

Equilibrium and thermodynamic studies of Cd (II) biosorption by chemically modified orange peel

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Abstract

Agricultural wastes have great potential of removing heavy metal ions from aqueous solution. Removal of Cd (II) from aqueous solutions onto chemically modified orange peel was studied at different pH, contact time, initial metal concentrations, adsorbent doses and temperature. Batch experiments were carried out under optimized conditions to evaluate the adsorption capacity of orange peel chemically modified with NaOH. The results showed that maximum adsorption capacity of modified orange peel, approximately 97.0 %, was observed 3 mg l⁻¹ of initial Cd(II) concentration pH 6 for 4 g l⁻¹ adsorbent dosage, 200 min contact time and 298 K temperature. Adsorption efficiency of modified orange peel decreased with increase in temperature indicated exothermic nature of adsorption. A negative value of ΔG° (-8.59 kJ mol⁻¹) confirmed the feasibility of adsorption process and spontaneous nature of adsorption. A negative value of ΔH° (-28.08 kJ mol⁻¹) indicated exothermic nature while a negative ΔS° (-66.86 J K⁻¹ mol⁻¹) value suggested decrease in degree of freedom of the adsorbed species. The results showed that biosorption process of Cd(II) ions by chemically modified orange peel is feasible, spontaneous and exothermic under studied conditions. Chemically by modified orange peel investigated in the present study showed good potential for the removal of cadmium from aqueous solutions.

Key words

Adsorption capacity, Cadmium, Chemically modified orange peel, Thermodynamic parameters

Publication Info

Paper received:

28 November 2014

Revised received:

03 June 2015

Re-revised received:

03 July 2015

Accepted:

08 August 2015

Introduction

Inorganic effluents emanating from industries, such as metal finishing, electroplating, plastics, pigments and mining, contain toxic metal ions which tend to bioaccumulate in food chain. Once they enter the food chain, large concentration of heavy metal accumulate in human body. If these metal ions accumulate in high concentration in body, they can cause serious health disorders (Arbind *et al.*, 2015). Therefore, it is urgent to remove these toxic heavy metals from wastewater. Although heavy metal removal from aqueous solutions can be achieved by conventional methods like chemical precipitation, reverse-osmosis, oxidation/reduction, electro-chemical treatment, evaporative recovery, filtration, ion exchange and membrane technologies, they may be ineffective or cost-expensive,

especially when metal ion concentration in solution are in the range of 1–100 mg l⁻¹ (Liang *et al.*, 2009; Parajuli *et al.*, 2005).

Recently, adsorption technology has become one of the alternative treatments (Kumar and Bandyopadhyay, 2006; Singh *et al.*, 2006), especially widespread industrial use of low-cost adsorbents for wastewater treatment is strongly recommended due to their local availability, technical feasibility, engineering applicability and cost effectiveness. However, using biological adsorbents directly may suffer from lack of specificity and poor adsorption capacity. It is observed that appropriate modification of raw adsorbents by crown esters, amines, polyethylamine and sulphur bearing groups like sulfides, thiols, dithiocarbamates, dithiophosphates and xanthates can eliminate the drawbacks

and improve their performances significantly (Panda *et al.*, 2008).

Cadmium is a toxic heavy metal of significant environmental and occupational concern. It is released in water from smelting, metal plating, cadmium nickel batteries, phosphate fertilizers, mining, pigments, stabilizers, alloy industries and sewage sludge (Kadirvelse and Namasivayam, 2000). Contamination of drinking-water may occur as a result of the presence of cadmium as an impurity in galvanized pipes or cadmium-containing solders in fittings, water heaters, water coolers and taps. Cadmium has been classified as a potent carcinogen and teratogen, affecting lungs, kidneys, liver and reproductive organs (Wsslkes, 2000; Sharma, 2008). The harmful effects of cadmium include a number of acute and chronic disorders, such as renal damage, emphysema, hypertension and testicular atrophy (Kadirvelse *et al.*, 2000).

A wide variety of biosorption have been investigated for adsorption of cadmium ions, including algae, bacteria and agricultural by-products (Feng and Aldrich, 2004 Pagnanelli, *et al.*, 2003; Zhengjm *et al.*, 2011; Kumsar, U. 2011; Arbind *et al.*, 2013; Arbind and Vipin, 2015). Application of these raw plant materials as biosorbents is limited due to leaching of organic compounds such as cellulose, lignin, pectin and lignocelluloses into solution. Chemical modification on solid biomasses have been used to improve their physical, chemical and biosorption capacity (Yenench *et al.*, 2011; Anirudhin *et al.*, 2006).

