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Adsorption of Divalent Cobalt from Aqueous Solution onto Chitosan–Coated Perlite Beads as Biosorbent

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Abstract: Chitosan coated perlite beads are prepared by drop-wise addition of a liquid slurry containing chitosan and perlite to an alkaline bath. The resulting beads are characterized using FTIR, SEM, EDXRF, and Surface area analysis and the chitosan content of the beads is 23% as determined by a pyrolysis method. Adsorption of Co (II) metal ions from aqueous solution on chitosan coated perlite beads is studied under both equilibrium and dynamic conditions. In the present investigation, a first order reversible rate equation is used to understand the kinetics of metal removal and to calculate the rate constants at different initial concentrations. The equilibrium characteristics of metal ion on newly developed biosorbent are studied and the experimental adsorption data are well fitted to Freundlich and Langmuir adsorption isotherm models and the model parameters are evaluated. The effect of pH, agitation time, concentration of adsorbate, and amount of adsorbent on the extent of the adsorption are investigated. The sorbent loaded with metal is regenerated with 0.10 mol dm^{-3} sodium hydroxide solution. The adsorption desorption cycles indicated that the chitosan coated perlite could be regenerated and reused to remove Co (II) from waste water.

Keywords: Adsorption, desorption, chitosan, perlite, cobalt

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INTRODUCTION

The negative effect of the generation and the disposal of residues in the environment has intensified researches aiming the development of clean technologies and treatment strategies for these pollutants. Industrial rejects containing synthetic organic compounds and heavy metals are amongst the most dangerous residues, increases in generation due to expansion of the industrial activities and the base manufacture sector (1). Heavy metals are readily assimilated into the food chain and therefore are easily accumulated in the ecosystem. When the concentration levels of these metals in the environment rise above the values determined by environmental agencies, degradation of the natural resources will occur (2). The treatment of wastewaters containing heavy metal could be achieved with settling as settleable metal hydroxides, activated carbon adsorption, ion exchange, reverse osmosis, electrochemical treatment, evaporation, and biological methods. However, in many situations, these processes do not work efficiently. For example, heavy metal precipitation produces sludges that must be treated and disposed of, normally at high cost. Similarly, the use of commercially available activated carbon is limited, especially to developing countries, because of its relatively high cost and the difficulties associated with its regeneration (3). New technologies are currently being researched, such as biotechnological processes, in order to reduce ambient pollution, combining with low costs and high efficiency in heavy metal removal (4).

Biosorption of heavy metals from aqueous solutions is a relatively new technology for the treatment of industrial wastewater (5). Adsorbent materials (biosorbents) derived from suitable biomass can be used for the effective removal and recovery of heavy metal ions from wastewater streams. The major advantage of biosorption technology is its effectiveness in reducing the concentration of heavy metal ions to very low levels using inexpensive biosorbent materials. Therefore, new types of biosorbent materials able to effectively sequester heavy metals have been explored (6, 7).

Chitosan (2-acetamido-2-deoxy- β -D-glucose, (N-acetylglucan)) is a partially deacetylated polymer of chitin and a major component of arthropods, and is readily available from sea food processing wastes (8, 9). Because chitosan has unique physiological and biological properties, it has been widely used as a versatile starting material for the preparation of various products in biomedical engineering (10). In recent years, chitosan has also increasingly been studied as an adsorbent for the removal of heavy metal ions from aqueous solutions because the amino and hydroxyl groups on the chitosan chain act as a chelation or reaction site for the substances to be removed (11–13).

Several investigators have attempted to modify chitosan to facilitate mass transfer, to expose the active binding sites and to enhance the adsorption capacity. Kawamura et al. (14) studied the adsorption of Cu (II) and Ni (II) on polyaminated, highly porous chitosan chelating resin. Caihua and Yuwu (15) synthesized a series of resins based on chitosan and investigated

adsorption capacity, adsorption rate and selectivity of different metal ions. EDTA- and DTPA-chitosan (16) are prepared and the adsorption characteristics for Cu (II) and Ni (II) ions are examined. Crosslinked chitosan acetate crown ethers (17) and grafted chitosan diamine crown ethers (18) are synthesized and the adsorption capacity for different metal ions is evaluated. Schmuhl et al. (19) studied the adsorption capacity of crosslinked and uncross-linked chitosan for Cu (II) and Cr (VI) ions. Nickel imprinted chitosan resin (20) and crosslinked chitosan with copper as templates (21) are prepared to improve the adsorption capacity and selectivity for trace metal ions.

Batch isothermal equilibrium and continuous column adsorption experiments are conducted to evaluate, a new composite chitosan, for the removal of hexavalent chromium from synthetic as well as field samples obtained from chrome plating industries by Boddu, et al. (22). Thus, several studies are conducted to improve the properties of chitosan and to enhance its adsorption capacity and selectivity for trace metal ions. Very few attempts are made to coat chitosan on a supporting material and to characterize its adsorption capacity (23, 24).

In the present investigation an attempt is made to synthesize a new composite biosorbent by coating chitosan on the surface of perlite, an inorganic porous alumino-silicate and formed into beads. It is expected that the swelling and gel formation of chitosan can be reduced in this way, thus allowing regeneration and repeated use of the chitosan adsorbent in a column. The chitosan coated perlite beads (CHCP) are characterized by using FTIR, SEM and EDXRF, BET, and pyrolysis studies. A simple and economic preparation of the adsorbent is performed and adsorption experiments are conducted to determine the metal adsorption mechanisms. Then, models are used to describe the experimental kinetics and isotherms. The kinetic and equilibrium parameters calculated, such as the maximum fixation capacities, are tentatively correlated to the adsorption capacity of Co (II). Finally, the influence of pH and amount of adsorbent dose parameters on the metal adsorption are also studied.

EXPERIMENTAL

Materials

Perlite is not a trade name but a generic term for naturally occurring siliceous rock. Perlite, which is composed mainly of alumina and silica, is used as a substrate for the preparation of beads. The distinguishing feature, which sets perlite apart from other volcanic glasses, is that, when heated to a suitable point in its softening range, it expands from four to twenty times of its original volume. This expansion process also creates one of perlite's most distinguishing characteristics, its white color, while the crude rock may range from transparent light gray to glassy black. The expanded form of perlite is obtained from Silbrico

Corporations, IL, USA. Chitosan, cobalt sulphate are procured from Aldrich Chemical Corporation. Oxalic acid and sodium hydroxide are purchased from Fisher Scientific Company. A stock solution containing 1000 ppm of Co (II) is prepared using double distilled water. All the working solutions are obtained by diluting the stock solution with double distilled water.

