Removal of chromium from water effluent by adsorption onto Vetiveria zizanioides and Anabaena species

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ABSTRACT

Bioadsorption phenomenon is more or less like a chemical reaction and several parameters are bound to affect the process. The pH, amount of adsorbent and agitation time influence the biosorptive potentiality. Hence, the present study on adsorption of Cr(VI) by activated Vetivera roots and Blue green algae Anabaena supports that it is an effective low cost adsorbent for the removal of Cr(VI) from plating effluent. Langmuir and Freundlich adsorption isotherm correlate the equilibrium adsorption data. In batch experiments both Vetiveria and Anabaena species were found to be cost effective biosorbent for the efficient removal of Cr(VI) from the effluent and comparatively Anabaena species was found to adsorb maximum Cr(VI) (88.86%) at a low contact time of 60 min. The data obtained from the experiments and modeling would prove useful in designing and fabricating an efficient treatment plant for Cr(VI) rich effluent.

Keywords: Bioadsorption; Vetiveria; Anabaena; Adsorption Isotherm; Chromium

1. INTRODUCTION

The treatment of waste water containing metals is a challenging problem; Due to rise in rigorous environmental policies, scientists all around the world are desired to develop precise techniques to control the amount of heavy metal in waste water and drinking water. Chromium in particular has received a great deal of attention. The increased environmental burden of Cr(VI) may come from various industrial sources like those from electroplating, leather tanning, textiles and metal finishing industries. The presence of heavy metals in wastewater is not only of great environmental concern but also strongly declining microbial activity, as a result adversely affecting biological wastewater treatment processes.

Earlier the method of ion exchange has been widely employed to remove heavy metals in water bodies [1,2], but the cost is high. There are also reports available on the removal of heavy metals in effluent by complexation of dry biomass [3,4]. Unfortunately, these methods were not employed on large scale. Many researchers have reported the methods of biosorption on chemical modified solid surface [5], it takes some time for the adsorption of heavy metals in water bodies, especially, at ppm level.

Vetiveria zizanioides, due to its unique morphological and physiological characteristics, and tolerance to high levels of heavy metal and adverse conditions, has also been successfully used in the field of environmental protection [6,7]. It is excellent for the removal of heavy metals from contaminated soil [8,9] and rehabilitating landfills [10]. Even though it is not an aquatic plant, vetiver can be established and survive under hydroponic conditions [11]. It can purify eutrophic water [12], garbage leachates [13] and wastewater from pig farms [14]. Therefore, vetiver has high potential to be used for industrial wastewater treatment [12].

Among the most promising types of biosorbents studied is the algal biomass [15,16]. This is due to the presence of various functional groups such as carboxyl, amino, sulphate and hydroxyl groups, which can act as binding sites for metals [17]. Anabaena Bory ex Bornet & Flahault (Cyanobacteria), a blue green alga, is among a number of cyanobacteria that present gas vacuoles (aerotope) and form dense populations on the surface of lakes and reservoirs, the so-called blooms. Anabaena being structurally similar might also possesses the capabilities of
heavy metal removal from effluents as this alga contain lipopolysaccaride envelop, that is proven to be helpful in ionic exchange properties/intracellular accumulation/adsorption onto cell surface.

The present study characterizes waste water from chrome plating effluent, and finally to optimize conditions pertaining to removal and recovery of Cr(VI) by these selected biosorbents, *Vetiveria* and *Anabaena* species.

2. MATERIALS AND METHODS

To envisage the biosorption potentiality of *Anabaena* and *Vetiveria*, various methods pertaining to physicochemical analysis of chrome plating effluent, preparation of biosorbents, optimization and adsorption isotherm studies were performed.

2.1. Physiochemical Analysis

Effluents from chrome plating industry were collected in plastic containers as per standard methods [18]. The industrial effluent was analyzed as per standard methods [19]. Bio chemical Oxygen Demand (BOD) measured by the methods described in APHA [20] procedure. The sample was diluted sufficiently so that the demand of oxygen does not exceed the amount of available oxygen. Dilution extract for dilution of sample was prepared by adding one 1 ml each of phosphate buffer, magnesium sulphate solution, calcium chloride solution and ferric chloride in one liter of distilled water, then after diluted sample was filled in BOD bottles. For subsequent dilution of sample, two BOD bottles were prepared. Initial Dissolved Oxygen (DO) was noted from the first one and second one was incubated at 20°C for five days. DO of diluted sample was recorded and water blank was diluted before incubation and kept for 5 days of incubation. BOD was calculated in mg/l from the difference between initial and final DO by the following formula.