Therefore orange peel, as chemically modified form, can be used as adsorbent of Cd (II) ions as it has strong potential due to its main components of cellulose, pectin, hemicellulose and lignin which contain functional groups as possible binding sites for metals (Feng *et al.*, 2009b; LI XM *et al.*, 2008). The aim of the present study was to investigate the adsorption capacity of orange peel that was chemically modified with sodium hydroxide for removing Cd (II) ions from aqueous solutions. Batch adsorption experiments were carried out to evaluate the adsorption characteristics for different pH, contact time, initial metal ion concentration, biosorbent dosage and temperature on the bases of biosorption efficiency.

Materials and Methods

Preparation of Cd (II) stock solution : All the chemicals used were of analytical grade (E Merek. India). Stock solution (1000 mg l⁻¹) of Cd (II) was prepared by dissolving 1.37g cadmium nitrate [Cd (NO₃)₂ . 4H₂O] in 100 ml beaker. For biosorption experiments, Cd (II) solutions (100 mg l⁻¹) were prepared from stock solution by dilution. Calibration standards (5, 10, 20, 50 and 100 mg l⁻¹) were prepared and

used for calibrating the atomic absorption spectrophotometer. pH of the solution was adjusted using either 0.1 M HNO₃ or 0.1 M NaOH solution.

Preparation of chemically modified orange peel (CMOP): Biowaste material used for the study was obtained from a local market. Orange peels were washed with distilled water, dried in an oven at 80°C to constant mass and crushed into smaller particles of approximate size ≤ 200 μm. Crushed orange peel was treated with NaOH to improve the efficiency of metal uptake. In the present study, 100 g of dried orange peel biomass was treated with 1 l of (0.1M) NaOH for 48 hr with shaking at 120 rpm. After repeated decantation and filtration, the modified biomass was washed with distilled water until pH value of solution was neutral. CMOP was then oven dried at 80°C to constant mass, put in air tight bottles and stored in desiccators for further use in batch experiments.

Batch equilibrium studies: 50 ml of Cd (II) solution (100 mg l⁻¹) at uncontrolled pH was taken in 250 ml conical flask with fixed dosage (4 g l⁻¹) of adsorbent. The mixture was agitated in a shaker at a speed of 120 rpm at room temperature for a time which was sufficient for cadmium uptake process to reach equilibrium. Batch adsorption studies were performed at room temperature at different pH (3, 4, 5, 6, 7, 8 and 9), adsorbent dose (1, 2, 3, 4, 5 and 6 g l⁻¹), initial Cd (II) concentration (1, 2, 3, 4, 5, 6 and 7 mg l⁻¹) and contact time (40, 80, 120, 160, 200, 240 and 280 min) to obtain the equilibrium data. All the experiments and analysis were carried out in duplicate and the maximum analytical error was found to be less than 5%. After attaining of equilibrium, the samples were filtered through Whatman No. 40 filter paper and the residual Cd (II) concentration in the filtrate was estimated by Perkin Elmer AAnalyst 800 Atomic Absorption Spectrophotometer (AAS).

Results and Discussion

Gonen and Serin (2010) studied the binding of Cd (II) to raw orange waste and suggested that hydroxyl groups (-OH) and carboxyl groups (-COOH) are responsible for binding of metal ions. Similar trend was reported by Feng *et al.* (2009 a, b). Therefore, metal binding capacity can be enhanced by increasing the number of carboxylate groups in orange peel. Orange waste consists mainly of cellulose, hemicelluloses, galacturonic acid and lignin contains methyl ester. Methyl ester can be activated by converting carboxylic ligand by treating with NaOH solution (Mandina *et al.*, 2013).

