

Removal of Cr (VI) From Aqueous Solutions Using Moringa Olifera As A Biosorbent

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ABSTRACT

The removal of Cr (VI) from aqueous solution was performed using Moringa olifera seeds powder as a biosorbent by batch adsorption technique. The operating variables studied were adsorbent dose, particle size, and agitation speed, pH of solution, contact time and initial Cr (VI) concentration. Adsorption process was found to be highly pH dependent. The optimum pH range for adsorption of Cr (VI) was found to be between 2 and 3. Adsorption isotherms were modeled with the Langmuir, Freundlich, Dubinin Radushkevich and Tempkin isotherms. Langmuir equation is found to best represent the equilibrium data for Cr (VI) Moringa olifera seed system than other isotherms ($R_2=0.9946$). The maximum monolayer adsorption capacity was found to be 40.0 mg g⁻¹ at 298k.

Keywords: Adsorption, batch technique, isotherms, sorbent

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INTRODUCTION

Advances in water and wastewater treatment technology need spur for the development of technologies that may be more effective and less costly. Nowadays, the contamination of water by toxic heavy metals through the discharge of industrial waste water is a world wide environmental problem. The term "heavy metal" refers to the metallic elements having density greater than or equal to 6.0 gcm⁻³[1]. The most familiar metals are Cd (8.65 gcm⁻³), Cr (7.19 gcm⁻³), Co (8.90 gcm⁻³), Cu (8.95gcm⁻³), Pb (11.34 gcm⁻³), Hg (13.53 gcm⁻³), Ni (8.91 gcm⁻³) and Zn (7.14 gcm⁻³). Among these toxic metals Cr has major impact on environment and it has both beneficial and detrimental properties. In aqueous phase chromium mostly exists in two oxidation states such as trivalent Cr(i.e., Cr³⁺, Cr(OH)₂ or Cr(OH)₃, etc.) and hexavalent Cr(i.e., HCrO₄⁻, CrO₄²⁻ or Cr₂O₇²⁻), Most of the hexavalent compounds are toxic, carcinogenic and mutagenic and even it can cause lung cancer also[2,3]. Cr (III) is essential for human nutrition (especially in glucose metabolism) and it is relatively innocuous and immobile. Cr (VI) ions mostly exists as H₂CrO₄ form at high acidic medium (pH =1.0). At pH 2-6 there is equilibrium between Cr₂O₇²⁻ and HCrO₄⁻ species, if the Cr (VI) concentration is less than 0.02 M, HCrO₄⁻ is predominant form, when Cr(VI) concentration is greater than 0.02 M the dichromate ion (Cr₂O₇²⁻) is the predominant species and under alkaline condition (pH>8) it exists as chromate CrO₄²⁻ anion[4]. Chromium and its compounds are widely used in electroplating, leather tanning, cement, dyeing, metal processing, wood preservatives, paint and pigments, textile and steel fabrication industries. These industries produce large quantities of toxic metal wastewater effluents. But the maximum exit Cr (VI) concentration based on USEPA guidelines for potable water is 0.05 mg/l and the United Nations Food and Agricultural Organization recommended maximum level for irrigation waters is 0.1 mg/l [5]. In general, a wide range of processes have been reported to eliminate the Cr(VI) from water and wastewater such as chemical precipitation, electrochemical reduction, sulphide precipitation, cementation, ion-exchange, reverse osmosis, electrodialysis, solvent extraction and evaporation,etc.[6]. The application of such methods is however cost intensive and is unaffordable for large scale treatment of wastewater. Hence, more economical means such as adsorption for the removal of toxic metals have been sought for. Therefore, there is a need to search an effective low cost adsorbent for economical waste water treatment. A variety of natural plant biomass like green algae, rice bran, sugar industrial waste, tamarind hull, tea waste, *Azadirachta indica*(neem) leaf powder, pomegranate peel, olive bagasse and hazelnut shell, etc. are used in the previous investigations. Literature survey reveals that the plant biomass is capable of reducing Cr (VI) to Cr (III) due to the active participation of its several anionic functional groups like hydroxyl, carbonyl, carboxyl, sulfhydryl and phosphoryl groups [6–11]. In the present work, we describe the use of Moringa olifera seed powder (MSP) as an effective and inexpensive material for the removal of hexavalent chromium from aqueous solution. The effects of adsorbent dose, pH, contact time and initial metal ion concentration on the adsorption capacity were investigated.

