

Effect of acidic and basic pretreatment of wild algal biomass on Cr (VI) biosorption

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Abstract: In the present study, effect of acidic and basic pre-treatment of wild algal biomass for their hexavalent chromium removal capacity was investigated. Wild algal biomass was subjected to chemical pretreatments with acid (perchloric acid with formaldehyde in 1:1 ratio (PF)), base (0.5 N NaOH), and only distilled water washed (DW). Batch experiments were conducted to determine the adsorption properties of pretreated wild algal biomass. It was observed that biomass was capable of removal of Cr (VI) metal ions from aqueous solution. The removal percentage was significantly depends on contact time, equilibrium pH, initial metal concentration and biosorbent load. Removal equilibrium was attained in less than 2 hours. Optimum pH for Cr(VI) was found to be 2 pH, and optimum algal dose was 10g/L. It was also observed that removal percentage was increased after acidic pre-treatment of wild algal biomass. In contrast, it was decreased significantly after basic pre-treatment. The order of maximum metal uptakes for Cr (VI) was PF>DW>NaOH. The sorption data of DW obtained at pH 2.0 conformed well fitted in both Langmuir and Freundlich isotherm models ($R^2 > 0.99$). The study concluded that the algal biomass pre-treated with perchloric acid and formaldehyde is more efficient biosorbent than sodium hydroxide pretreated algae and raw algae biomass for solution containing hexavalent chromium.

Keywords: Algae, Biosorption, Heavy metal, Pollution

I. Introduction

Rapid and unorganized urban and industrial developments have contributed continuously to the elevated levels of heavy metals which depleting natural resources and deteriorating the environmental quality [1]. About 90 per cent of sewage and 70 per cent of industrial wastes in developing countries are discharged untreated or partially treated wastes into water courses [2]. There are several technologies for treatment of wastewater like reverse osmosis, electrodialysis, ultrafiltration, chemical precipitation, ion exchange and phytoremediation are commonly used in industries. However, these technologies are often expensive, generating toxic non eco-friendly sludge or other waste products that require careful disposal and ineffective when the metals concentration are low (range 1-100 mg.L⁻¹) [3]. During the last few decades, biosorption process has emerged as an alternative solution of conventional technologies for the removal of toxic metals from water/wastewater [4]. Among promising biosorbents, algae have been found to be effective biosorbent due their huge abundance and high metal uptake capacities. Metal sorption capacity of biosorbent can be altered by pretreatment. The various chemical treatments used for biomass modification include washing the biomass with detergents, cross-linking with organic solvents, and alkali or acid treatment. The pretreatment could modify the surface characteristics either by removing or masking the groups or by exposing more metal-binding sites [5]. In the present study, the effect of pretreatment on metal uptake capacity of biosorbent for the different pretreatment methods used has been studied. Wild algae was chemically modified by acidic (perchloric acid with formaldehyde (PF)), basic pretreatments (NaOH), or only washed by distilled water (DW).

II. Material And Methods

Bioabsorbent processing: Wild algae samples were collected from native water reservoirs. Algal biomass was dried in an oven at 60 °C to constant weight, grind and sieved with the help of 85 BSS sieve. The 0.18 mm particle size fraction of biomass was used through the experiments.

Pretreatment: For basic pretreatment, 50 g wild algae was mixed with 500 ml solution of 0.5 N NaOH in 1000 ml beaker. The mixture was stirred with the help of magnetic stirrer for 8 hours and then centrifuged and washed with distilled water. For acidic pretreatment, 100g of wild algae was mixed with perchloric acid (HClO₄) and formaldehyde (HCHO). (25+25) ml equal v/v of HClO₄ + HCHO diluted to 1000 ml of distilled water. The mixture was stirred with the help of magnetic stirrer for 8 hours and then centrifuged and washed with distilled water to remove excess ClO₄⁻ and aldehyde. For blank sample, wild algae was washed simply with distilled water and dried at 60 °C. All of the dried pretreated algae samples were preserved at 4 °C for future use.

