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Original Research Paper

Biosorption of Cadmium from Aqueous Solutions using Blue Green Algae

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ABSTRACT

The kinetics and optimum conditions for the adsorption of Cd(II) ions on to dead blue green algae (BGA) mixed species were investigated with a view to explore the possibility of utilising it as a low cost adsorbent for the removal of Cd(II) from aqueous medium. Biosorption of Cd(II) was studied by varying different experimental conditions viz; contact time, solution pH, bio-sorbent dosage and Cd(II) concentration. Cd(II) adsorption onto BGA was observed to be depend on solution contact time, pH, bio-sorbent dosage and concentrations of Cd(II) in solution. The biosorption process followed pseudo-first order model (R^2>0.99). Reuses of the biosorbent were also studied.

INTRODUCTION

Toxic heavy metals enter the aquatic streams mainly through a variety of industrial activities. Even though various regulatory bodies set limits for heavy metal discharge into aquatic streams, heavy metals are being added to water bodies at a much higher concentration than the prescribed limits, causing health hazards. Cadmium [Cd(II)] is highly toxic and its accumulation in the human body causes erythrocyte destruction, nausea, muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformation (Patterson & Passino 1987, Lehoczky et al. 1998). "Itai-Itai" disaster that occurred in Japan in the year 1968 was due to contamination of water of Jintsu river with Cd(II) (Kjellstrom et al. 1977). Permissible limit of Cd(II) in industrial discharges is set at 0.01mg/L by the Ministry of Environment and Forests (MOEF), Government of India. Conventional methods for the removal of heavy metal ions from aqueous solutions are chemical precipitation, ion exchange, reverse osmosis and electrochemical treatment (Elouear et al. 2008, Santhy & Selvapathy 2004, Chan-jun & Jung-Heon 2005). However, these methods have limitations, because they often involve high capital and operational cost and may also be associated with the generation of secondary wastes. Among the various water-treatment techniques described, adsorption is versatile due to its high efficiency, easy handling, cost effectiveness and availability of various materials which can be used as adsorbents (Beauvais & Alxendratos 1998). Adsorbents like activated carbon (Hajar Merrikhpour & Mohsen Jalali 2012) Mn-oxide coated granular activated carbon (Fan et al. 2005) and alumina or chitosan (Cervera et al. 2003) were used for the removal of Cd(II). Biosorbents have advantage over physical adsorbents, in that they do not cause secondary pollution. Use of biosorbents like bacteria (Scott & Palmer 1990) and yeast (Volesky et al. 1995) was reported in the literature for the removal of Cd(II). Researchers also used different agricultural wastes such as coconut coir pith (Kadirvelu et al. 2003), sawdust (Yu et al. 2000), banana pith (Low et al. 1995), cottonseed hulls (Marshall & Champagne 1995) and peanut hull carbon (Perisamy & Namasivayam 1996). Many other biomaterials were also used for removal of Cd(II) from aqueous solutions (Kumar et al. 2012a, Leyva Ramos et al. 2012a, Rao & Rehman 2012, Volesky 1990). Most of the methods reported describe that the pretreatment of the adsorbent before adsorption studies which are tedious. Systematic studies on the reuse and regeneration of the biosorbent were not reported. In the present study, blue green algae species was used as biosorbent for removal of Cd(II) from aqueous solutions. Detailed investigations were carried out and experimental conditions were optimized to achieve maximum removal of Cd(II). The results obtained are presented and discussed in this communication.

MATERIALS AND METHODS

Materials: Blue green algae (BGA) samples were collected from Nacharam Lake, located in the vicinity of Indian Institute of Chemical Technology (IICT). The algae were dried in sunlight and ground into fine powder using mortar and pestle. Later, chloroform and methanol 2:1 ratio was added and kept in a bath sonicator for 30 min for further cell disruption and kept in shaking incubator for 6 hrs. The supernatant containing lipid extract was discarded and remaining waste algae powder was dried in hot air oven at 60°C and used for further experiments.

A standard stock solution containing Cd(II) (1000 mg/L) was prepared by dissolving 163.21 mg Cd(II) chloride in distilled water in a 1000 mL volumetric flask. All working standards were obtained from this stock solution by dilution. Analytical grade reagents were used throughout this work.

Instrumental analysis: pH measurements were conducted using a pH meter equipped with standard calomel electrode (SCE). Batch adsorption mixtures were agitated at required shaking speed on a constant shaker and a centrifuge machine was used for the separation of biomass from Cd(II) solutions, and residual Cd(II) ion concentration in solution was determined using Atomic Adsorption Spectrometer (AAS) (Perkin Elmer -GBC 932 AA).