Preparation of Chitosan Coated Perlite Beads

Perlite is first mixed with 0.20 mol dm^{-3} oxalic acid and the mixture is stirred for 12 h at room temperature and filtered. The filtered perlite is washed with deionized water, dried overnight at 70°C , and sieved through 100-mesh size. The acid treated perlite is stored in desiccator. About 30 g of medium molecular weight chitosan is slowly added to 1L of 0.20 mol dm^{-3} oxalic acid solution under continuous stirring at $40\text{--}50^\circ\text{C}$ to facilitate the formation of viscous gel. About 60 g of acid treated perlite powder is mixed with deionized water and slowly added to the diluted gel and stirred for 12 h at $40\text{--}50^\circ\text{C}$. The highly porous beads are then prepared by drop wise addition of perlite gel mixture into a 0.70 mol dm^{-3} NaOH precipitation bath (25). The purpose of adding acidic perlite-chitosan mixture to NaOH solution is to assist rapid neutralization of oxalic acid, so that the spherical shape could be retained. The beads are separated from NaOH bath, and washed several times with deionized water to a neutral pH. The beads are dried in a freeze drier oven and by air.

Experimental Procedure

Batch Equilibrium Studies

In order to explore the effect of influencing factors, such as pH, contact time, the quantity of the adsorbent, and the initial concentrations of metal solution, a series of batch experiments are conducted. The stock solution is diluted to required concentrations (50, 100, 150, and 200 ppm). Batch adsorption experiments are performed by agitating a specified amount of adsorbent in 100 ml of metal solution of desired concentration at varying pH in 100 ml stopper bottles. The pH of the suspension is adjusted with 0.10 mol dm^{-3} HCl and 0.10 mol dm^{-3} NaOH. The reaction mixture is agitated at 100 rpm for a known period of time at room temperature in a mechanical shaker. After equilibrium, the aqueous-phase concentration of metal is analyzed with flame atomic absorption spectrometer (FAAS) (Perkin-Elmer 2380) with a deuterium background corrector. All measurements are carried out in an air/acetylene flame. A 10 cm long slot-burner head, a lamp, and an air acetylene flame are used. The operating parameters for the working elements are set as recommended by the manufacturer. Adsorption of metal on the glassware is found to be negligible and is determined by running blank experiments. Each experiment is repeated at least 3 times and mean values are taken. The

absolute deviation is found to be 3.0%. The amount adsorbed per unit mass of adsorbent at equilibrium ' Q_e ' (mg g⁻¹) is obtained using the equation.

$$Q_e = \left(\frac{C_o - C_e}{m} \right) v \quad (1)$$

where C_o and C_e denote the initial and equilibrium metal ion concentrations (ppm) respectively. v is the volume of the solution in liters and m is the mass of the adsorbent used (g).

Column Adsorption and Desorption Studies

Column studies are carried out in a column made of pyrex glass of 1.35 cm id and 15.0 cm length. The column is filled with 1 g of the chitosan coated perlite beads by tapping so that the column is filled without gaps. The influent solution containing known concentration of an aqueous metal solution is allowed to pass through the bed at constant flow rate, 0.016 cm³ s⁻¹, in down flow manner. All the experiments are carried out at room temperature. The effluent solution is collected at different time intervals and the concentration of the metal ion in the effluent solution is monitored by FAAS. The effluent solution is diluted appropriately prior to analysis.

After the column is exhausted, the column is drained off the remaining aqueous solution by pumping air. Desorption of solutes from loaded adsorbent are carried out by solvent elution method using 0.10 mol dm⁻³ NaOH as an eluent. Then a sodium hydroxide solution is pumped into the column and maintained at constant temperature at a fixed flow rate (0.016 cm³ s⁻¹). From the start of the experiment effluent samples at different intervals, are collected at the bottom of the column for analysis. After the regeneration, the adsorbent column is washed with distilled water to remove sodium hydroxide from the column before the influent metal solution is reintroduced for the subsequent adsorption–desorption cycle. Thus, adsorption–desorption cycles are performed thrice using the same bed to check the sustainability of the bed for repeated use. Breakthrough curves for cobalt are obtained by plotting the volume of the effluent versus the ratio of the column outlet concentration to the initial concentration, $C_{\text{outlet}}/C_{\text{inlet}}$.

RESULTS AND DISCUSSION

Characterization of Chitosan Coated Perlite (CHCP) Beads

Pyrolysis Studies

The amount of chitosan coated on perlite is obtained by measuring the weight loss of biosorbent from pyrolysis. These experiments are conducted at high

temperature (800°C) to determine the amount of chitosan coated over perlite. Two ceramic crucibles, one containing acid washed pure perlite and the other containing chitosan coated perlite (CHCP) beads, are placed inside a furnace heated to 800°C. The chitosan burnt out at this temperature and the chitosan content is determined from the weight difference. The results indicated that 23% of chitosan is coated over perlite. The surface morphology of the pure perlite appears to change significantly following coating with chitosan.

Fourier Transform Infrared (FTIR) Studies

The FTIR spectrum provides some understanding of the adsorption mechanism of metal ions by chitosan. Figure 1 represents the FTIR spectrum of chitosan. The broad band around 3550 cm^{-1} indicates the presence of NH_2 and OH groups. The absorption band around 1050 cm^{-1} may be attributed to $-\text{C}-\text{O}-\text{C}-$ stretching frequency, which indicates the presence of a pyranose ring. The peaks at these wave numbers are intact, indicating that the functional groups are not disturbed during the coating process. Moreover, the lone pairs of electrons present in OH and NH_2 groups involve in the complexation with metal ion (26). Hence the absorption bands for OH and NH_2 are shifted from 3550 cm^{-1} to 3450 cm^{-1} (Fig. 2) after adsorption of cobalt. This result confirms the participation of unprotonated amino and hydroxyl groups as active binding sites for the adsorption of metals on chitosan. Formation of a complex between chitosan and metal ion is shown in Fig. 3.