pH is one of the most important controlling parameters in all the adsorption process. In order to establish the effect of pH on adsorption of Cd (II) onto modified orange peel, batch adsorption studies at different pH values were carried out in the range of 3.0-9.0. No significant variation in

adsorption capacity between pH 6 and 9 (Fig.1) was observed. From the results it is evident that maximum adsorption of Cd (II) was 97.6 % at pH 6.0. Adsorption of cadmium on pH may be related to the functional groups of biomass and or solution chemistry (Annadurrai *et al.*, 2002). Lower uptake of metal, at low pH might be due to higher concentration and higher mobility of H^+ ions, which is preferentially adsorbed rather than metals ions (Annadurrai *et al.*, 2002; Ajmal *et al.*, 2003). It has also been suggested that at highly acidic condition, adsorbent surface ligands are be closely associated with H_3O^+ that restricts access to ligands by metal ions as a result of repulsive forces. Similar results have been reported by several researchers (Feng *et al.*, 2009b; Mandina *et al.*, 2013; Kumar *et al.*, 2010). At high pH, due to lower number of H^+ ions and greater number of ligands with negative charges results in greater intake of Cd^{2+} ions. If $pH > 3$, carboxylic groups (-COOH) present in orange peel gets deprotonated and gets negatively charged, therefore association with positively charged metal ions is enhanced (Norton *et al.*, 2004). Decrease in adsorption rate at high pH values may be due to the competitiveness of oxy-anion of Cd^{2+} and OH^- ions in bulk. These results suggest that pH affects solubility of metals and ionization state of functional groups like carboxylate, phosphate and amino groups present in cell walls of the biosorbent (Moussavi *et al.*, 2010; Ahamadpour *et al.*, 2010).

Effect of biosorbent dosage on percentage removal of Cd(II) was investigated by varying adsorbents dosage in the range of 1.0 g l^{-1} to 6.0 g l^{-1} . It was observed that the percentage removal of Cd (II) increased from 86% at 1 g l^{-1} to 97.7 % at 4 g l^{-1} with increase in adsorbent dosage (Fig. 2). Maximum percentage removal of Cd (II) was 97.7% at 4.0 g l^{-1} of biosorbents dosage and constant initial metal ions concentration of 3 mg l^{-1} . The phenomenon of increase in percentage removal of Cd (II) with increase in adsorbent dose explains that with increase in adsorbent dose, more and more surface becomes available for metal ion to adsorb and this increases the rate of adsorption (Rio *et al.*, 2002). A significant increase in uptake was observed when dose was increased from 1 to 4 g l^{-1} . Any further addition of the adsorbent beyond this did not cause any significant change in adsorption which might be due to completion of Cd(II) on the sites available (kumar *et al.*, 2010, Moussavi *et al.*, 2010).

It was observed that adsorption rate increased from 86.3% to 96.7% with increase in contact time from 40 to 200 min (Fig.3). Maximum Cd (II) removal was achieved (96.7%) within 200 min after residual Cd(II) concentration in the test solution became constant. It might be explained by the fact that initially for adsorption large number of vacant sites were available which slowed down later due to exhaustion of remaining surface sites and repulsive force between solute molecule and bulk phase (Sarvanane *et al.*, 2002). Lower

adsorption rate in the later stage (after 200 min) was due to difficulty encountered by Cd ions in occupying the remaining vacant surface sites due to the forces between the solute molecules of solid and bulk phase (Ucun *et al.*, 2002). This might also be due to intraparticle diffusion process dominating over adsorption (Voleky *et al.*, 2003). The results also indicated that chemically modified orange peel showed better adsorption capacities than raw orange peel.

In the present study, the effect of initial concentration of Cd (II) for adsorption was investigated with initial concentration of Cd (II) ranging from 1.0 mg l^{-1} to 7 mg l^{-1} , dosage of CMOP 4 g l^{-1} and pH value 6 (Fig.4). It was observed that adsorption of Cd (II) first increased from 72% to 97.3% then decreased from 97.3% to 65% with increase in metal concentration from 1 to 3 mg l^{-1} , and then from 3 to 7 mg l^{-1} respectively. At higher concentration, most of the Cd (II) was left unadsorbed due to saturation of adsorption sites. As the ratio of adsorptive surface to ion concentration decreased with increase in metal ion concentration and so removal of metal ions was reduced. At low initial concentration of metal ions, more binding sites are available. But as the concentration increased, the number of ions competing for available binding sites in the biomass increased (Gupta *et al.*, 2003).