Batch adsorption tests: All the adsorption experiments were conducted in duplicate 25± 2°C. A known quantity of BGA was (1.5 g) mixed with 150 mL of solution containing Cd(II) ions at an initial concentration 100 ppm. The mixture was agitated at a constant speed of 120 rpm for a period of 8 hrs. Aliquots were drawn from the reaction mixture and centrifuged. Remaining Cd(II) concentration in solution was determined. All the experiments were performed in duplicate.

Optimization of contact time: Contact time of Cd(II) solution with the biosorbent for maximum adsorption was determined by carrying out experiments keeping the quantity of biosorbent and pH constant. Experiments were conducted at different contact time intervals (15 to 600 min) to determine the most effective time for Cd(II) uptake by BGA. Samples were drawn periodically for analysis to determine the concentration of Cd(II) adsorbed.

Optimization of pH: The effect of change in solution pH was studied using Cd(II) solution at different pH values (6.0-8.5). pH pre-adjustments were achieved by the addition of small amounts of 0.1M HNO_3 and 0.1 M NaOH as appropriate. In each experiment, aliquots of the test mixture were drawn to determine the concentration of Cd(II) remaining in the test solution.

Optimization of the quantity of biomass: Tests were conducted to optimize the quantity of biomass by keeping the solution pH and time of contact. The quantity of biomass used was varied between 0.5 and 3.0 g for 150 mL of the test solution. The concentration of Cd(II) in the solution was determined periodically using AAS in each experiment.

Kinetics: Kinetics of adsorption of Cd(II) to BGA were investigated. Ten separate 250 mL flasks were taken for the experiments. The mixture in each flask was rotated at 120 rpm for 8 hrs. Samples were drawn for every one hour from each flask at the time for analysis. Remaining concentration of Cd(II) in each sample after adsorption at different time intervals was determined by AAS.

Reuse: Reuse of the adsorbent was also investigated. The biomass was reused for 4 cycles by adding 150 mL of fresh Cd(II) solution each time to examine the efficiency of adsorption of the biomass at different concentrations viz; 50, 25,15,10 and 5 ppm under optimized experimental conditions.

Reuse by washing (adsorbent): Adsorption of Cd(II) by reusing the adsorbent after each experiment was studied at different concentrations viz; 100, 50 and 10 ppm to understand the efficiency of adsorption of the adsorbent after washing. The biomass was washed 5 times with 100 mL distilled water and used for adsorption experiments for 4 cycles.

RESULTS AND DISCUSSIONS

Optimization of contact time: Biosorption process is dependent on the contact time of the biosorbent with Cd(II) solution (ref). Therefore, experiments were carried out by varying contact time 15 to 600 min, keeping the quantity of biosorbent constant (1.5 g) and the solution pH (6.5). The results obtained are shown in Fig. 1. The results indicated that the biosorption of metal was rapid in the first 15 min, then was gradually increased till the equilibrium become almost constant thereafter. Therefore, it was concluded that contact time of 480 min was optimum for the adsorption of Cd(II).

Optimization of pH: The pH of the aqueous solution affects the metal solubility and the concentration of counter ions on the functional group of the cell wall of the biosorbent. Consequently, pH is considered as the most important parameter that could affect the biosorption of metal ions from solutions (King et al. 2007). The effect of solution pH value on the biosorption of Cd(II) ions was evaluated. The time of contact was kept at 8 hrs and the biomass quantity was kept constant at 1.5 g. Solution pH was varied from 6.0 to 8.0. The effect of change of pH on Cd(II) adsorption is shown in Fig. 2. It was observed that, as the pH was going towards alkaline condition, the extent of biosorption was decreasing upto solution pH of 7.5. However, there was a slight increase in the biosorption at pH of 8.0. In general, the optimum Cd(II) uptake by various biomasses occurs in acidic media of pH values 4.4 to 5.5. Optimum pH of Cd(II) biosorption on BGA occurred at near neutral pH values (6.5), which is desirable for treatment of contaminated natural water. Therefore, all the experiments were carried out at solution pH 6.5.