Chromium detection: The residual concentrations of chromium (VI) in the aqueous solution were determined using diphenyl carbazide method [6] at 540 nm using spectrophotometer. The pink colored complex, formed from 1, 5-diphenylcarbazine and Cr (VI) in acidic solution, was able to be spectrophotometrically

analyzed at 540 nm. To measure total Cr concentration, the Cr (III) was first converted to Cr (VI) at high temperature (130–140 °C) by the addition of excess potassium permanganate prior to the 1, 5-diphenylcarbazide reaction. The Cr (III) concentration was then calculated by subtracting the Cr (VI) concentration from the total Cr concentration.

Biosorption experiments: Batch experiments were performed in 250 ml Erlenmeyer flasks containing 100 ml of 10 mg/L Cr (VI) solutions. The experimental set up was incubated on a rotary shaker at 150 rpm at 30 °C for 2-3 h and biosorbents loaded with adsorb metal separated from solution by filtration. Sorption process parameters such as adsorption time, metal concentration, initial pH values and biosorbent load were optimized. The pH of each solution was adjusted with 0.1 N NaOH and HCl. The percent biosorption of metal ion was calculated as follows:

$$\text{Percentage removal (\%)} = \frac{C_i - C_f}{C_i} \times 100$$

Where, C_i and C_f are initial and final concentrations of metal ions, respectively.

The biosorption capacities were evaluated using Langmuir and Freundlich isotherms [7].

III. Results And Discussion

Effect of contact time: The sorption studies at different contact times help in determining the sorption capacities of biomass at varying time intervals. The effect of contact time on the percentage removal of Cr (VI) from synthetic solutions with initial metal ion concentration of 10 mg/l for Cr (VI) using the algal dose of 10 g/l are shown in Figure 1. It can be observed that all of the pretreated samples showed similar trend of removal. A rapid removal of Cr (VI) took place in the first 30 min, and thereafter the removal became asymptotic. Figure 1 showed a rapid removal of 65% at 15 min and remained almost constant to 80 – 85 % with minute fluctuations. It was attributed the fact that initially all functional groups on biosorbent were vacant and solute concentration was high [8]. However, after 1 hour, very few active sites were left on algal cell wall. Maximum percentage removal of 85% was achieved within a period of 1-2 hours. Therefore, for all experiments, optimum contact time was taken as 2 hours.

Effect of pH: pH controls the metal ion dissolution and the magnitude of the electrostatic charge in the medium [9]. It influences both the speciation of Cr (VI) in the aqueous solution and the binding sites availability on the surface of biosorbent [10]. Effect of pH on biosorption was studied over a range of 1 to 5. The results indicated that the Cr (VI) biosorption by non-living cells of algae was affected by initial pH of the solution and may be due to ionic attraction. Therefore, at low pH values the cell surface becomes more positively charged, reducing the attraction between metal ions and functional groups on the cell walls. As evident from Figure 2, at initial pH 1.0 nearly 99 % Cr (VI) was removed. While at initial pH 5.0, 80% Cr (VI) could be removed. High percentage removal at low pH was attributed to the fact that hexavalent chromium may be transformed in to trivalent form at low pH. To verify this speciation assumption, we analyzed the total Cr (Cr (VI) and Cr (III)) concentration in the medium after equilibrium. At low pH high Cr (III) concentration existed (result not showed) and sharply decreased with pH increase. It was determined that at pH 2 we have maximum removal efficiency. Acidic pretreatment showed high sorption around 90% while NaOH was least with 88 % at pH 2. This may be due to modifications on the cell wall components which remove the surface impurities and expose available active metal binding sites embedded in the cell wall.

