



Low-Cost *Schizandra chinensis* Fruit Peel for Co(II) Removal from Aqueous Environment: Adsorption Properties and Mechanism

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Biosorption is an ecofriendly wastewater treatment technique with high efficiency and low operating cost involving simple procedure for the removal and recovery of heavy metal ions from aqueous media. In present investigation, *Schizandra chinensis* fruit peel powder was utilized as biosorbent for the removal of Co(II) from aqueous media. The biosorbent was characterized by using Fourier transform infrared spectroscopy, scanning electron microscopy and energy dispersive X-ray techniques analysis. From FT-IR analysis it was found that hydroxyl, methoxy and carbonyl groups are involved in the removal of Co(II) from aqueous environment. The effect of various parameters for Co(II) removal by using *Schizandra chinensis* fruit peel powder are evaluated in batch biosorption method. Biosorption kinetics data was evaluated with kinetic models and the kinetic data was well fitted with pseudo-second-order kinetic model. The equilibrium data was in tune with the Langmuir isotherm model by revealing the maximum sorption capacity of 9.47 mg g⁻¹ at pH 6.5, contact time 40 min. This study demonstrated that the *Schizandra chinensis* fruit peel powder biosorbent was a promising, efficient, economic and biodegradable sorbent.

Keywords: Wastewater, Biosorption, Heavy metal, Cobalt, *Schizandra chinensis* fruit peel, Kinetic, Equilibrium, Adsorption mechanism.

INTRODUCTION

Heavy metals are significant environmental pollutants owing to their indefinite persistence in the environment and many of them are toxic even at very low concentrations. Many industrial activities (*e.g.* metal plating, fertilizer industry *etc.*) introduce heavy metals to environment *via* their waste effluents^{1,2}. Cobalt is a typical heavy metal because it has variety of industrial applications such as production of satellite alloys, paints, mining, metallurgical, electro plating, pigments and electronic. It was also present in the waste water from nuclear power plants and industrial effluents. Cobalt may causes serious health problems such as asthma leading to the damage of heart, its failure, damage to the functioning of thyroid gland and liver in humans³⁻⁵ and also causes genetic changes in living cells⁵⁻⁷. Cobalt ionization radiation exposure is associated with increasing risk of developing cancer⁵. Thus various regulatory bodies have set permissible limits for cobalt in drinking water. The EPA permissible limits of cobalt in the irrigation water and livestock wastewater are 0.05 and 1.0 mg/L respectively⁸⁻¹⁰ (Environmental Bureau of Investigation, Canadian Water Quality Guidelines).

Thus various techniques have been developed and employed for the treatment of cobalt from aqueous solutions.

The most conventional methods used for Co(II) removal from aqueous solutions include chemical precipitation, ion exchange/chelation, electrolytic recovery, liquid-liquid extraction and membrane separation⁹⁻¹¹. However, application of these methods are limited due to their technical and economical constraints, such as disadvantages like incomplete metal removal, high energy requirements, generation of toxic sludge or other waste products that require careful disposal. Hence it is imperative to explore a cost-effective treatment method that is capable of removing Co(II) from aqueous effluents^{10,12-14}. This accelerated the search for highly efficient yet economically attractive treatment methods involving their removal from waste waters following the technique of biosorption^{8,15,16}. In this perspective a number of researchers have been used biosorption technique for the removal of Co(II) from aqueous solution^{10,12,17-24}. Biosorption has potential advantages over other traditional wastewater treatment technologies including low cost, high efficiency, minimization of chemical and low biological sludge, no additional nutrient requirement, regeneration of biosorbent and possibility of metal recovery and environmental friendly, particularly when natural biomass is used²⁵⁻³¹. One of important natural biomass is peel of various fruits, which can serve as a potential adsorbent for the removal

of various types of environmental pollutants, especially metal ions³²⁻³⁵. *Schizandra chinensis* is a vine with flowers and fruits that grows in Russia, China, Korea and Japan, is an excellent source of biomass for the chelating of heavy metals and its applications to eliminate these contaminants from underground water as well as contribute or reduce the organic pollution due to this kind of wasters in places with string fruit in Korea. The biomass of *Schizandra chinensis* consists of nine lignans bioactive compounds³⁶. The fruits of *Schizandra chinensis* have been used to treat chronic cough, spontaneous sweating, palpitation and spermatorrhea as tonic and sedative in various prescriptions in traditional Chinese medicines^{37,38}.

This work is to demonstrate that the use of modified waste material from *Schizandra chinensis* fruit peel (SCFP) as a biosorbent for the removal of Co(II) from aqueous solutions. Various experimental parameters such as equilibrium, pH effect, biosorbent dosage, contact time and initial metal ion concentration were performed in order to optimize the process variables for the removal of Co(II). Langmuir, Freundlich and Temkin adsorption isotherm models were used to determine the mechanism of the biosorption process. The developed method was successfully applied for the removal of Co(II) from aqueous solutions. The report is first of its kind about using biomass, SCFP as a biosorbent for the removal of metal ions.

EXPERIMENTAL

Preparation of the biosorbent: *Schizandra chinensis* fruits peel was collected from Oriental Medical College, Gyeongju, South Korea. The peel was removed from the fruits and was cut into small pieces. These pieces were air dried and grounded in a mill to get fine powder. The powder was washed twice with deionizer water and dried at 60 °C for 24 h, then boiled in double distilled water by changing the water repeatedly until water becomes colourless, which indicates that the removal of water soluble colour compounds. The washed and boiled fine powder was oven dried at 70 °C for 24 h and stored in desiccators to prevent from moisture adsorption. This was named as SCFP biosorbent.