Removal of cadmium decreased from 97% to 88.3% (Fig. 5) on increasing the temperature of the process from 298 to 338 K at 3 mg l^{-1} initial concentration of Cd, pH 6.0 and at constant adsorption dose of 4 g l^{-1} . Decreasing pattern of adsorption with increasing values of temperature revealed the exothermic nature of cadmium adsorption on CMOP. Moreover, decreasing values of adsorption distribution coefficient (K_d) at increasing temperature also proved the exothermic nature of the present process. Increased escaping tendency of cadmium at elevated temperature might be another explanation to this finding. In order to determine thermodynamic feasibility and thermal effect of adsorption, change in Gibbs energy (ΔG^0) entropy (ΔS^0) and enthalpy (ΔH^0) associated with the process were calculated. The ΔS^0 and ΔH^0 values determined from intercept and slope of Van't Hoff plots (Fig. 6) is presented in Table 1.

Gibbs energy change (ΔG^0) was found to be $-8.59 \text{ k J mol}^{-1}$ for Cd (II) biosorption at 298K. The negative value of ΔG^0 confirmed feasibility and spontaneous nature of Cd (II) biosorption on CMOP. Increase in ΔG^0 with increase in temperature (Table 1) showed decrease in feasibility of biosorption at higher temperature. A negative ΔH^0 ($-28.08 \text{ k J mol}^{-1}$) indicated exothermic nature, while a negative ΔS^0 ($-66.86 \text{ J K}^{-1} \text{ mol}^{-1}$) value suggested decrease in randomness at solid/solution interface during Cd (II) biosorption on CMOP (Aksu and Isoglu, 2005; Feng *et al.*, 2009a; Gonen and Serin, 2010). It has been reported that ΔG^0 values up to -20 k J mol^{-1}