Effect of Cr (VI) concentration and biosorbent load: The initial concentration of metal provides an important driving force to overcome all mass transfer resistance of metal ion between the aqueous and solid phases [11]. Hence, effect of different concentration of chromium ion (15, 20, 25, and 30 mg/l) was studied in conjunction with algal dose (5, 10, and 15 g/L) variation as shown in Figure 3. It is clear that the removal of Cr (VI) depended on the initial metal concentration and biosorbent dose. The Cr (VI) percentage removal decreases with increase in Cr (VI) concentration. Higher initial Cr (VI) concentration increased the number of collisions between Cr (VI) ions and the adsorbent, which decrease the adsorption process. In contrast, percentage removal of Cr (VI) increased with the increase of biosorbent dosages due to increased available surface area and number of binding sites. Maximum removal of 96.8 % was observed at an algal dose of 15 g/l from the solution with initial Cr (VI) ions concentration as 15 mg/l.

Biosorption isotherm models: Figure 4 (a) indicates the linear relationship between the amount (mg) of Cr(VI) ions sorbed per unit mass (g) of biomass against the concentration of Cr(VI) ions remaining in solution (mg/L). The coefficient of determination (R^2) was found to be 0.9986 for Cr (VI) biosorption, indicating that the biosorption of the metal ions onto biomass well fitted the Langmuir model. The b value was found as 0.01568 L/mg for Cr(VI) ion . The maximum biosorption capacity (q_m) was found to be 7.007 mg/g for Cr(VI) ion. The Figure 4 (b) shows the Freundlich isotherms obtained for the biosorption of Cr(VI) ions onto biomass using Eq. (3). The values of K_F and $1/n$ were found to be 3.807 and 1.0056 for Cr(VI) biosorption. It can be seen from the value of R^2 that both Langmuir and Freundlich model well fitted the equilibrium sorption data.

IV. Figure And Legend

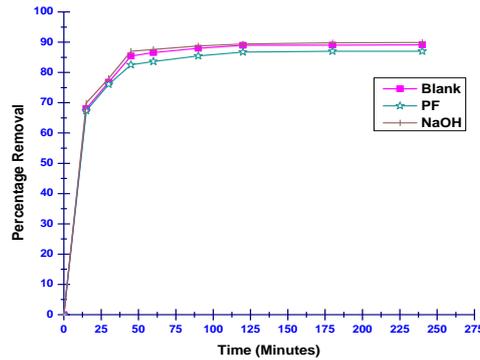


Figure-1: Effect of contact time on biosorption of Cr (VI)

(Metal concentration: 10 mg/L; Biomass dosage: 10 g/L; pH: 5; temperature 30°C).

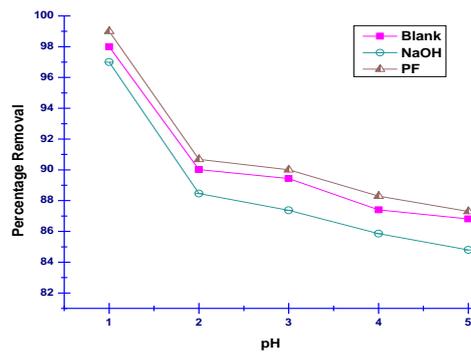


Figure-2: Effect of pH on biosorption of Cr (VI) (Contact time: 2 hours; Metal concentration: 10 mg/L; biomass dosage: 10 g/L h; temperature 30°C).