Chemicals and equipments: Standard metal solution (analytical grade) containing 1000 mg L⁻¹ of Co(II) was prepared from cobalt acetate [Co(CH₃COO)₂·4H₂O] purchased from Sigma-Aldrich (Ireland). Working solutions were prepared by diluting the standard solution with distilled water. pH of the samples was measured by pH meter (pH 340i, WTW, Germany) after calibration using standard buffer solutions for three times. The metal concentrations in solution were determined using Varian Spectra AA220 model atomic absorption spectrometer (AAS). The morphology and elemental composition of the biosorbent was analyzed using scanning electron microscope with an energy dispersive X-ray spectroscopy (S-4300 & EDX-350, Hitachi, Japan). Surface area and pore sizes of the biosorbent were measured by Brunauer-Emmett-Teller method (BET) (Autosorb-1, Quanta chrome instrument, USA) based on N₂ gas adsorption on the surface of biosorbent at 60 °C. The functional groups present in the biosorbents were analyzed by using spectrum GX & Auto image (Perkin-Elmer, USA) FTIR spectra from 4000 to 400 cm⁻¹ spectral range using Ge coated KBr beam splitter.

Batch biosorption studies: Batch biosorption studies were carried out by shaking 0.1 g of biomass (SCFP) with 50 mL of the aqueous solutions of Co(II) ions at pH 6.5 in different conical flask using a temperature controlled shaker (25 ± 2 °C). The solution–biosorbents mixtures were stirred at 200 rpm and at the end of pre-determined time interval the reaction mixtures were filtered out and analyzed for its metal ion concentrations by using AAS. The biosorption experiments were also conducted to determine the equilibrium time (10-60 min), initial concentrations (6-20 mg L⁻¹) and dosage of the adsorbent (1-4 g L⁻¹) for maximum biosorption. All the investigations were carried out in duplicate to avoid any discrepancy in experimental results and metal solution controls were kept throughout the experiment to maintain quality control. The percentage of metal biosorption was measured using the equation:

$$\text{Biosorption (\%)} = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

where C_i and C_e or C_f are the initial and equilibrium or final concentration of metal ion (mg L⁻¹), respectively in the solution. Biosorption capacity was calculated by using the mass balance equation for the biosorbent:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

where q_e is the biosorption capacity (mg g⁻¹), V is the volume of metal ion solution (L) and m is the weight of the biosorbent (g).

Kinetics biosorption studies were also carried out in order to determine the contact time required to reach the equilibrium at constant pH, biosorbent dosage and metal initial concentration with varying contact time. The amount of adsorption capacity at time t, was measured using the following equation:

$$q_t = \frac{(C_o - C_t)V}{m} \quad (3)$$

where C_t (mg L⁻¹) is the concentration of metal ion at particular time, t in the present experiment.

RESULTS AND DISCUSSION

Physical characterization of the *Schizandra chinensis* fruits peel (SCFP) biosorbent: Characteristics of SCFP biomass such as bulk density, moisture content, ash content, surface area, surface composition and other physical parameters were measured (Table-1). The bulk density of the biomass was found to be 0.45-0.55 g mL⁻¹ with 1.2 % moisture and 12.54 % of ash content, respectively. The BET surface area of biomass was found to be 445 m² g⁻¹ by using N₂ gas adsorption method. The pore volume and pore mean diameter were also measured and reported in Table-1. From the pore mean diameter (43.5 Å) of biomass, it was confirmed as mesopores sorbent [20 Å < d < 500 Å; International Union of Pure and Applied Chemistry (IUPAC)].

Optimization of batch biosorption: Biosorption of heavy metal ions onto the surface of a SCFP is affected by several factors, such as biomass concentration, initial pH, initial metal ion concentration, time and temperature. In order to optimize

TABLE-1
PHYSICAL CHARACTERISTICS OF
SCFP POWDER BIOSORBENT

Physical characteristics	Values
Bulk density	0.45-0.55 g mL ⁻¹
Moisture content	1.20 %
Ash content	12.54 %
Surface area	445 m ² g ⁻¹
Pore volume	0.718 cm ³ g ⁻¹
Pore mean diameter	43.45 Å

the effect of these parameters batch biosorption experiments were carried out as follows:

Effect of biomass dosage: The number of sites available for biosorption depends upon the amount of the biosorbent. Effect of biosorbent dosage (1 to 4 g L⁻¹) on metal (20 mg L⁻¹) removal efficiency was studied at pH 6.5 at 25 ± 2 °C controlled water bath for 40 min. The percentage of metal ions uptake was found to be on the rise with the increasing concentration of the biosorbent but the amount of metal adsorbed per unit mass decreased considerably. The increase in the biosorption percentage or decrease in unit biosorption with increase in the dose of biosorbent is due to the increase in active sites on the adsorbent and thus making easier penetration of the metal ions to the biosorption sites. It may be due to the formation of biosorbent agglomerates or interactions between sorbent atoms reducing available surface area and blocking some of the biosorption sites^{39,40}. Maximum removal of Co(II) ions was observed with an biosorbent dose of 2 g L⁻¹ and there after a slow increase in the percentage removal was seen reaching a constant value with respect to the biosorbent dosage.

Effect of pH: The pH of the solution is well known characteristic that affects the surface charge of adsorbents by the protonation of functional groups in the biomass, as well as the degree of ionization and chemistry of the metal ions. The optimum pH for Co(II) biosorption was investigated by adding 2 g L⁻¹ SCFP biomass to aqueous metal solution and was adjusted to various pH values (2 to 12) using 0.1 mol L⁻¹ NaOH or 0.1 mol L⁻¹ HCl. Flasks were shaken for 40 min at 200 rpm at 25 ± 2 °C. As shown in Fig. 1, the metal uptake was increased with increase of pH in the range of 2 to 6 and after that it was almost constant and achieved maximum sorption capacity values above pH 6. At lower pH lower biosorption capacity was observed this is due to the fact that the concentrations of protons and hydronium (H₃O⁺) ions was higher and this compete for the binding of active sites on the surface of the biosorbent with metal ions. Further with increasing pH there is a decrease in competition between the protons surrounded by the adsorbent and metal ions. When the pH of the solution was increased from pH 2 to 6 the number of negatively charged sites increased and resulting in increased biosorption. Further the biosorption capacity was almost constant above the > pH 6.5 there is no significant change in adsorption was observed.