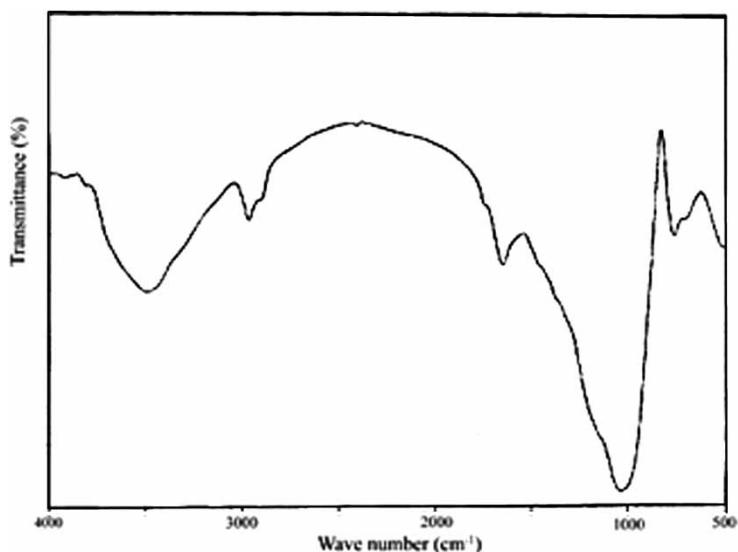


Figure 1. FTIR spectrum of chitosan coated perlite beads.

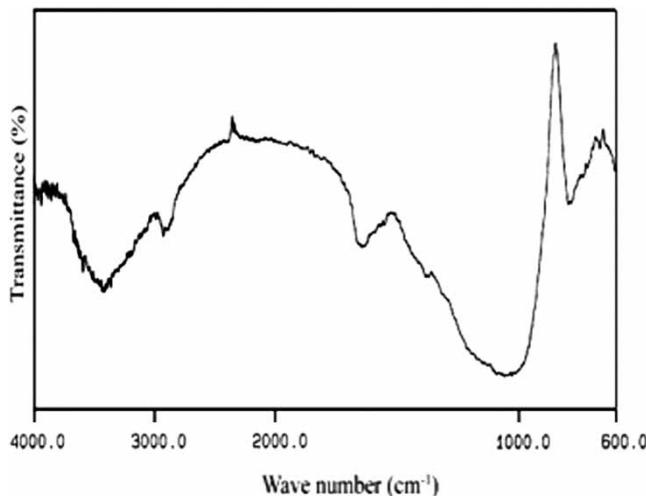


Figure 2. FTIR spectrum of chitosan coated perlite beads after adsorption of Co (II).

Physical and Chemical Characteristics of CHCP Beads

The surface area, density, pore volume, pore diameter, and porosity of the composite biosorbent are determined with BET and pycnomatic ATC instruments. The surface area is measured by assuming that the adsorbed nitrogen forms a monolayer and posses a molecular cross sectional area of 0.162 nm^2 . The isotherm plots are used to calculate the specific surface area (N_2/BET method) and average pore diameter of CHCP, while micropore volume is calculated from the volume of nitrogen adsorbed at $p/p_0 = 1.4$. The sorbent material shows an average surface area of $112.25\text{ m}^2\text{ g}^{-1}$ and pore volume of $0.47\text{ cm}^3\text{ g}^{-1}$. The ion exchange capacity of CHCP beads is determined by using an ionometer in which the amino groups exchanged by the sodium ions with the use of NaOH electrolyte. The physical and chemical characteristics of CHCP are summarized in Table 1.

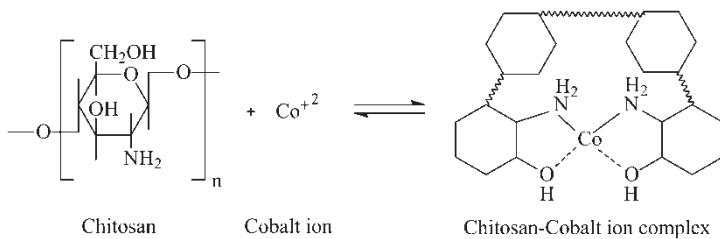


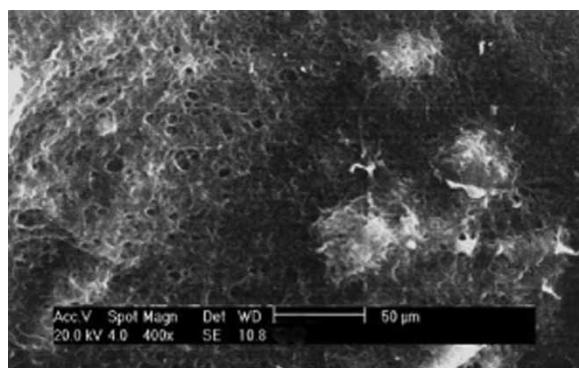
Figure 3. Formation of complexation between chitosan and cobalt ion.

Table 1. Surface properties of chitosan coated perlite (CHCP) beads

S. no.	Property	Chitosan coated perlite
1	Surface area ($\text{m}^2 \text{ g}^{-1}$)	112.25
2	Porosity (%)	43.41
3	Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	0.47
4	Pore diameter (cm g^{-1})	0.97
5	Density (g cm^{-3})	3.13
6	Ion exchange capacity (mmol g^{-1})	0.92

Scanning Electron Microscopic (SEM) Studies

Scanning electron micrographs (SEM), recorded using a software controlled digital scanning electron microscope, are given in Figs. 4 to 6. The SEM of various samples is taken to study the surface morphology. The surface morphology of the pure perlite appears to change significantly following coating with chitosan. The SEM micrograph of the outer surface of CHCP beads is shown in Fig. 4. The average size of particles is 100–150 μ and that the shape of composite particle can be described as spherical. The figure also illustrates the surface texture and porosity of CHCP beads with holes and small openings on the surface, thereby increasing the contact area, which facilitates the pore diffusion during adsorption. The beads are cut into half and then the SEM of the internal surface is recorded and included in Fig. 5. The porous nature is clearly evident from this micrograph. The surface morphology and texture of coated perlite are completely different compared to the uncoated perlite. The inner surface appears to have a similar type of texture and morphology as the outer surface. Figure 6 describes the

