite	0.92	[19]
Saudi activated bentonite	7.3	[2]
Montmorillonite	6.92	[18]
Clearing nut seed powder	4.25	This study

that the adsorption process is feasible, spontaneous and exothermic in nature. The FTIR analysis indicated the presence of various functional groups in clearing nut seed powder such as hydroxyl, C-N and C-O functional groups which might be participated in metal ion removal. The SEM analysis suggested that adsorbent possesses an irregular surface structure with tiny pores on it, which could be related to the metal uptake by the adsorbent. The surface modified clearing nut seed powder showed higher potential for the removal of Co(II) ions when compared with surface unmodified clearing nut seed powder. However, further investigations should be carried out to identify the optimum conditions for the removal of Co(II) ions from aqueous solutions using surface modified clearing nut seed powder as an adsorbent.

### Declarations

### Author contribution statement

Kavitha H. Ranaweera, Pahan I. Godakumbura, B. Asiri Perera: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

### Funding statement

This work was supported by the University of Sri Jayewardenepura, Sri Lanka.

#### Competing interest statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

### References

- [1] N. Gandhi, D. Sirisha, K.C. Shekar, Bioremediation of wastewater by using strychnos potatorum seeds (clearing nuts) as bio adsorbent and natural coagulant for removal of fluoride and chromium, J. Int. Aca. Res. Multidis. 3 (1) (2014) 253–272.
- [2] S.S. Al-Shahrani, Treatment of wastewater contaminated with cobalt using Saudi activated bentonite, Alexandria Eng. J. 53 (2014) 205–211.
- [3] L. Leyssens, et al., Cobalt toxicity in humans-A review of the potential sources and systemic health effects, Toxicology 387 (2017) 43–56.
- [4] H. Ghassabzadeh, et al., Characterizations of Co (II) and Pb (II) removal process from aqueous solutions using expanded perlite, Desalination 261 (1-2) (2010) 73–79.
- [5] K.M.O.Y.Z. Mohiuddin, H.M.K. Otomo, N. Shikazono, Heavy metals contamination in water and sediments of an urban river in a developing country, Int. J. Environ. Sci. Technol. (2011) 723–736.
- [6] O.T.E. Oyeku, Heavy metal contamination of groundwater resources in a Nigerian urban settlement, Afr. J. Environ. Sci. Technol. 4 (2010) 201–214.