Effect of pH on biosorption can also explained based on the Co(II) species distribution as the function of solution pH^{9,41}. According to Huang *et al.*⁴¹ the chemical precipitation of Co(II) started at above the pH 8. This means Co(II) remains as the prevailing species up to a pH value of 8. Above pH 8, the

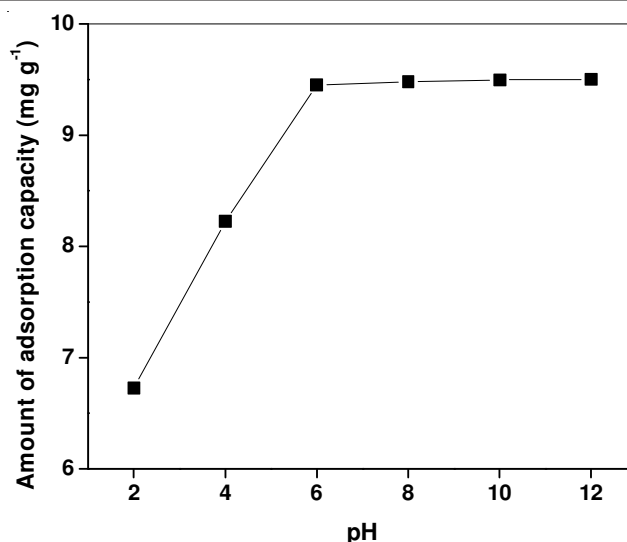


Fig. 1. Effect of pH on biosorption of Co(II) using SCFP (2 g L⁻¹) as biosorbent at 20 mg L⁻¹ Co(II) initial concentration, 25 ± 2 °C temperature and 200 rpm shaking speed for 40 min equilibrium time

Co(II) species are available as [Co(OH)]⁺ and Co(OH)₂. Above pH 8, Co(II) was adsorbed onto negative surface of biosorbent along with chemical precipitation of Co(II) as hydroxide at above pH 8. Hence, pH 6.5 was choosing for further studies.

Effect of contact time and Initial concentration: Effect of contact time is one of the most important factors that affecting the biosorption efficiency. In order to study the effect of contact time on metal ion removal batch sorption experiments were carried with metal ions (initial concentration 6 to 20 mg L⁻¹) and SCFP biomass (2 g L⁻¹) as a function of contact time (10 to 60 min) in a temperature controlled shaking water bath at 25 ± 2 °C. It has been observed that the within the first 10 min rapid biosorption of metal ion was observed (Fig. 2). After this period the amounts of biosorption was slowed down until it reaches the equilibrium. The possible reason for the phenomenon is a large number of vacant surface sites which are available for biosorption during the initial stage and after a lapse of time the remaining vacant surface sites find it difficult to get occupied due to repulsive forces between the solute molecules on the solid and aqueous phases. Similar results were observed by some researcher for the different adsorbate-sorbent system^{42,43}. Based on the results 40 min was fixed for further batch biosorption experiments to assume that the equilibrium is achieved. As shown in Fig. 2, when increase initial concentration of Co(II) from 6 to 20 mg L⁻¹ the absolute sorption per unit weight of biosorbent increased. However, the percentage of Co(II) biosorption decreases with increasing initial concentration. It is due to the available active sorption sites became fewer at higher initial concentration. It concluded that the Co(II) biosorption is concentration dependent. Similar results were reported by some of researchers for different sorption systems⁹.

Kinetic studies of biosorption: The biosorption kinetics studies have carried out to determine the rate of biosorption which is important for designing treatment systems. The kinetics of biosorption of Co(II) onto SCFP biomass were investigated for three initial concentrations varying between 6 to 20 mg L⁻¹. The experimental data were analyzed by the

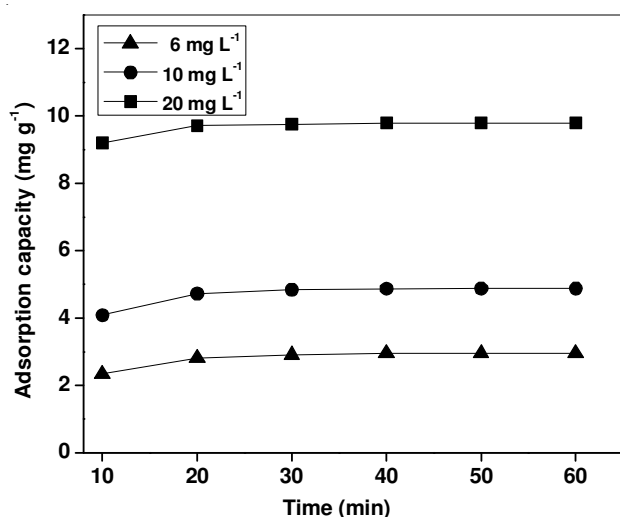


Fig. 2. Effect of contact time and initial metal ion concentration on biosorption of Co(II) using SCFP (2 g L^{-1}) as biosorbent at $25 \pm 2 \text{ }^\circ\text{C}$ and 200 rpm shaking speed and varying the Co(II) initial concentration from 6 to 20 mg L^{-1}

pseudo first-order and pseudo-second-order kinetic models. The conformity between experimental data and the model predicted values was expressed by correlation coefficient (R^2).