**Figure 4.** SEM of outer surface of chitosan coated perlite bead.

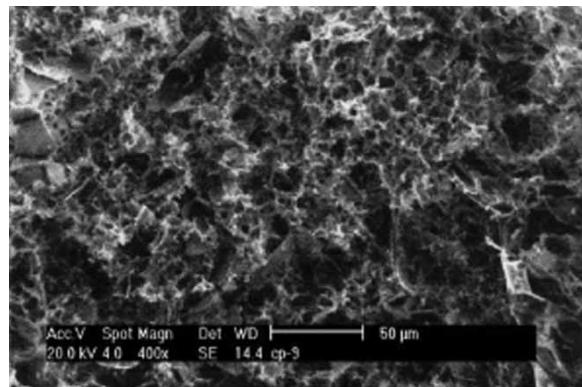


Figure 5. SEM of cross section of chitosan coated perlite bead.

surface characteristics and morphology of the beads after their exposure to Co (II) metal solution. It can be observed that there is a change in the morphology of the beads after adsorption. Surface morphological studies revealed that the process of metal adsorption on CHCP beads is predominantly a surface phenomenon and this is confirmed by the SEM images.

Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometry Analysis

Energy dispersive X-ray fluorescence (EDXRF) spectroscopy, a non-destructive analytical technique, allows the simultaneous identification of elements in different matrices (27, 28). In the present study the ED X-ray microanalysis is performed to investigate the elements present on chitosan

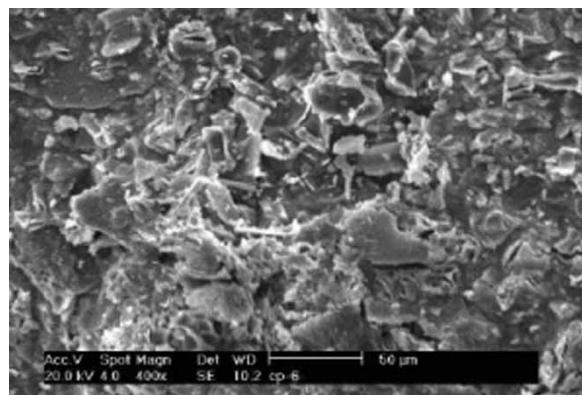


Figure 6. SEM of chitosan coated perlite after adsorption of Co (II).

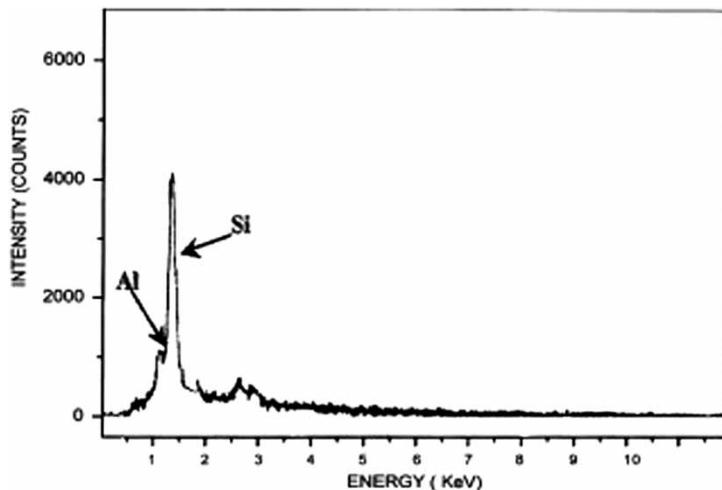


Figure 7. EDXRF spectrum of unexposed chitosan coated perlite.

beads before and after their exposure to metal solution. The EDXRF spectrum of unexposed CHCP beads is presented in Fig. 7. The ED X-ray microanalysis shows peaks assigned to aluminum and silicon, which are the two major constituents of perlite. The EDXRF spectrum of CHCP treated with aqueous metal solution of Co (II) shows the presence of peaks of different metal ions as seen in Fig. 8. This observation provides evidence for metal uptake by chitosan. Strong peaks of K_{α} and K_{β} values at 6.92 and 7.69 KeV are due to adsorption of Co (II). It is evident from the SEM and ED X-ray

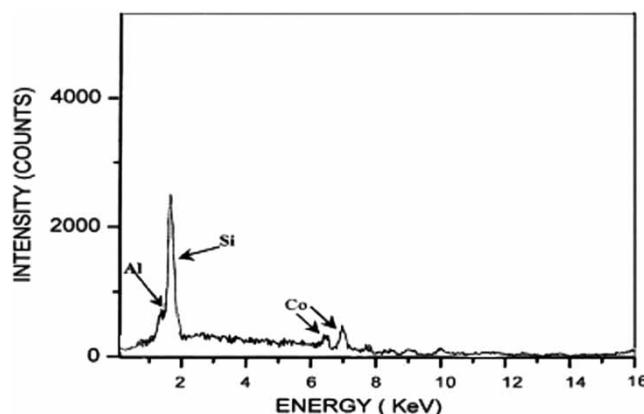


Figure 8. EDXRF spectrum of chitosan coated perlite after adsorption of Co (II).

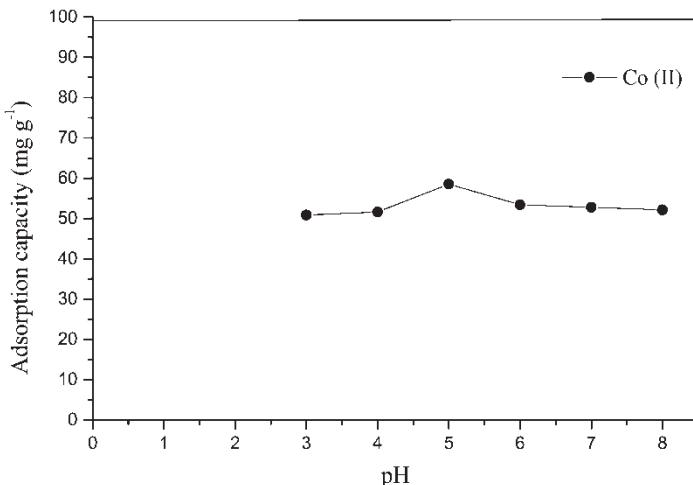


Figure 9. Effect of pH on adsorption of Co (II) on chitosan coated perlite beads.

microanalysis that highly porous chitosan beads are capable of adsorbing metal ions from their aqueous solution.