Optimization of the quantity of biomass: Different biosorbent dosages ranging from 0.5 g to 3.0 g/150 mL were used to study the effect of biosorbent dose on the biosorption of Cd(II) ions (Fig. 3). The data revealed that the biosorption efficiency of Cd(II) ions on BGA was significantly affected

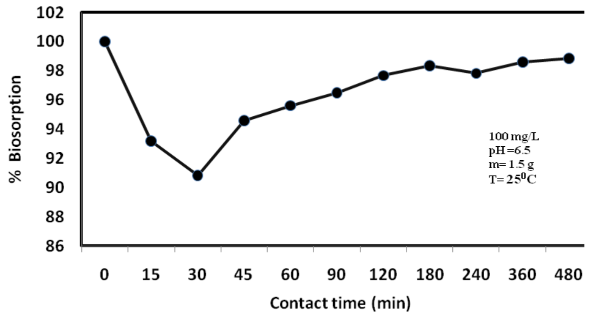

Fig. 1: Effect of contact time on % biosorption of Cd(II) by blue green algae sp.

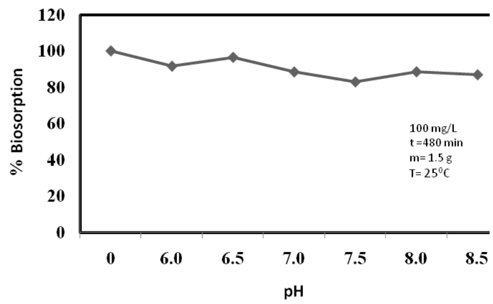

Fig. 2: Effect of solution pH on % biosorption of Cd(II) by blue green algae as biosorbent.

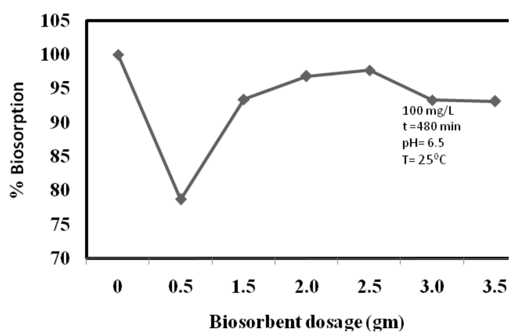

Fig. 3: Effect of biosorbent dosage on biosorption of Cd(II).

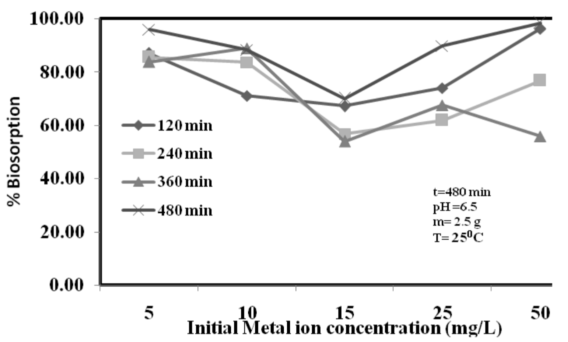

Fig. 4: Effect of initial metal ion concentration on % biosorption cadmium by blue green algae species at different time interval under optimized conditions.

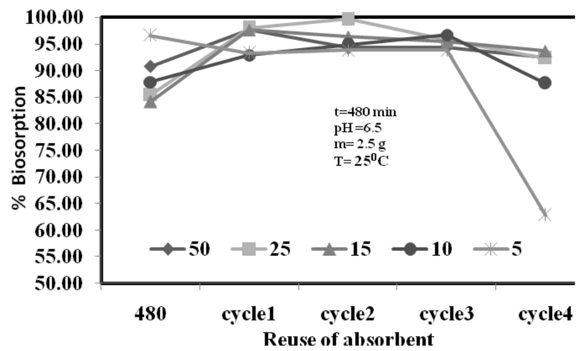

Fig. 5: Reuse of the blue green algae for the removal of Cd(II) under optimized conditions.

by the dose of BGA. In other words, the biosorption of Cd(II) ions increased with increase in biosorbent dose and almost became constant at higher dosage at 2.5 g of the bios-orbent per 150 mL for Cd(II) respectively. This behaviour could be explained by the formation of aggregates of biomass at higher doses, which decreases the effective surface area for biosorption (Karthikeyan et al. 2007, Gaur et al. 2009). Therefore, at 2.5 g/150 mL of Cd(II) solution was selected as the optimum dose of the biosorbent for the rest of the study.