The linear pseudo-first order model was proposed by Lagergren⁴⁴, describes the rate of sorption is proportional to the number of sites unoccupied by the solutes is expressed as follows:

$$\log(q_e - q_t) = \log(q_e) - (K_1/2.303)t \quad (4)$$

where q_t and q_e are the metal ion concentrations (mg g^{-1}) at any time (t) and at the equilibrium (mg g^{-1}), respectively and K_1 is the first order rate constant (min^{-1}) which is obtained from slope of the $\log(q_e - q_t)$ versus t at different initial concentration of Co(II) (Fig. 3). The constant value K_1 and correlation coefficient (R^2) summarized in Table-2. The correlation coefficient values for biosorption of Co(II) indicates that the pseudo-first order kinetics was not fitted well to biosorption kinetic data. The pseudo-first order model works effectively only in the region where biosorption process occurs rapidly.

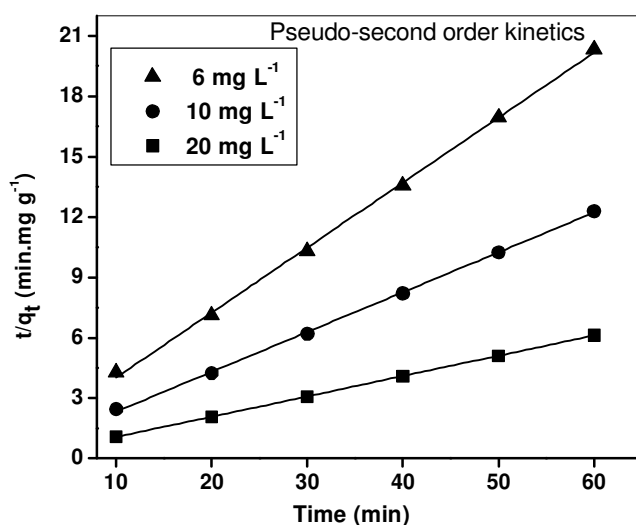
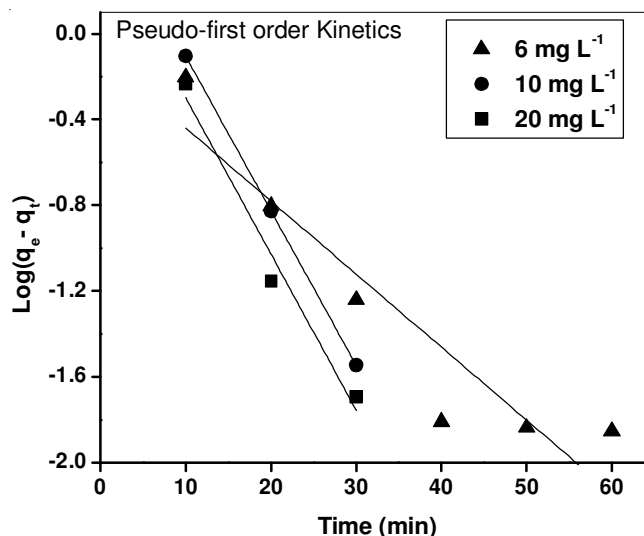


Fig. 3. Pseudo-first order and pseudo-second order kinetics for Co(II) biosorption on to SCFP biomass as a biosorbent

TABLE-2 KINETICS PARAMETERS OF Co(II) BIOSORPTION ON TO SCFP BIOSORBENT			
Kinetics parameters	Initial metal ion concentration (mg L^{-1})		
	6	10	20
$q_{e,\text{exp.}}$ (mg g^{-1})	2.949	4.879	9.787
Pseudo-first-order kinetics			
$q_{e,\text{cal.}}$ (mg g^{-1})	17.92	4.12	2.69
K_1 (min^{-1})	0.078	0.135	0.168
R^2	0.850	0.999	0.956
Pseudo-second-order Kinetics			
$q_{e,\text{cal.}}$ (mg g^{-1})	3.098	5.053	9.898
K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.131	0.113	0.188
h ($\text{mg g}^{-1} \text{min}^{-1}$)	1.26	2.89	18.38
R^2	0.999	0.999	0.999

Ho *et al.*⁴⁵ noticed that the use of the Lagergren model for prediction of the biosorption kinetics is not suitable for the entire sorption period. Thus, Ho *et al.*⁴⁵ developed pseudo-second order kinetic model expressed in the following form:

$$t/q_t = 1/(K_2 q_e^2) + (1/q_e)t \quad (5)$$

where q_t is the metal ion concentration (mg g^{-1}) at time (t) and is the metal ion concentration the equilibrium (mg g^{-1}) and is the pseudo second order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). A plot was drawn between t/q_t and t using eqn. 5 and fit liner curve (Fig. 3). From the slope and intercept of the curve q_e , K_2 and correlation coefficient (R^2) were calculated and the obtained results were summarized in Table-2. The correlation coefficient values obtained from pseudo-second-order model were ranged from 0.998 to 0.999 indicate the applicability of pseudo-second-order model for the biosorption data of Co(II) on to SCFP biomass. From the comparison of the two kinetic models, we can conclude that the biosorption of Co(II) onto the SCFP biomass follows the pseudo second-order kinetics.

Isotherm studies of biosorption: A biosorption isotherm is characterized by certain values, which express the surface properties and affinity of the biosorbent^{46,47}. Sorption equilibrium data can be described by a number of isotherm models available in the literature. In this study, Langmuir, Freundlich and Temkin isotherm models were selected to analyze the experimental data at different adsorbent dosage at $25 \pm 2 \text{ }^\circ\text{C}$.