Calculation: BOD = \( A \times \text{Dilution Factor} \)

\[ A = (C_0 - C_1) - (D_0 - D_1) \]

where, \( D_0 \) = DO in dilution water; \( D_1 \) = DO in dilution water, after incubation; \( C_0 \) = DO in sample; \( C_1 \) = DO in sample after incubation; \( D_0 - D_1 \) = oxygen depletion in dilution water; \( C_0 - C_1 \) = oxygen depletion due to biomass in diluted original sample; Dilution factor = 10².

2.2. Total Dissolved Solids

Total Dissolved Solids (TDS) was examined by taking 20 ml of the sample, after filtering through a dry whatman filter paper. The filtrate was taken in a pre-weighed porcelain crucible and evaporated to dryness in a hot air oven. The evaporated sample was further dried for an hour at 105°C in a hot air oven. The crucible was cooled in desiccators and weighed. TDS was calculated with standard formula:

Calculation:

\[ \text{TDS (mg/l)} = \frac{(\text{Final Wt} - \text{Initial Wt})}{\text{Vol. of sample}} \]

2.3. Total Suspended Solids

Total Suspended Solids (TSS) was calculated by collecting 20 ml of the sample filtered through a pre-weighed whatman filter paper and then after drying it in a hot air oven for an hour. Filter paper was cooled in desiccators and weighed. From the readings, TSS was calculated by using the formulae

Calculation:

\[ \text{TSS (mg/l)} = \frac{(\text{Final Wt} - \text{Initial Wt})}{\text{Vol. of sample}} \]

2.4. Estimation of Chloride

Chloride estimation was done as per the method described in APHA [19]. Chloride solution was titrated against silver nitrate taking potassium chromate as indicator. The end point was noted through the formation of reddish brown precipitate. The volume of silver nitrate consumed was noted.

Amount of chloride present in 1 liter of solution was calculated by:

\[ \text{Normality} \times 35.5 \times 1000 \text{ mg/l} \]

2.5. Estimation of Sulphate

20 ml of sample was initially filtered to remove the suspended solids and was further taken for analysis. To
this, 4 ml of 10% Barium chloride solution and 2 ml of dilute Sulphuric acid was added; which results into a white precipitate of Barium sulphate.

\[ \text{BaCl}_2 + 2\text{SO}_4^{2-} \rightarrow \text{Ba}_2\text{SO}_4 + 2\text{Cl}^- \]

The solution was filtered through Whatman filter paper, whose initial weight was priorly known. Thenafter it was filtered, the filter paper was completely dried in hot air oven and final weight was noted.

Amount of sulphate = Final Wt. – Initial Wt./20 mg/l

2.6. Estimation of Chromium

The chromium present in the given sample was estimated spectrophotometrically by Diphenyl carbazide method [21]. Different concentrations of chromium standard solutions and sample solutions were taken in test tubes. To each test tube, 1ml each of 0.1 N concentrated Hydrochloric acid and Phosphoric acid was added, and allowed to rest for 5 minutes. Then after 0.05 ml of Diphenyl carbazide was added and tubes are allowed for further 15 minutes rest, to develop colour.

The absorbance was observed spectrophotometrically at 540 nm. A graph between absorbance and concentration of solution was plotted. Accordingly the amount of chromium present in the samples is estimated. The other parameters like pH and Dissolved Oxygen were measured by using pH meter and DO meter respectively.

2.7. Preparation of Bio Adsorbent

2.7.1. Vetiveria

The V. zizanioides root was washed well with distilled water and treated with 0.1 N NaOH solution for a period of 10 hrs, for delignification. It was further treated with 0.1 N sulphuric acid for about 4 - 5 hrs to remove the alkalinity, washed with distilled water till the washing water became colorless. The treated adsorbent material was dried in sun light and stored in desiccators.

2.7.2. Anabaena

Anabaena sps. were cultured in Allen-Arnon medium (gm/l), with the composition: Potassium nitrate, 2.02 g; Di potassium hydrogen phosphate tri hydrate, 0.456 g; Magnesium sulphate hepta hydrate, 0.24 g; Sodium chloride, 0.234 g; Calcium chloride, 0.074 g; Fogg’s micro-nutrient solution, 1 ml; Fe-EDTA complex, 0.8 ml; Distilled Water, 1000 ml. The wet biomass of Anabaena was utilized directly for biosorption experiment.

2.8. Optimization of Biosorption Parameters

To study the adsorption capacity of the Anabaena and Vetiveria, batch experiments were conducted at room temperature. The effect of pH ranging from 2 - 5; contact time ranging between 30 - 150 minutes at 180 rpm; adsorbent dosage ranges from 0.5 - 3 g. The suspension from 100 ml of effluent was filtered through Whatman filter paper no. 41 and the filtrate was analyzed for residual Cr(VI) concentration. The elution studies were performed with 0.1 N HCl, 0.1 N H_2SO_4, 0.1 N HNO_3 and 0.1 M EDTA.