Effect of pH on Metal Adsorption

Metal ion adsorption on the sorbent material is pH dependent. In order to optimize the pH for maximum removal efficiency, experiments are conducted at a wide range of pH from 3 to 8 using 0.1 g of CHCP beads with 100 ml of 100 ppm metal solution at room temperature. These results are graphically represented in Fig. 9. The results indicate that the extent of adsorption varies with pH. Under acidic conditions (below pH 3) the chitosan undergoes dissolution. Due to this dissolution, experiments are conducted above pH 3. There is no considerable change in the adsorption capacity of cobalt with increase in solution pH 3.0 to 8.0. It is observed that at higher pH values above 8.0, Co (II) ions are precipitates as their insoluble hydroxides. Nevertheless, it has to be mentioned that at alkaline region, metals precipitate as insoluble hydroxides (29).

Sorption Kinetics

Sorption kinetics is an important physicochemical parameter to evaluate the basic qualities of a good sorbent. Data on removal of Co (II) by CHCP beads as a function of time at pH 5.0 at various initial concentrations (50–200 ppm) are represented graphically in Fig. 10. From this figure it is observed that the adsorption capacity of Co (II) increased monotonically to saturation with time and maximum adsorption is attained at 150 min.

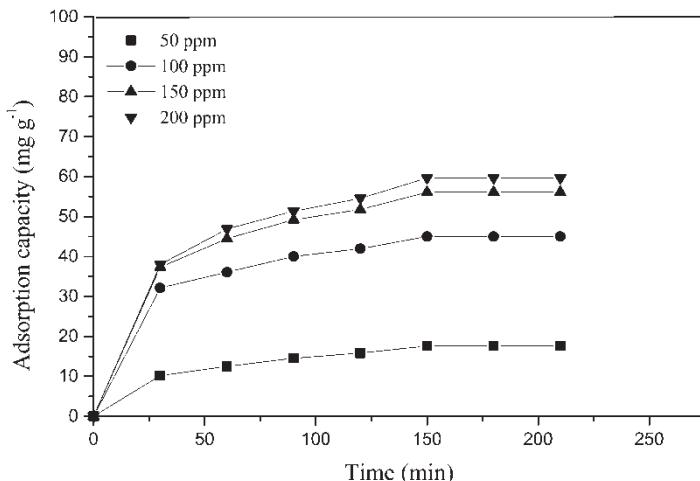


Figure 10. Effect of agitation time on adsorption of Co (II) on chitosan coated perlite beads at different initial concentrations.

Therefore, these times are sufficient to attain equilibrium for the maximum removal of Co (II) from aqueous solution on CHCP beads. The kinetics of adsorption of these metal ions on CHCP beads is determined using the Lagergren's equation.

$$\log (Q_e - Q_t) = \log Q_e - \left(\frac{K_{ad}}{2.303} \right) t \quad (2)$$

where Q_e is the amount of sorbate adsorbed per unit weight of sorbent at equilibrium (mg g^{-1}), Q_t is the amount of sorbate uptake per unit weight of sorbent at any time t (mg g^{-1}), t is the time in minutes, and K_{ad} is the rate constant of adsorption. The values of K_{ad} , calculated from the slopes of the plot of $\log (Q_e - Q_t)$ versus t , are given in Table 2 along with the correlation coefficients (R^2). There is no significant change in the values of K_{ad} at various concentrations of Co (II). From this observation it may be concluded that the adsorption of this metal on the CHCP beads follows first order kinetics.

Effect of Adsorbent Dose

The dependence of adsorption of Co (II) on the amount of CHCP beads is studied by varying the adsorbent doses from 0.05 g to 0.5 g, at room temperature and at the optimal pH, while keeping the volume and concentration of the metal solution constant. The results are graphically represented in Fig. 11. It is apparent that the percent removal of Co (II) increases rapidly with increase in the dose of the adsorbent. The extent of adsorption attains maximum with

Table 2. Adsorption rate constants of Lagergren plots for Co (II) on chitosan coated perlite beads

Initial concentrations of metal solution (ppm)	Co (II) metal ion	
	K_{ad}	R^2
50	0.0160	0.997
100	0.0168	0.996
150	0.0172	0.997
200	0.0160	0.999

0.4 g of CHCP beads and the maximum percentage removal is about 94.6% with CHCP.

Equilibrium Modeling

Modeling of equilibrium data is a fundamental aspect for the industrial application of biosorption since it gives information for comparison among different biomaterials under different operational conditions and also enables to optimize design and operation procedures (30). To examine the relationship between the amount sorbed (Q_e) and aqueous concentration (C_e) at equilibrium, sorption isotherm models are widely employed. Among them the Langmuir and Freundlich equations are the most widely used. To get the equilibrium data (Q_e and C_e) experiments are conducted by varying initial concentrations of Co (II) ranging from 10–100 ppm at the optimal

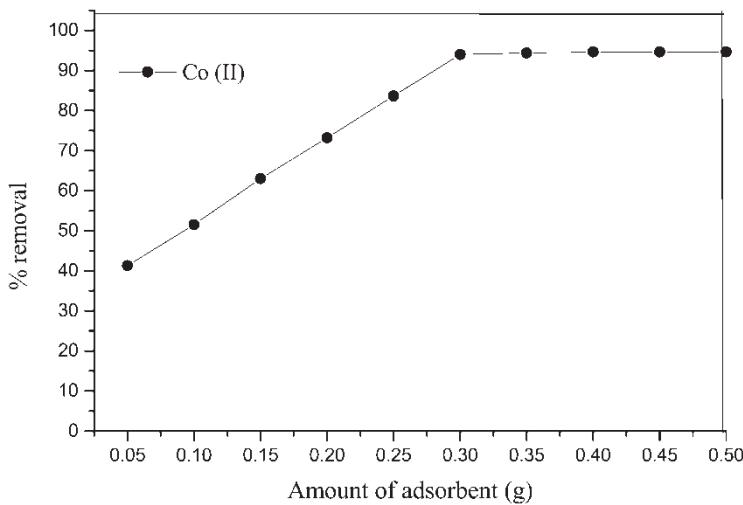


Figure 11. Effect of dose of adsorbent (CHCP beads) on percent removal of Co (II).