The Langmuir isotherm model⁴⁸ which describes, that the sorption process takes place at a specific sorption surface with homogeneous adsorption energy. It is based on the assumption that the maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules⁴⁹. This model is expressed as follows:

$$C_e/q_e = 1/b(1/K_L) + 1/b(C_e) \quad (6)$$

where q_e is the metal uptake capacity and C_e is the concentration of metal ions in the solution at equilibrium, b is the maximum uptake capacity when the surface is completely covered with metal ions that represents the affinity between the biosorbent and the metal ion and K_L is the Langmuir equilibrium constant or rate of adsorption. The plot drawn between C_e/q_e versus C_e and fitted linear curve was shown in Fig. 4. The slope of curve indicates $(1/b)$ and where as an intercept indicates $1/bK_L$. The correlation coefficients (R^2), values observed for Co(II) biosorption onto SCFP were 0.985 and 0.998 at 2 and 4 g L⁻¹ adsorbent dosages respectively. This indicates that the biosorption of Co(II) onto SCFP biomass was compatible with the Langmuir isotherm. The isotherm constants of Langmuir, K_L and b were calculated and are reported in Table-3. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L and as expressed in the follows^{49, 50}:

$$R_L = 1/(1 + K_L C_0) \quad (7)$$

where C_0 is the highest initial concentration of adsorbate (mg L⁻¹) and K_L (L mg⁻¹) is the Langmuir constant. The R_L values indicates the shape of the isotherm to be either favourable ($0 < R_L < 1$), Linear ($R_L = 1$), unfavourable ($R_L > 1$), or irreversible ($R_L = 0$). The R_L value in the present investigations were found to be 0.255 and 0.090 ($0 < R_L < 1$) at 25 °C with 2 and 4 g L⁻¹ adsorbent dosage respectively, indicating that the sorption of Co(II) on SCFP biomass is favourable.

TABLE-3
ISOTHERM PARAMETERS OF Co(II)
BIOSORPTION ON TO SCFP BIOSORBENT

Adsorption isotherm and its constants	Adsorbent dosage (g L ⁻¹)	
	2	4
Langmuir adsorptions isotherms constants		
Maximum adsorption capacity, b (mg g ⁻¹)	9.47	18.23
K_L (L mg ⁻¹)	0.146	0.504
R^2	0.985	0.998
Freundlich adsorption isotherms constants		
K_F (mg g ⁻¹) (L mg ⁻¹) ^{1/n}	13.52	6.80
N	1.136	1.124
R^2	0.998	0.998
Temkin adsorption isotherms constants		
K_T (L mg ⁻¹)	17.14	16.87
B	7.82	3.94
R^2	0.922	0.917

The Freundlich isotherms is an empirical expression that takes into account the heterogeneity of the surface and multi-layer adsorption to the binding sites located on the surface of the sorbent. The Freundlich⁵¹ model is expressed as follows:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (8)$$

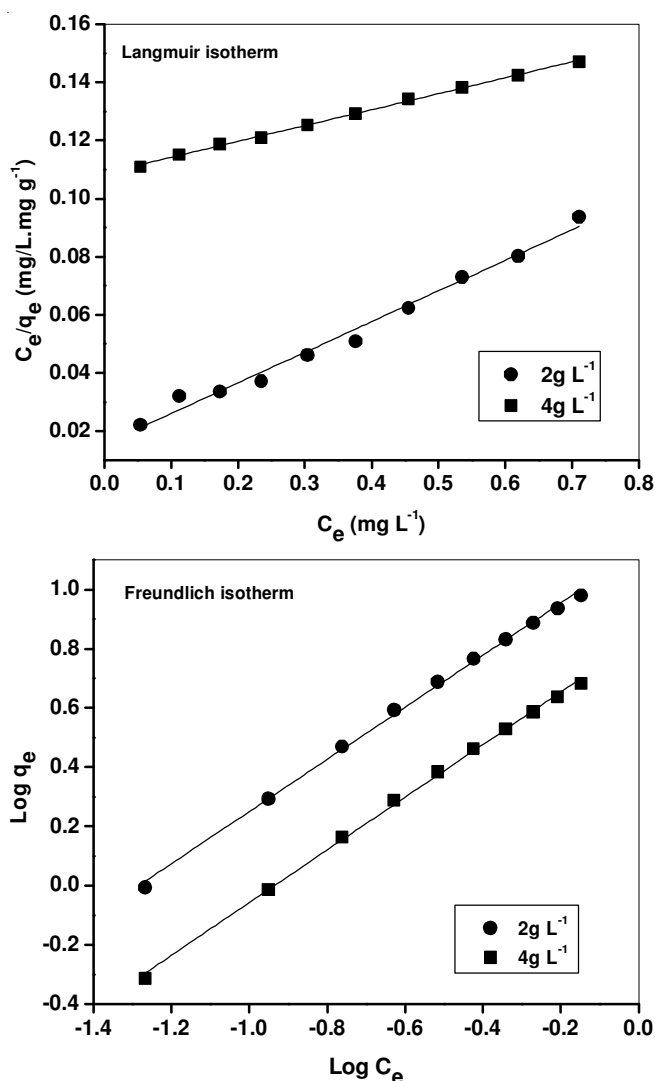


Fig. 4. Langmuir and Freundlich adsorption isotherms of Co(II) on to SCFP biomass as a biosorbent

Based on Freundlich eqn. 8, a plot drawn between $\ln C_e$ and $\ln q_e$ (Fig. 4) should be a straight line with a slope $(1/n)$ is an empirical constant indicates the biosorption intensity and an intercept $\ln K_F$ where K_F is the biosorption equilibrium constant. The correlation coefficients (R^2), 0.998 at two different adsorbent dosages (2 and 4 g/L) and $n > 1$ indicates that the biosorption of Co(II) onto SCFP is well fitted to Freundlich isotherm. The Freundlich isotherm parameters were reported in Table-3.

Temkin and Pyzhev⁵² considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms. The Temkin isotherm has been used in the following form:

$$q_e = RT/b \ln(K_T C_e) \quad (9)$$

This equation can be expressed in its linear form as:

$$q_e = B \ln K_T + b \ln C_e \quad (10)$$

where $B = (RT/b)$, which is obtained from the slope of plot q_e versus $\ln C_e$. The intercept of curve indicates $B \ln K_T$. The isotherm constants K_T and BK_T is the Temkin equilibrium binding constants (L/mg) corresponding to the maximum binding energy and constant B is related to heat of adsorption and the reset of term as usual have significance. The calculated

isotherms constants were reported in Table-3. It was not in tune with the adsorption data of Co(II) which was predicted by the R^2 values of this isotherms.