2.9. Adsorption Isotherms

Langmuir and Freundlich adsorption isotherm models were applied for Cr(VI) adsorption as per the method of Seidel-Morgenstern [22]. The Langmuir equation correlates the amount of adsorbate adsorbed with the equilibrium aqueous concentration can be given as

\[ \frac{1}{x/m} = \frac{1}{b} + \frac{1}{ab}C_e \]

where “x” is the amount of Cr(VI) adsorbed in mg/100 ml, “m” is the weight of Cr(VI) adsorbent (g), C_e is the residual concentration of Cr(VI) at equilibrium in mg/100 ml. Langmuir constants “a” and “b” are the measures of maximum adsorption capacity and energy of adsorption given in Table 1.

\[ R_L = 1 + bC_o \]

where C_o is the initial concentration of the adsorbate and “b” the Langmuir constant.

The value of R_L < 1, obtained in this study indicates the applicability of Langmuir adsorption isotherm.

The linear form of Freundlich equation is represented as follows [21].

\[ \log (x/m) = \log K_f + \frac{1}{n} \log C_e \]

where “x” is the amount of Cr(VI) adsorbed in mg/100 ml, “m” is the weight of adsorbent (g), C_e is the residual concentration of Cr(VI) at equilibrium in mg/100 ml. K_f and 1/n are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The values of adsorption intensity 1/n << 1 reveal the application of this adsorption isotherm.

3. RESULTS

3.1. Physicochemical Analysis of Chrome Plating Effluent

The effluent was slightly acidic in nature with the value of pH 4.1 - 5.5 and orange in colour. The COD and
BOD were too high, lies between 248 - 431 mg/l and 170 - 262 mg/l respectively. TSS and TDS were present in the concentration of 3.8 - 5.4 and 21.0 - 23.5 mg/l respectively. Concentration of DO, SO4 and Cl2 varied from 6.8 - 7.6, 0.53 - 1.01 and 0.40 - 0.80 mg/l respectively and the chromium content was 1.05 - 4.32 mg/l, which is beyond the limit value as analyzed by Tamilnadu Pollution Control Board Norms.

3.2. Optimization of Biosorptive Parameters

3.2.1. Vetiveria zizanioides

1) Effect of pH
pH is an important controlling factor in adsorption process and thus the role of hydrogen ion concentration was studied in the present investigation, covering range of 2 - 8. It was observed that, higher pH (4 - 8) has no effects on metal adsorption (Figure 1). At pH 3.5 chromium removal was increased 55% and at pH 2.5 metal sorption was maximum around 97%.

2) Effect of Agitation Time
The uptake of Cr(VI) from effluent by activated Vetiveria root increased from 22% to 93%, when agitation time was varied from 30 to 120 min and attained equilibrium after 150 min at 30°C (Figure 2). The increase in adsorption of Cr(VI) with increase in agitation time may be attributed to the increased intra-particle diffusion that occurred at longer shaking period.

3) Effect of Adsorbent Dosage
Increase in adsorbent dosage increased the adsorption of Cr(VI) species, batch adsorption studies were carried out at pH 2.5 and 30°C. The adsorbent dosage was varied from 0.5 g to 3.0 g of plant biomass and the removal of Cr(VI) was found to be increased from 30% - 80%. This is to be expected because for a fixed effluent concentration increasing total adsorbent doses, provides a greater surface area or adsorption site, thus the adsorption increases with adsorbent dosage as depicted in Figure 3.

4) Elution Studies
Because of the economic success and reuse of the biomass, elution studies have an importance for the bioadsorption process. The efficiency of elution and preservation of bioadsorption capacity of bioadsorbent are important factors to choose the elution agents. Based on the optimized conditions viz., pH 2.5, contact time 120 min and adsorbent dosage of 1 g for Vetiveria, various eluting agents such as 0.1 N HCl, HNO3, H2SO4 and 0.1 M EDTA were utilized to study the removal and recovery capacity. It was observed that 0.1 N H2SO4 eluted maximum 86.3% of Cr(VI) from the aqueous solution (Figures 4 and 5).

5) Adsorption Isotherm
Based on Freundlich and Langmuir formulae it was found that adsorption dosage of 1 g of Vetiveria was sufficient to adsorb maximum Cr(VI) i.e. 86.3% as depicted in Figures 6 and 7.

3.2.2. Anabaena

1) Effect of pH
The uptake of the metallic cations by Anabaena trimed down with increase in pH. Hence, the change of pH affects the adsorption process through dissociation of func-
Figure 4. Effect of eluting agents on Cr(VI) removal by *Vetiveria zizanioides*.