Studies on Cd(II) adsorption at optimized experimental conditions: Fig. 4 shows the effect of initial Cd(II) concentration on adsorption by BGA under optimized experimental conditions viz., 8 hrs contact time, 6.5 pH and 2.5 g/150 mL solution was studied. Experiments were carried out with 50, 25, 15, 10 and 5 ppm Cd(II) solutions. 92.47% of Cd(II) ions were adsorbed using an initial Cd(II) concentration of 50 ppm. Increase in the amount of Cd(II) adsorption was observed as an initial Cd(II) concentration increased from 5 ppm to 50 ppm; however, the percentage quantity adsorbed decreased. This shows that there is a progressive increase in mutual electrostatic interaction between sites of lower affinity for metal ions as the population occupied sites in the biosorbent surface increases (Gupta et al. 2006).

Reuse of biomass: Experiments were carried out to understand the sustainability of the biosorbent. Reuse of the same biosorbent was done by taking 50, 25, 15, 10 and 5 ppm concentrations of Cd(II) metal solution under optimized conditions. The biosorbent was reused without any treatment adding a fresh 150 mL metal solution and the same procedure was repeated up to 4 cycles. The results obtained are presented in Fig. 5. The percentage of biosorption was found to be high at higher concentrations and between 80-95% in first three cycles and less biosorption at cycle 4 at all concentrations because most of the metal molecules present in solution could be adsorbed on the available active sites of the biosorbent. The biomass could be reused 3 times efficiently.

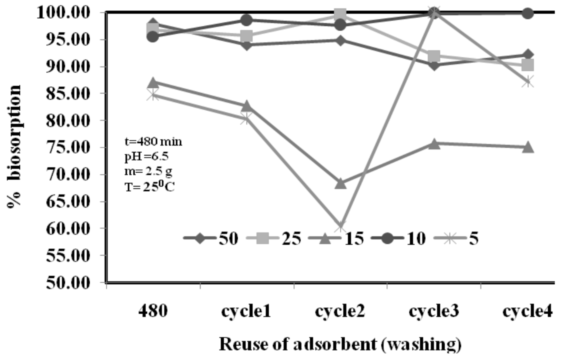

Fig. 6: Efficiency of the biosorbent for the removal of Cd(II) after washing with distilled water.

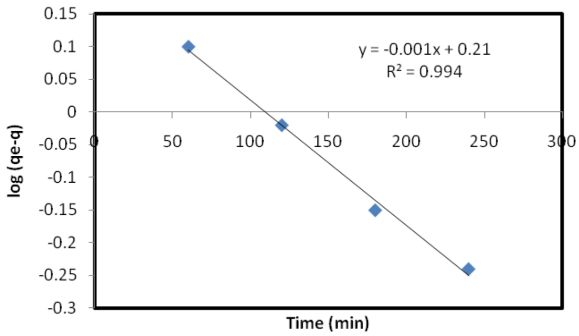

Fig. 7: Graph showing the kinetics of adsorption of Cd(II) on the blue green algae.

Reuse of biosorbent by washing: Adsorption experiments were carried out with 100, 50 and 10 ppm concentrations of cadmium metal solution under optimized conditions and the biosorbent after first cycle was washed 5 times with 100 mL distilled water and the biosorbent was used for adsorption experiments. The same procedure was repeated for the next 3 cycles. The results obtained are presented in Fig 6. The biosorption percentage was between 80-93% and decreased in the cycle 2. In cycle 3 and cycle 4 the biosorption percentage of the biosorbent after reuse was found to be very good. At 15 mg/L the biosorption was found to be very less due to non availability of active sites in the metal solutions. It could be concluded from the results obtained that the biosorbent could be reused for biosorption of cadmium four times.

Kinetics: A graph was drawn by taking contact time at different time interval on the x-axis and natural logarithm of the remaining concentration of Cd(II) on the y-axis log (q_e-q). The graph is shown in Fig.7. Kinetics of adsorption was determined from the graph. The graph was observed to be a straight line fit with a relatively good correlation coefficient ($r^2 = 0.99$). Therefore, it was concluded from the graph that adsorption followed pseudo first order.

CONCLUSIONS

The present study revealed that low cost biomass material obtained from the BGA was a promising material for the removal of Cd(II) ions from water. Metal adsorption was controlled by the contact time, initial metal ion concentration, sorbent dose and solution pH. Highest adsorption Cd(II) ions were found at solution pH of 6.5 using initial Cd(II) ion concentration 100 mg/L, adsorbent dose of 2.5 g/150 mL, 480 min of contact time, and agitation speed 120 rpm. Kinetic analyses indicated that the adsorption process followed the pseudo-first order kinetics.

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