From Table-3, the Langmuir and Freundlich adsorption isotherm models yielded best results as indicated by the highest R^2 values at different biosorbent dosage compared to Temkin adsorption isotherm models. Best fitting of the equilibrium data with both Langmuir and Freundlich isotherms suggest that biosorbent surface contains both homogeneous and heterogeneously distributed active sites.

Comparison of Co(II) biosorption on to SCFP with other biosorbents: Biosorption capacities of various biosorbents towards Co(II) removal reported in literature were compared with the SCFP biosorbent and the results are summarized in Table-4. From the present study it was found that the maximum biosorption capacity of SCFP biomass is found to have a relatively large biosorption capacity of 9.47 mg g^{-1} at $25 \pm 2^\circ \text{C}$ with 2 g L^{-1} biosorbent dosage. The biosorption capacity for Co(II) biosorption found in this study was comparable and was found to be higher than many other biosorbents, this indicates that it could be considered a promising material for the removal of Co(II) ions from aqueous solutions. From the results it was found that SCFP biomass appears to be economic as well as efficient biosorbent for the Co(II) removal from aqueous solutions.

TABLE-4
COMPARISON OF THE PRESENT SCFP BIOSORBENT
MAXIMUM BIOSORPTION CAPACITIES (b, mg g^{-1}) OF
Co(II) WITH VARIOUS BIOSORBENT

Biosorbent	Biosorption capacity (mg g^{-1})	Ref.
<i>Ficus religiosa</i> (peepul)	3.60	18
<i>Rhytidiadelphus squarrosus</i> (moss)	7.25	20
<i>Hypogymnia physodes</i> (Foliose lichen)	9.90	22
<i>Evernia prunastri</i> (fruticose lichen)	5.72	23
<i>R. arrhizus</i> (fungi)	2.90	24
<i>Saccharomyces cerevisiae</i>	5.80	24
<i>Schizandra chinensis</i> Fruit peel	9.47	Present study

Effect of ionic strength: Wastewaters from industries contain various types of suspended and dissolved compounds apart from the metal ions. These impurities could be acids, alkalis, salts or metal ions. Salt is an important factor to adverse the biosorption of metal ion. The effect of ionic strength (NaCl) on cobalt biosorption was studied by changing NaCl concentration from 0.005 to 0.045 mol L^{-1} which is the level of salt in natural water at $25 \pm 2^\circ \text{C}$ and 10 mg L^{-1} Co(II) initial concentration. The obtained results (Fig. 5) indicates that the increase concentration of ionic strength led to a slight decrease in the amount of adsorbed Co(II) this is due to the competitive interaction of salt ions and metal ions with surface active sites of biosorbent. However, the amount of adsorbed Co(II) was not significantly affected with ionic strength.

Desorption studies: The desorption studies of Co(II) from biomass were carried out with EDTA, HCl, HNO_3 and Na_2CO_3 . As the concentration of desorbing solutions (HCl, HNO_3 and EDTA) increases, more Co(II) ions were able to be desorbed.

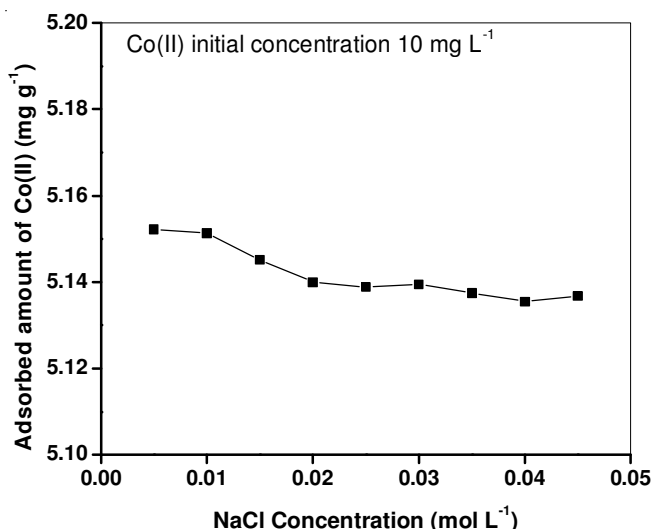


Fig. 5. Effect of ionic strength on biosorption of Co(II) on to SCFP (2 g L^{-1}) biosorbent at 10 mg L^{-1} Co(II) initial concentration, $25 \pm 2^\circ \text{C}$ temperature and 200 rpm shaking speed for 40 min equilibrium time

As shown in Table-5, more than 90 % of Co(II) ions were able to be desorbed from biomass using 0.025 mol L^{-1} HCl, HNO_3 and EDTA solutions. Especially, 98 % of Co(II) recovery was achieved with 0.025 mol L^{-1} EDTA. This may be the stability of the aqueous Co(II)-EDTA complex is more than the Co(II)-biosorbent interactions. This result showed that the test biosorbent could be reused without significant losses in its initial adsorption capacity. It will help to elucidate the adsorption and desorption behaviour of Co(II) in aqueous solutions for recovery and recycling of adsorbent at particular treatment of effluents.