Figure 5. Percentage removal/recovery capacity of Cr(VI) by *Vetiveria zizanioides*.

Figure 6. Langmuir adsorption isotherm for adsorption of Cr(VI) by *Vetiveria zizanioides*.

Figure 7. Freundlich adsorption isotherm for adsorption of Cr(VI) by *Vetiveria zizanioides*.

Figure 8. Effect of pH on Cr(VI) removal by *Anabaena*.

Figure 9. Effect of Agitation Time

The uptake of Cr(VI) from effluent by *Anabaena* was found to increased, when the agitation time varied around 30 to 120 min and equilibrium was attained after 150 min at 30°C (Figure 9).

Figure 10. Effect of Adsorption Dosage

At pH 2.5 batch adsorption studies were carried out at 30°C and adsorption of Cr(VI) species was found to be improved with increase in adsorbent dosage. The adsorbent dosage was varied from 0.5 g to 3.0 g of wet biomass of *Anabaena* (Figure 10).

4) Elution Studies

Depending on the optimized conditions viz., pH 2.5, contact time 60 min and adsorbent dosage of 1 g for *Anabaena* various eluting agents such as 0.1 N HCl, HNO₃, H₂SO₄ and 0.1 M EDTA were utilized to study the removal and recovery capacity. From the experiments it was observed that 0.1 M EDTA eluted maximum of 88.86% of Cr(VI) from the aqueous solution as seen in Figures 11 and 12.
5) Adsorption Isotherm

Based on Freundlich and Langmuir formulae it was found that adsorption dosage of 0.5 g of wet biomass of Anabaena was sufficient to adsorb maximum Cr(VI) i.e. 88.86% (Figures 13 and 14).

4. DISCUSSION

The key factors for preparation for bioadsorbent depend on its morphological properties such as particle size and shape, binding surface area, and overall effluent removal capacity. The two selected bioadsorbents were conditioned/optimized based on morphological properties, binding surface area, and overall Cr(VI) removal capacity. The eco-friendly approach on lower cost was found superior in all the parameters [23-25].

The pH of the metal solution is the most influential factor as it affects surface properties of the adsorbent and metal speciation. The uptake of the metallic cations by adsorbent is reduced at pH below 3 and above 8; lowest at its isoelectric pH and highest at alkaline pH range as observed by Pagnanelli et al. [26]. Hence, the change of...
pH affects the adsorption process through dissociation of functional groups on the adsorbent and adsorbate. Similar results were obtained by many researchers [27,28].

Variation in adsorbent dosage increased the removal of Cr(VI) up to 80%. This is to be expected because for a fixed effluent concentration increasing total adsorbent doses, provides a greater surface area or adsorption site. This kind of observation was reported by Stephen et al. [29] with the removal of Pb using lignite. Water lettuce (Pistia stratiotes L.), an aquatic plant, removed arsenate [30]. Young plants were harvested from a pollution-free pond and hydroponically cultured, effectively absorbed arsenic in a range from 0.25 to 5.0 mg/L. From 22.8% to 82.0% of the As was removed for a biomass loading of 20 g/L at pH 7.0 after 144 h. The sorption capacity was 1.43 mg/g of biomass. 

Morgenstern [22] revealed the suitable dosages that were employed in our study. Langmuir and Freundlich adsorption isotherm, Seidel-ria et al. [32] employed activated carbon prepared from Gracilaria and obtained more than 90% removal of Cu from waste water. With advantages of high metal biosorption and desorption capacities, the biomass of Azolla is a promising application as a cost-effective biosorbent material for the removal of copper and nickel ions from wastewater [32]. The Comparison of various literature studies of Cu$^{2+}$ removal by biosorption was considered by Ahmady-Ashchin [33].

The low elution efficiency of HNO$_3$ solution can be attributed to the greater affinities of divalent cations for the negative charged sites on the bioadsorbent than monovalent cations. HCl and EDTA showed the maximum efficiency for the desorption process. This result obtained with EDTA can be attributed to the strong complexing ability to Cr(VI). HCl was selected as an effective desorbing agent due to the similar result with EDTA, and low cost of HCl [34].

The mathematical calculations with reference to Langmuir and Freundlich adsorption isotherm, Seidel-Morgenstern [22] revealed the suitable dosages that were sufficient for maximum adsorption of Cr(VI) and that were employed in our study.

5. CONCLUSION

The selected bioadsorbents, Vetiveria and Anabaena have proved to be high capacitance, economically viable and low cost adsorbent for Cr(VI) removal. Adsorption of Cr(VI) on these two selected bioadsorbents shows high association with Langmuir and Freundlich isotherm model. This present study can conclude that both Vetiveria and Anabaena are favourable alternate of chromium removal from water effluents.

REFERENCES