- [7] D.M. Manohar, B.F. Noeline, T.S. Anirudhan, Adsorption performance of Al-pillared bentonite clay for the removal of cobalt(II) from aqueous phase, Appl. Clay Sci. 31 (3-4) (2006) 194–206.
- [8] V. Khandegar, A.K. Saroha, Electrocoagulation for the treatment of textile industry effluent–a review, J. Environ. Manag. 128 (2013) 949–963.
- [9] C. Blöcher, et al., Hybrid flotation—membrane filtration process for the removal of heavy metal ions from wastewater, Water Res. 37 (16) (2003) 4018–4026.
- [10] F. Fu, et al., Application of a novel strategy—advanced Fenton-chemical precipitation to the treatment of strong stability chelated heavy metal containing wastewater, Chem. Eng. J. 189–190 (2012) 283–287.
- [11] F.M. Pang, S.P. Teng, T.T. Teng, A.K.M. Omar, Heavy metals removal by hydroxide precipitation and CoagulationFlocculation methods from aqueous solutions, Water Qual. Res. J. 44 (2) (2009) 174–182.
- [12] A. Dabrowski, et al., Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, Chemosphere 56 (2) (2004) 91–106.
- [13] L.M. Ottosen, et al., Screening the possibility for removing cadmium and other heavy metals from wastewater sludge and bio-ashes by an electrodialytic method, Electrochim. Acta 52 (10) (2007) 3420–3426.
- [14] P. Senthil Kumar, et al., Adsorption of Cu(II), Cd(II) and Ni(II) ions from aqueous solution by unmodified Strychnos potatorum seeds, Eu. J. Env. Civil Eng. 17 (4) (2013) 293–314.
- [15] I. Ali, V.K. Gupta, Advances in water treatment by adsorption technology, Nat. Protoc. 1 (6) (2006) 2661–2667.
- [16] T. Dewangan, A. Tiwari, A. Bajpai, Removal of cobalt ions from aqueous solution by adsorption onto cross-linked calcium alginate beads, J. Dispersion Sci. Technol. 30 (1) (2009) 56–60.
- [17] G. Annadurai, R. Juang, D. Lee, Adsorption of heavy metals from water using banana and orange peels, Water Sci. Technol. 47 (1) (2003) 185–190.
- [18] W. Hu, et al., Competitive adsorption of U (VI) and Co (II) on montmorillonite: a batch and spectroscopic approach, Appl. Clay Sci. 157 (2018) 121–129.
- [19] Ö. Yavuz, Y. Altunkaynak, F. Güzel, Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite, Water Res. 37 (4) (2003) 948–952.
- [20] N. Packialakshmi, C. Suganya, V. Guru, Phytochemical and IR –Spectrum analysis of Strychnos potatorum linn, Int. J. Phytopharm. 4 (2) (2014) 63–66.
- [21] P. Mallikharjuna, et al., Phytochemical studies of Strychnos potatorum Lf-A medicinal plant, J. Chem. 4 (4) (2007) 510–518.
- [22] K.S. Vijay, S.N. Waman, Use of strychnos potatorum seed powder as a water purifier: a sustainable approach for rural development, Global J. Res. Anal. 4 (7) (2015) 135–137.
- [23] P. Senthil Kumar, Adsorption of Zn(II) ions from aqueous environment by surface modified Strychnos potatorum seeds, a low cost adsorbent, Pol. J. Chem. Technol. 15 (3) (2013) 35–41.
- [24] K. Anbalagan, P. Senthil Kumar, R. Karthikeyan, Adsorption of toxic Cr(VI) ions from aqueous solution by sulphuric acid modified Strychnos potatorum seeds in batch and column studies, Desalination Water Treat. 1 (2015) 37–41.
- [25] K. Anbalagana, et al., Removal and recovery of Ni(II) ions from synthetic wastewater using surface modified Strychnos potatorum seeds, Desalination Water Treat. 53 (2013) 171–182.
- [26] S. Vishali, P. Rashmi, R. Karthikeyan, Potential of environmental-friendly, agrobased materialStrychnos potatorum, as an adsorbent, in the treatment of paint industry effluent, Desalination Water Treat. 57 (39) (2015) 18326–18337.
- [27] M. Thirumavalavan, Y.-L. Lai, J.-F. Lee, Fourier transform infrared spectroscopic analysis of fruit peels before and after the adsorption of heavy metal ions from aqueous solution, J. Chem. Eng. Data 56 (5) (2011) 2249–2255.
- [28] M. Kavand, M. Soleimani, N. Asasian, Film-Pore-[Concentration-Dependent] surface diffusion model for heavy metal ions adsorption: single and multi-component systems. Process Saf. Environ. Protect. 1 0 7 (2017) 486–497.
- [29] M. Hamayun, et al., Equilibrium and kinetics studies of arsenate adsorption by FePO4, Chemosphere 99 (2014) 207–215.
- [30] Hussein S. Mohamed, et al., Adsorption of Cd<sup>2+</sup> and Cr<sup>3+</sup> ions from aqueous solutions by using residue of Padina gymnospora waste as promising low-cost adsorbent, Heliyon 5 (2019).
- [31] B.M.W.P.K. Amarasinghe, R.A. Williams, Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater, Chem. Eng. J. 132 (1-3) (2007) 299–309.
- [32] Y.S. Ho, Citation review of Lagergren kinetic rate equation on adsorption reactions, Scientometrics 59 (2004) 171–177.
- [33] Y.S. Ho, Review of second-order models for adsorption systems, J. Hazard Mater. 136 (3) (2006) 681–689.
- [34] T.W. Weber, R.K. Chakravorti, Pore and solid diffusion models for fixed-bed adsorbers, AIChE J. 20 (2) (1974) 228–238.
- [35] G.E. Boyd, A.W. Adamson, L.S. Myers, The exchange adsorption of ions from aqueous solutions by organic zeolites. II. Kinetics, J. Am. Chem. Soc. 69 (1947) 2836–2848.
- [36] P. Senthil Kumar, et al., KINETICS AND EQUILIBRIUM STUDIES OF Pb2+ ION REMOVAL FROM AQUEOUS SOLUTIONS BY USE OF NANO-SILVERSOL-COATED ACTIVATED CARBON, Braz. J. Chem. Eng. 27 (2) (2010) 339–346.
- [37] Y. Liu, New insights into pseudo-second-order kinetic equation for adsorption, Colloid. Surface. 320 (2008) 275–278.
- [38] G.M. Al-Senani, F.F. Al-Fawzan, Adsorption study of heavy metal ions from aqueous solution by nanoparticle of wild herbs, Egypt. J. Aquat. Res. 44 (3) (2018) 187–194.
- [39] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.
- [40] H.M.F. Freundlich, Over the adsorption in solution, J. Physicochemical 57 (1) (1906) 385–470.