TABLE-5
DESORPTION STUDIES OF Co(II) FROM SCFP BIOSORBENT

Desorbing solution	Concentration of desorbing solution (mol L^{-1})	Desorption of metal ion (%)
EDTA	0.001	56.45
	0.005	76.25
	0.010	87.24
	0.020	90.25
	0.025	98.26
HCl	0.001	22.56
	0.005	36.57
	0.010	85.28
	0.020	89.96
	0.025	92.15
HNO_3	0.001	33.46
	0.005	49.98
	0.010	78.26
	0.020	90.26
	0.025	95.74

Foreign ions effect on biosorption of Co(II): For the determination of interference caused by the presence of other metal cations, Ni(II), Li(II), Cu(II) and Pd(II) were added to the Co(II) (10 mg L^{-1}) solution. The obtained results were shown in Fig. 6. Presence of additional metal cations in the sorption medium in general was inhibitory to Co(II) biosorption by SCFP. This might be due to competition of divalent metal cations for complexation with the active binding sites of

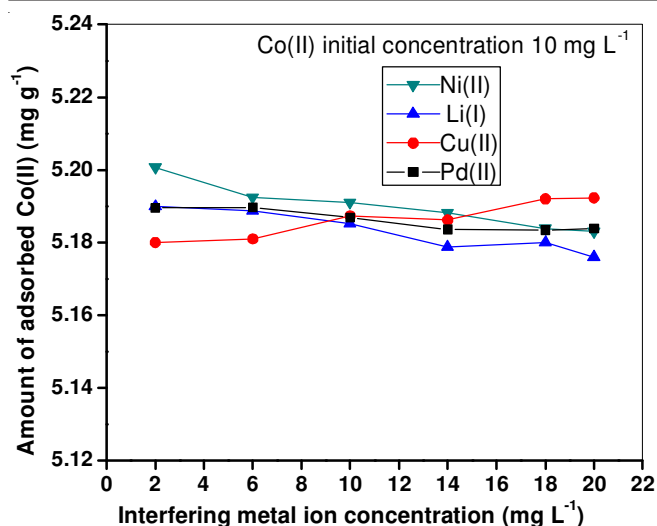


Fig. 6. Effect of associated metal ions on biosorption of Co(II) on to SCFP (2 g L^{-1}) biosorbent at fixed Co(II) initial concentration (10 mg L^{-1}), $25 \pm 2 \text{ }^\circ\text{C}$ temperature and 200 rpm shaking speed for 40 min equilibrium time

biomass leading to decrease in Co(II) uptake. However, decrease of biosorption capacity of Co(II) was not significantly affected with associated metal ions which were studied here.

Biosorption mechanism: Biosorption is a complex process therefore it is essential to understand mechanisms participating on the biosorption processes. Therefore, in our work we employed FTIR and SEM-EDX techniques to understand the biosorption mechanism.

The FT-IR spectrum of biomass (Fig. 7) shows a number of absorption peaks indicating the presence of various types of functional groups. A broad and strong absorption peak at 3433 cm^{-1} is observed this peak corresponds to aromatic and aliphatic OH groups. The peak at 3006.78 cm^{-1} indicating alkenes in aromatic ring and the strong peaks at 2926.22 and 2854.70 cm^{-1} are related to the C-H vibration of alkyl and ethylene groups of side chains and aromatic methoxyl groups. A weak absorption peak at 2280.56 cm^{-1} corresponds to C-C triple bond at side chain of aromatic ring. The strong absorption peak at 1744.92 cm^{-1} assigned as carbonyl stretching vibrations. The absorption peak at 1638.28 cm^{-1} is indicating the aromatic ring alkenes while the peaks at 1460.51 and 1377.56 cm^{-1} are typical vibrations in alkynes skeleton on aromatic ring. The absorption peaks between 1319.54 and 1161.65 cm^{-1} indicating to C-O stretching vibrations in side chains of aromatic ring units and the vibrations bands at 1059.76 and 804.11 cm^{-1} are indicating presence of substituted phenyl rings. The absorption peaks observed between 660.73 to 448.09 cm^{-1} related to C-X ($\text{X} = \text{Cl}^-, \text{S}^{2-}$) stretching vibrations. To identify the functional group that are involved in biosorption process FTIR spectra of Co(II) loaded biomass was compared with the FTIR spectra of biomass. The FT-IR spectrum of Co(II) loaded biomass (Fig. 7) indicating that the absorption peaks observed in SCFP biomass wavenumber were shifted, such as from 3433.28 to 3449.48 , from 2926.22 to 2928.81 , from 1744.92 to 1745.59 , from 660.73 to 722.41 and 448.06 to 424.15 cm^{-1} . The shift in these peaks indicates the involvement of hydroxyl, methoxy and carbonyl functional groups in binding of Co(II).

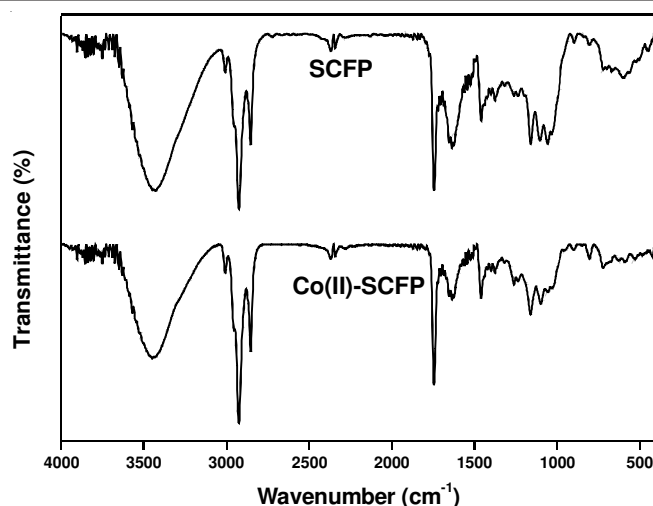


Fig. 7. FT-IR spectrum of SCFP biomass and Co(II)-SCFP biomass

Further SEM-EDX analysis was carried and the SEM morphology of biomass and metal loaded biomass were shown in Fig. 8. It was observed that the biomass has rough surface morphology this is favourable for biosorption of metal ions. The surface morphology of Co(II) loaded biomass (Fig. 8) exhibited different morphology than SCFP biomass, where shiny surface morphology was observed, indicating the surface of the SCFP biomass was covered by metal ions. The EDX analysis of SCFP biomass (Fig. 8) showed that the C was 65.93 weight % and oxygen was 29.46 weight % which are present in high percent and the calcium (0.73 weight %), sulfur (1.35 weight %) and chlorine (2.54 %) are present in low percentage. The presence of sulfur in SCFP is advantageous, because sulfur groups which are soft bases, have chemical affinity towards cobalt. Thus presence of sulfur in SCFP qualifies it as a potential adsorbent. From the overall results it was found that chemisorption plays an important role in the removal of Co(II) from aqueous solution by SCFP biosorbent.