pH value, while the biomass weight in each sample (0.1 g) is kept constant. The Langmuir isotherm is based on the assumption of monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate on the plane of the surface. The experimental data are fitted to the Langmuir isotherm equation,

$$Q_e = \frac{Q^o b C_e}{1 + b C_e} \quad (3)$$

where Q_e is the amount of metal adsorbed (mg g^{-1}), C_e is the equilibrium concentration of metal ion (ppm), Q^o and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The equilibrium data are also fitted to Freundlich equation, which takes the form,

$$Q_e = K_f C_e^{1/n} \quad (4)$$

where K_f and n are Freundlich constants. Experimental data of the present study are fitted to equation (4) and the parameters (K_f and n) are evaluated from the plot of $\log Q_e$ versus $\log C_e$. The Langmuir and Freundlich adsorption isotherms are shown in Figs. 12 and 13. The values of Langmuir constants Q^o and b and Freundlich parameters K_f and n along with the correlation coefficients (R^2) are presented in Table 3. Among, these two models, the experimental data are well-fitted to the Langmuir model compared to Freundlich model.

Column Adsorption Studies

Metal biosorption dynamics in a fixed bed flow through a sorption column is eventually conducted for multiple reuse of the biosorbent. Column adsorption

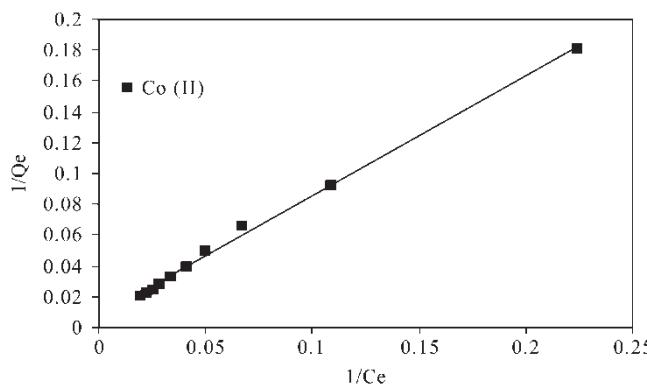


Figure 12. Langmuir isotherms for adsorption of Co (II) on chitosan coated perlite beads.

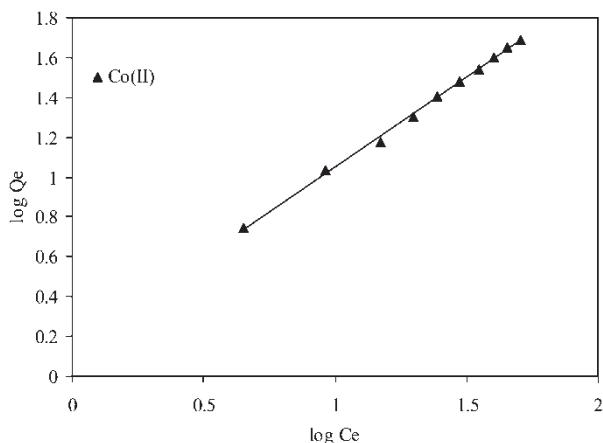


Figure 13. Freundlich isotherms for adsorption of Co (II) on chitosan coated perlite beads.

studies of Co (II) on CHCP beads at room temperature are investigated using aqueous solution at 99.51 ppm influent concentrations (C_o), at the optimal pH value (5.0). Experimental breakthrough curves, obtained by plotting a graph between the ratio of effluent concentration to initial concentration versus the volume of the effluent, are shown in Fig. 14. The measurement of the sorbent mass is more precise than the determination of the respective volume. Therefore, the sorbent quantity is being preferably used instead of the bed height (31). These data are obtained by passing the single metal ion solution through a bed packed with 1 g of CHCP beads in a downward flow at a rate of $0.016 \text{ cm}^3 \text{ s}^{-1}$ and determining the concentration of metal ions at different time intervals in the effluent solution. When the column gets saturated, it is regenerated and subsequently used for the next adsorption process. The adsorption–desorption cycles are repeated thrice.

Breakthrough is supposed to be attained when the concentration of solute in the effluent is equal to the influent concentration and remains unchanged there on (32). Faster and effective adsorption of Co (II) occurs during the initial phase. Subsequent metal adsorption decreases as a consequence of

Table 3. Parameters of Langmuir and Freundlich isotherms for adsorption of Co (II) on chitosan coated perlite beads

Metal ion	Langmuir constants			Freundlich constants		
	Q^o	b	R^2	K_f	n	R^2
Co (II)	135.1	0.0095	0.9967	1.406	1.108	0.9978

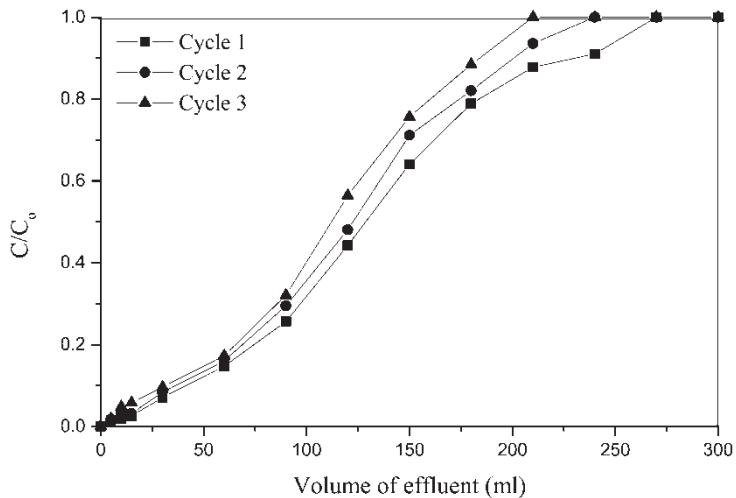


Figure 14. Column break through curves for adsorption of Co (II) on chitosan coated perlite beads.

the progressive saturation of the binding sites. It is observed that the column gets saturated after passing 270 ml of Co (II) metal solution in the first cycle. The adsorption capacity of the biosorbent is obtained by dividing the concentration of metal adsorbed by the total amount of biosorbent used. From the data it can be concluded that CHCP beads are a good biosorbent for the removal of cobalt from aqueous medium.