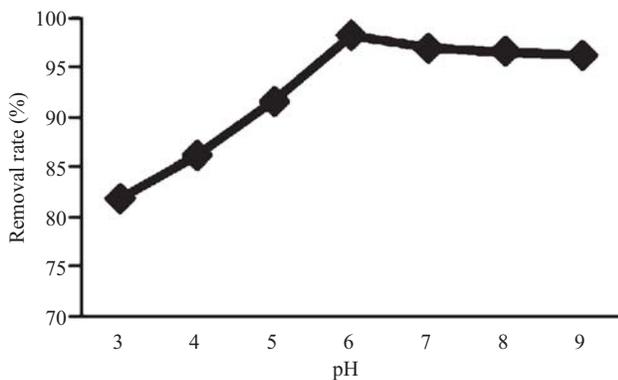


Fig. 1 : Effect of pH on Cd(II) removal rate

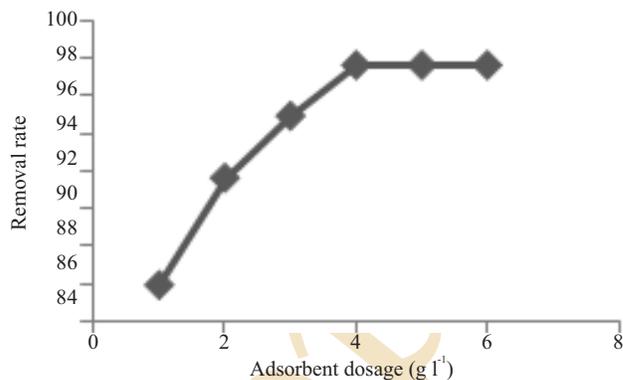


Fig. 2 : Effect of Adsorbent dosage on Cd(II) removal rate

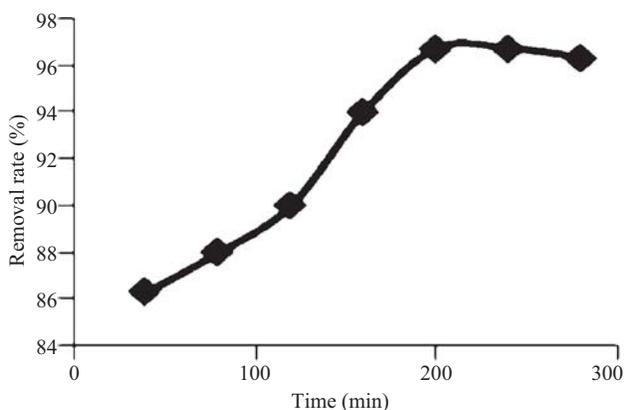


Fig. 3 : Effect of Time on Cd(II) removal rate

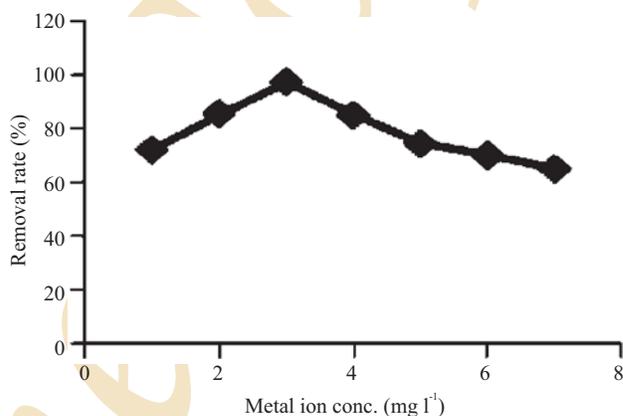


Fig. 4 : Effect of metal ion concentration on Cd(II) removal rate

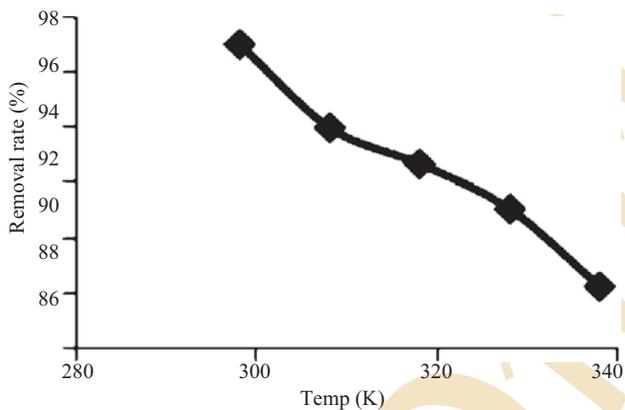


Fig. 5 : Effect of temperature on Cd(II) removal rate

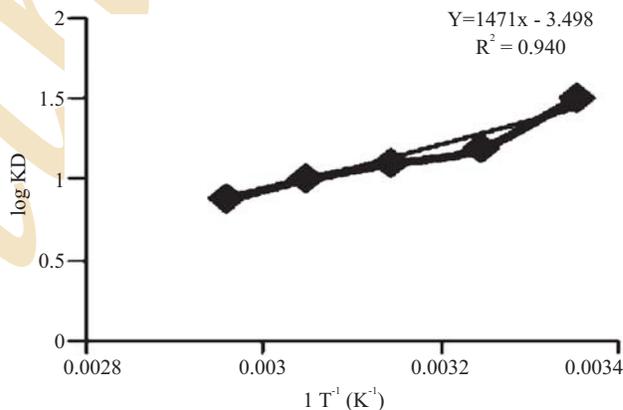


Fig. 6 : Van't Hoff plot for Cd(II) adsorption onto CMOP

are consistent with electrostatic interaction between adsorption sites and metal ion (physical adsorption), while ΔG^0 values more negative than -40 kJ mol^{-1} involve charge sharing or transfer from biomass surface to metal ion to form a coordinate bond (chemical adsorption) (Horsfall *et al.*, 2004). The ΔG^0 values obtained in the present study for cadmium were $< -10 \text{ kJ mol}^{-1}$, which indicated that physical adsorption was predominant mechanism in the adsorption

process (Abdel Ghani and Elchaghaby, 2007).

Finally, it is concluded that chemically modified orange peel using sodium hydroxide enhanced the removal of Cd (II) from aqueous solution. Experimental studies showed that rapid removal of Cd (II) strongly depended on the pH of solution, adsorbent dosage, contact time and initial concentration of Cd (II) solution. Negative (ΔG^0) values

Table 1 : Thermodynamic parameters for adsorption of Cd (II) onto CMOP

Temp (K)	logK _d	ΔG° (kJ mol ⁻¹)	ΔS° (JK ⁻¹ mol ⁻¹)	ΔH° (kJ mol ⁻¹)
298	1.5090	-8.590		
308	1.1948	-7.025		
318	1.1016	-6.687	-66.86	-28.08
328	1.0047	-6.291		
338	0.8791	-5.672		

indicate thermodynamically feasible and spontaneous nature of Cd (II) biosorption on CMOP. Therefore, the present study developed an inexpensive, highly available, effective metal ion adsorbents from natural waste as an alternative to existing commercial adsorbents.

Acknowledgment

The authors are thankful to the Principal of P.G. Center, D.S. College, Katihar (BNMU) and the Director of Kishanganj College of Engineering and Technology, Kishanganj, Bihar for providing research facilities.

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