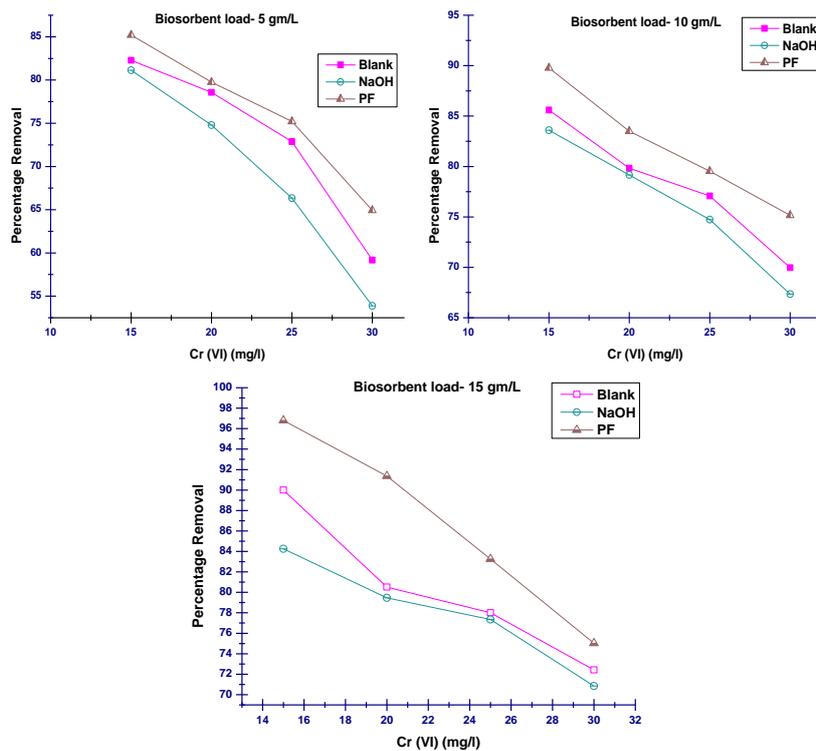


Figure 3. Effect of initial metal concentration (15, 20, 25, and 30 mg/l) and biomass dosage: (a) 5, (b)10 and (c)15 g/L on Cr (VI) biosorption (Contact time: 2 hours; pH: 2 ; Temperature 30°C).

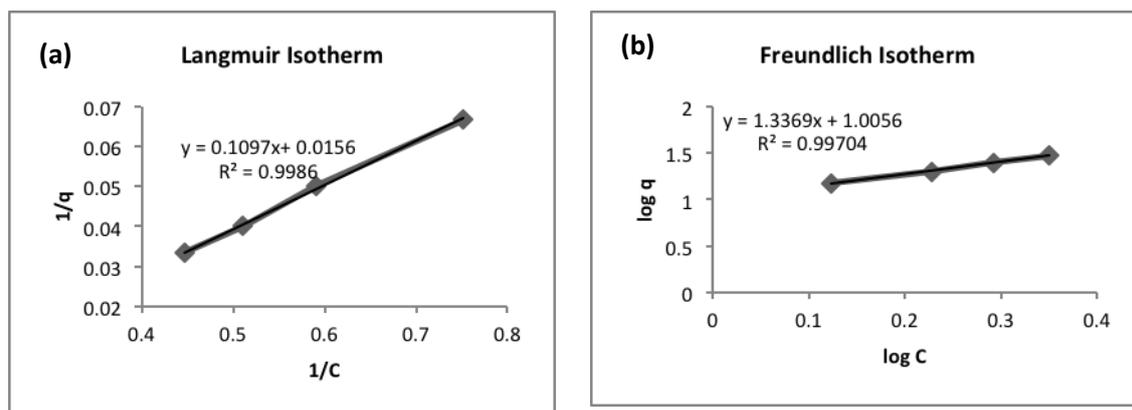


Figure 4. Biosorption isotherms of DW (a) Langmuir (b) Freundlich (Biomass dosage: 10 g/L; contact time: 2 hours ; pH: 2; temperature:30°C).

V. Conclusions

The effect of acid and basic pretreatment of algae for the removal of chromium has been studied. Results showed that removal efficiency was reduced in sodium hydroxide pretreatment compared to raw algae (DW). However, effect of acidic pretreatment has been studied and we found that by using (perchloric acid+ formaldehyde) for pretreatment the removal efficiency increases as compared to raw algae (DW) and NaOH treated. The order of maximum metal uptakes for Cr (VI) was PF>DW>NaOH. The coefficients of correlation (R^2) of both Langmuir and Freundlich model well were fitted the equilibrium chromium sorption data. Moreover, further detailed studies should be conducted in order to clarify the causes of enhancement or decrease in adsorption capacity for wild algal biomasses.

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