Desorption Studies

When the bed gets exhausted or the effluent coming out of the column reaches the allowable maximum discharge level, the regeneration of adsorption bed to recover the adsorbed material and/or to regenerate the adsorbent becomes quite essential. The regeneration could be accomplished by a variety of techniques such as thermal desorption, steam washing, solvent extraction etc. Each method has inherent advantages and limitations. In this study several solvents are tried to regenerate the adsorption bed. 0.10 mol dm^{-3} NaOH solution is found to be effective in desorbing and recovering metal ions quantitatively from the adsorption bed. NaOH is used as a solvent of choice because of its solubility parameters and solvation forces of NaOH outweigh the attractive forces of CHCP for metal ions. Desorption of these divalent metal ions from CHCP is believed to be mainly due to deprotonation of chitosan amine groups above pH 10. Due to this, metal ions migrate from the adsorbed state to the solvent phase. The fixed bed columns of CHCP beads saturated with Co (II) is regenerated by passing 0.10 mol dm^{-3} NaOH solution as an eluant at a fixed flow rate of $0.016 \text{ cm}^3 \text{ s}^{-1}$. To evaluate the

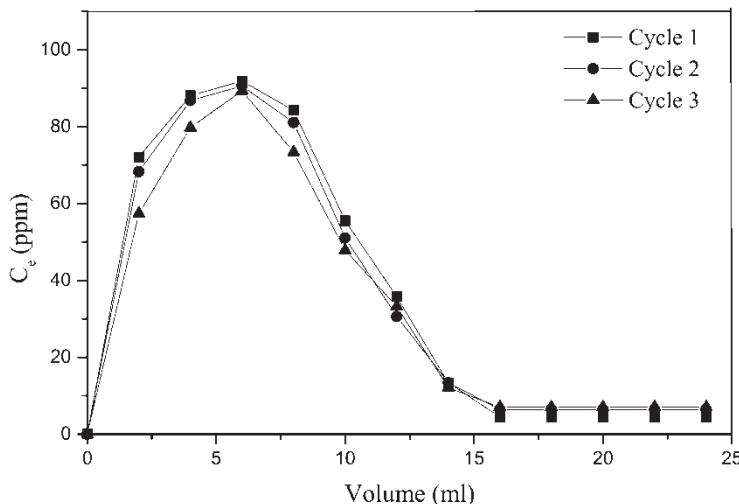


Figure 15. Regeneration curves of chitosan coated perlite beads loaded with Co (II).

metal recovery efficiency, the percentage of metal ions recovered is calculated from the breakthrough and recovery curves. More specifically, maximum desorption occurs at 6 ml of 0.10 mol dm^{-3} NaOH solution and complete regeneration of metal ions occurs at about 16 ml. These adsorption–desorption cycles are repeated thrice. It is observed that there is an early saturation of the bed with metal ion in 2nd and 3rd cycles. The desorption profile is graphically represented in Fig. 15. From the plots it is observed that the rate of desorption increases sharply reaching maximum with 6 ml of 0.10 mol dm^{-3} NaOH and decreases attaining minimum with about 16 ml 0.10 mol dm^{-3} NaOH solution. The regenerated column is further used for the removal of Co (II). The results indicate that the column gets saturated early and the adsorption capacity decreases slightly. As a result the percent desorption also decreases from first cycle to second cycle. Similar behavior is observed in case of third cycle of adsorption–desorption experiments.

CONCLUSION

Chitosan is effectively coated on an inert substrate, perlite, and is made in the form of spherical beads. Pyrolysis results indicated that 23% of chitosan is coated on perlite. The aim of this work is to find the biosorption characteristics of CHCP beads as a successful biosorbing agent for the removal of cobalt from aqueous solutions. EDXRF, FTIR studies of beads that are exposed to cobalt solution indicated that amine and hydroxyl groups are the main adsorption sites for the cobalt ions. SEM micrographs and surface area analysis studies

of chitosan coated adsorbent showed highly porous in nature. Experiments are performed as a function of pH, agitation time, initial metal ion concentration, and the amount of the adsorbent. Maximum removal of Co (II) on CHCP is at pH 5.0. The Langmuir adsorption model and the Freundlich model are used for the mathematical description of the biosorption of Co (II) ions onto chitosan biomass. It is seen that the adsorption equilibrium data fitted very well to both the models. The results show that chitosan is good adsorbing media for metal ion and had high adsorption yields for the treatment of wastewater containing Co (II) ions. Consequently, chitosan biosorption technologies are still being developed and much more work is required. Some practical applications have been achieved, and the fundamentals look promising: chitosan have the potential to remove metal ions to very low concentration and to accumulate large amounts of specific toxic elements. But, very little comparative or comparable information, especially economical analysis, are available.

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REFERENCES

1. Braile, P.M. and Cavalcanti, J.E.W. (1993) *Manual of Industrial Wastewater Treatment in São Paulo*; CETESB publication: p. 180, (in Portuguese).
2. Amorim, W., Hayashi, A.M., Pimentel, P.F., and Da Silva, M.G. C. (2003) A study of the process of desorption of hexavalent chromium. *Braz. J. Chem. Eng.*, 20: 132.
3. Lalvani, S.B., Wiltowski, T., Hubner, A., Weston, A., and Mandich, N. (1998) Removal of hexavalent chromium and metal cations by a selective and novel carbon adsorbent. *Carbon*, 36: 1219–1226.
4. Costa, A.C.A., Gonçalves, M.M.M., Mesquita, L.M.S., and Granato, M. (1995) Effluent treatment to remove heavy metals using biological resin. *Metalurgia and Materials*, 51: 872, (in Portuguese).
5. Volesky, B. (2001) Detoxification of metal-bearing effluents: biosorption for the next century. *Hydrometallurgy*, 59: 203.
6. Chang, J.S., Law, R., and Chang, C.C. (1997) Biosorption of lead, copper and cadmium by biomass of *Pseudomonas aeruginosa* PU21. *Water Res.*, 31: 1651.
7. Pagnanelli, F., Mainelli, S., and Toro, L. (2005) Optimization and validation of mechanistic models for heavy metal bio-sorption onto a natural biomass. *Hydrometallurgy*, 80: 107.