Applications: The present bio-sorption method was successfully applied for the determination of Co(II) ions in synthetic water samples (Table-6). The synthetic water samples were prepared by adding various amounts of cobalt to the water samples. Calculated the relative standard deviation (< 1.052) and percentage of Co(II) recovery ($> 99 \%$) for the validation of measurements and method. It is clear from the results, the present green biosorption method was validated and aptly suited for the Co(II) recovery and determination without waste generation.

TABLE-6
RECOVERY AND DETERMINATION OF Co(II)
FROM SYNTHETIC WATER SAMPLES USING
SCFP BIOMASS AS BIOSORBENT

Sample No.	Added Co(II) (mg L^{-1})	Amount of found Co(II) ^a (mg L^{-1})	RSD (%)	Recovery of Co(II) (%)
1	5.0	4.96	1.023	99.20
2	10.0	10.12	0.945	101.20
3	12.0	11.98	0.532	99.80
4	18.0	19.01	0.982	105.60
5	20.0	19.87	1.052	99.35
6	22.0	21.98	0.794	99.90

^aAverage of five determinations.

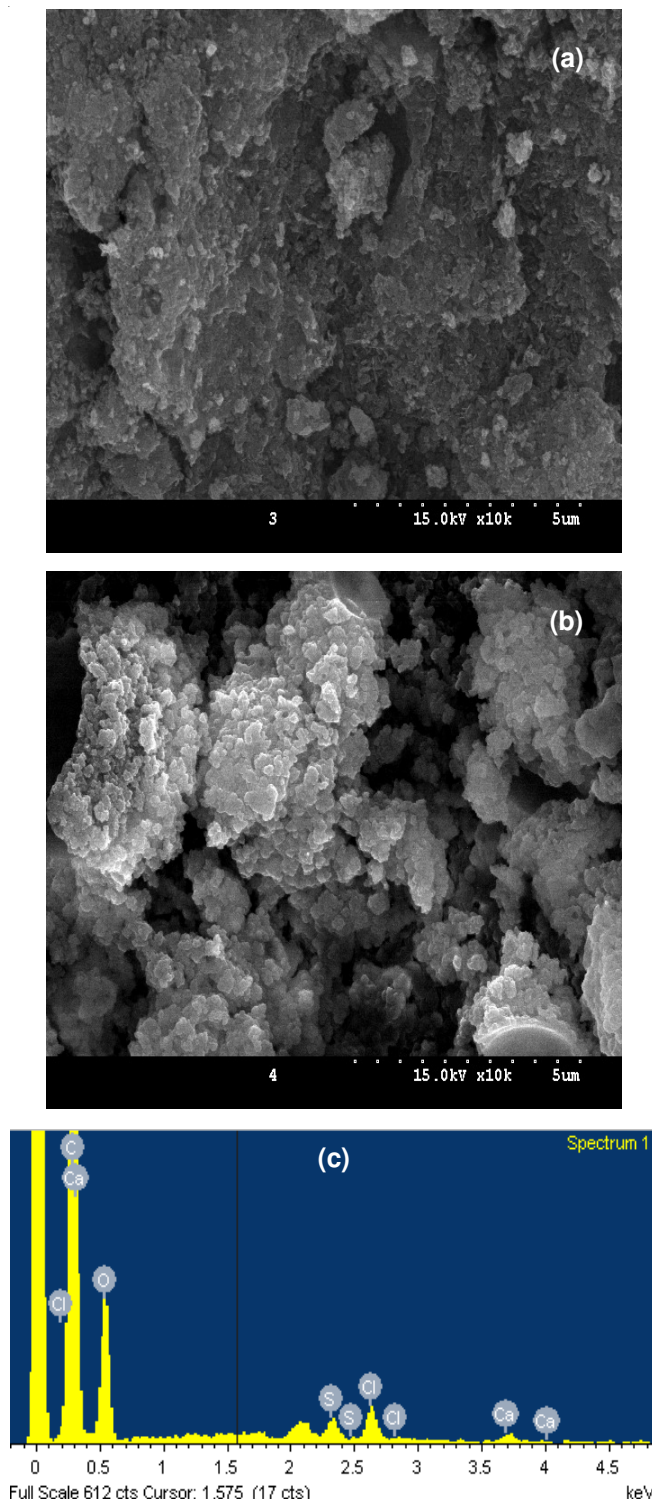


Fig. 8. Surface morphology (SEM images) of (a) Before biosorption of Co(II) on to SCFP, (b) after biosorption of Co(II) on to SCFP biosorbent at same magnifications and (c) SEM-EDX spectrum of SCFP biosorbent

Conclusion

Schizandra chinensis fruits peel (SCFP) was an eco friendly potential biosorbent for heavy metals removal. This work examined the efficiency of this sorbent in the removal of Co(II) ions from the aqueous solutions. Biosorption affected by various parameters, such as biomass concentration, pH and temperature was studied. The kinetic studies revealed that the

biosorption process followed the pseudo-second order kinetic model. Adsorption isotherm models such as Freundlich, Langmuir and Temkin models to the biosorption data of Co(II) for evaluation of adsorption efficiency of the biosorbent. The maximum biosorption capacity of Co(II) was 9.47 mg/g at 25 ± 2 °C with 2 g L⁻¹ adsorbent dosage and an optimum pH 6.5, which indicating that the present biomass was considered to be promising and potential biosorbent for the removal of Co(II). The biosorption capacity of present SCFP was near or more than the reported results of various biosorbents sorption capacity. This may be successful application for the regular adsorption/biosorption of metal ions in the large scale from metallurgical industries.

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