#### K.H. Ranaweera et al.

- [41] M.D.L. Radushkevich, The equation of the characteristic curve of the activated charcoal USSR, *Phys. Chem. Sect* 55 (1947) 331.
- [42] A. Ali, K. Saeed, F. Mabood, Removal of chromium (VI) from aqueous medium using chemically modified banana peels as efficient low-cost adsorbent, Alexandria Eng. J. 55 (3) (2016) 2933–2942.
- [43] A.M. Aljeboree, A.N. Alshirifi, A.F. Alkaim, Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon, Arabian J. Chem. 10 (2017) S3381–S3393.
- [44] Y. Liu, Is the free energy change of adsorption correctly calculated? J. Chem. Eng. Data 54 (2009) 1981–1985.
- [45] S.I. Lyubchik, et al., Kinetics and thermodynamics of the Cr(III) adsorption on the activated carbon from co-mingled wastes, Colloid. Surface. Physicochem. Eng. Aspect. 242 (1-3) (2004) 151–158.
- [46] M.F. El-Shahat, A.M.A. Shehata, Extraction of p-nitroaniline from aqueous solutions onto activated carbon prepared from treated camphor wood, Int. J. Emer. Tech. Adv. Eng. 4 (1) (2014).
- [47] L. Deng, et al., Sorption and desorption of lead (II) from wastewater by green algae Cladophora fascicularis, J. Hazard Mater. 143 (2007) 220–225.

- [48] K. Jayarama, et al., Biosorption of lead from aqueous solution by seed powder of Strychnos potatorum L, Alexandria Eng. J. 71 (2009) 248–254.
- [49] S. Sarkar, M. Sarkar, Ultrasound assisted batch operation for the adsorption of hexavalent chromium onto engineered nanobiocomposite, Heliyon 5 (4) (2019), e01491.
- [50] M.E.D.S. Argun, Removal of heavy metal ions using chemically modified adsorbents, J. Int. Environ. Appl. Sci. 1 (2006) 27–40.
- [51] E.T. Musapatika, M.S. Onyango, O. Aoyi, Cobalt (II) removal from synthetic wastewater by adsorption on South African coal fly ash, South Afr. J. Sci. 106 (9-10) (2010) 1–7.
- [52] D. Hymavathi, G. Prabhakar, Studies on the removal of Cobalt (II) from aqueous solutions by adsorption with Ficus benghalensis leaf powder through response surface methodology, Chem. Eng. Commun. 204 (12) (2017) 1401–1411.
- [53] J.K. Gunjate, Adsorption of cobalt onto coal based granular activated carbon: kinetics and equilibrium studies, Int. J. Appl. Environ. Sci. 12 (6) (2017) 1045–1058.
- [54] B. Krishna, P. Venkateswarlu, Influence of Ficus Religiosa Leaf Powder on Bisorption of Cobalt, 2011.