8. Chen, J.P. and Chang, K.C. (1994) Immobilization of chitinase on a reversibly soluble-insoluble polymer for chitin hydrolysis. *J. Chemical Technol. Biotechnol.*, 60: 133.
9. Ilyina, A.V., Tikhonov, V.E., Varlamov, V.P., Radigina, L.A., Tatarinova, N.Y., and Yamskov, I.A. (1995) Preparation of affinity sorbents and isolation of individual chitinases from a crude supernatant produced by *Streptomyces kurssanovii* by a one-step affinity chromatographic system. *Biotechnol. Applied Biochem.*, 21: 139.
10. Nomanbhay, S.M. and Palanisamy, K. (2005) Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. *Electronic J. Biotechnol.*, 8: 43.
11. Jeon, C. and Holl, W.H. (2004) Application of the surface complexation model to heavy metal sorption equilibria onto aminated chitosan. *Hydrometallurgy*, 71: 421.
12. Inoue, K., Yoshizuka, K., and Baba, Y. (1996) Adsorption of metal ions on chitosan and its derivatives. In *New Development in Ion Exchange*; Abe, M. and Suzuki, T. (eds.); Kodansha: Tokyo, 543.
13. Juang, R.S. and Ju, C.Y. (1998) Kinetics of sorption of Cu(II)-thylenediamine-tetraacetic acid chelated anions on cross-linked, polyaminated chitosan beads. *Ind. Eng. Chem. Res.*, 37: 3463.
14. Kawamura, Y., Mitsuhashi, M., Tanibe, H., and Yoshida, H. (1993) Adsorption of metal ions on polyaminated highly porous chitosan chelating resin. *Ind. Eng. Chem. Res.*, 32: 386.
15. Caihua, N. and Yuwu, X. (1996) Studies on syntheses and properties of chelating resins based on chitosan. *J. Appl. Polym. Sci.*, 59: 499.
16. Inoue, K., Yoshizuka, K., and Ohto, K. (1999) Adsorptive separation of some metal ions by complexing agent types of chemically modified chitosan. *Anal. Chim. Acta*, 388: 209.
17. Tan, S., Wang, Y., Peng, C., and Tang, Y. (1999) Synthesis and adsorption properties for metal ions of crosslinked chitosan acetate crown ethers. *J. Appl. Polym. Sci.*, 71: 2069.
18. Yang, Z., Wang, Y., and Tang, Y. (2000) Synthesis and adsorption properties for metal ions of mesocyclic diamine-grafted chitosan-crown ether. *J. Appl. Polym. Sci.*, 75: 1255.
19. Schmuhl, R., Krieg, H.M., and Keizer, K. (2001) Adsorption of Cu(II) and Cr(VI) ions by chitosan: Kinetics and equilibrium studies. *Water SA*, 27: 1.
20. Tianwei, T., Xiaojing, H., and Weixia, D. (2001) Adsorption behavior of metal ions on imprinted chitosan resin. *J. Chem. Technol. Biotechnol.*, 76: 191.
21. Zuoying, C., Huacai, G., and Shengli, L. (2001) Studies on synthesis and adsorption properties of chitosan cross-linked by glutaraldehyde and Cu (II) as template under microwave irradiation. *European Polym. J.*, 37: 2141.
22. Boddu, V.M., Krishnaiah, A., Jonathan, L.T., and Smith, E.D. (2003) Removal of hexavalent chromium from wastewater using a new composite chitosan biosorbent. *Environ. Sci. Technol.*, 37: 4449.
23. Kalyani, S., Priya, A.J., Rao, S.P., and Krishnaiah, A. (2005) Removal of copper and nickel from aqueous solutions using chitosan coated perlite as biosorbent. *Sep. Sci. Technol.*, 40: 1483.
24. Hasan, S., Krishnaiah, A., and Ghosh, T.K., Viswanath, D. S., Boddu, V. M., Smith, E. D. (2006) Adsorption of divalent cadmium (cd(II)) From aqueous solutions onto chitosan-coated Perlite beads. *Ind. Eng. Chem. Res.*, 45: 5066.
25. Kawamura, Y., Yoshida, H., Asai, S., Kurahashi, I., and Tanibe, H. (1997) Effects of chitosan concentration and precipitation bath concentration on the material properties of porous crosslinked chitosan beads. *Sep. Sci. Technol.*, 32: 1959.

26. Oyrton, A.C., Montciro Jr, and Aioldi, C. (1999) Some thermodynamic data on copper-chitin and copper-chitosan biopolymer interactions. *J. Colloid. Interface Sci.*, 212: 212.
27. Aravindhan, R., Madhan, B., Rao, J.R., Nair, B.U., and Ramasami, T. (2004) Bioaccumulation of chromium from tannery wastewater: an approach for chrome recovery and reuse. *Environ. Sci. Technol.*, 38: 300.
28. Lindgren, E. (2000) *X-ray Fluorescence Analysis Energy Dispersive in Encyclopedia of Analytical Chemistry*; John Wiley and Sons: Chichester.
29. Reddad, Z., Gerete, C., Andres, Y., Ralet, M.C., Thibault, J.F., and Cloirec, P.L. (2002) Ni(II) and Cu(II) binding properties of native and modified sugar beet pulp. *Carbohydr. Polym.*, 49: 23.
30. Benguella, B. and Benaissa, H. (2002) Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies. *Water Res.*, 36: 2463.
31. Hawari, H.A. and Mulligan, C.N. (2006) Heavy metals uptake mechanisms in a fixed-bed column by calcium-treated anaerobic biomass. *Process Biochem.*, 41: 187.
32. Vijayaraghavan, K., Jegan, J., Palanivelu, K., and Velan, M. (2005) Biosorption of copper, cobalt and nickel by marine green alga *Ulva reticulata* in a packed column. *Chemosphere*, 60: 419.