MATERIALS AND METHODS

Preparation of adsorbent in a solid waste. The collected materials were then washed with distilled water for several times to remove water soluble impurities and surface adhered particles. The washed materials were dried in a hot air oven at 50° C for 48 h. Dry moringa olifera seeds ground in ball mill and the resulting crumbs were sieved to different particle sizes: 125-180, 180-250, 250-355 and 355-500 µm. Finally, the products obtained were stored in glass bottle for further use. No other chemical or physical treatments were used prior to adsorption experiments.

Preparation of Cr (VI) solutions

A stock solution of Cr (VI) (1000 mg/l) was prepared by dissolving appropriate quantity of AR grade $K_2Cr_2O_7$ in 1000 ml of Elix water from Millipore purification unit. The stock solution was further diluted with deionised water to desired concentration for obtaining the test solutions. The initial metal ion concentrations ranged from 50 to 400 mg/l were prepared.

Batch experiments

Adsorption experiments were carried out in batch mode at ambient temperature. In order to investigate the nature of Cr (VI)–MSP interaction, initially the effect of pH on percentage removal was carried out and then further experiments on the effect of contact time, initial concentration and adsorption dose were conducted by using optimized pH. Only one parameter was changed at a time while others were maintained constant. In the first set of experiment, percentage adsorption was studied at various pH of (1–8) at MSP of 0.5 g/50 ml, initial Cr (VI) of 50 mg/l and the predetermined time (45 min) in a rotary shaker at a speed of 170 rpm. Next second set of experiments were conducted with various contact time, various initial Cr (VI) concentration (from 50 to 400 mg/l) at constant adsorbent (0.5 g/50 ml) dose and at optimized pH 3.0. In the third set of experiment MSP dose was varied (0.1–1.0 g/50 ml) while other parameters such as initial Cr (VI) concentration (50 mg/l), optimum time (45 min) and optimum solution pH kept constant. After completion of every set of experiments the supernatant was separated by filtration using Whatman filter paper no. 42 and only 10 ml of each sample was stored for residual chromium analysis. The pH of each solution was adjusted using required quantity of 1N HCl (or) 1N NaOH before mixing the adsorbent.

Metal analysis

Final residual metal (Cr (III) and Cr (VI)) concentration after adsorption was directly measured by flame atomic absorption spectrometer (Perkin-Elmer Model 2380) with an air– acetylene flame.

RESULTS AND DISCUSSION [12-19]

Effect of Adsorbent dose

To study the effect of adsorbent dose(g) on the uptake of Cr (VI), experiments were done with 50 ml of 50 mg/l ion solutions, while the amount of adsorbent added was varied from (0.1 – 1.0 g Cr (VI) from aqueous solution increased with the adsorbent dose and reached a plateau at 0.5g of sorbent. The increase in ion removal was due to the increase in the available sorption surface sites.

Effect of pH

The effect of pH on percentage removal of chromium. It was observed that the adsorption of Cr (VI) decreased with increase in initial pH from 2.0 to 7.0. The maximum removal was occurred at initial pH 3.0 for MSP. At lower pH the surface area of the adsorbent was more protonated and competitive negative ions adsorption occurred between positive surface and free chromate ion. Adsorption of Cr (VI) at pH 3.0 shows the binding of the negatively charged chromium species ($HCrO_4^-$) occurred through electrostatic attraction to the positively charged (due to more H^+ ions) surface functional groups of the adsorbent. But in highly acidic medium (pH \approx 2) H_2CrO_4 (neutral form) is the predominant species of Cr (VI) as reported by Agarwal et al. Hence, at pH 2 percentage adsorption decreased due to the involvement of less number of ($HCrO_4^-$) anions on the positive surface. At higher pH due to more OH^- ions adsorbent surface carrying net negative charges, which tend to repulse the metal anions (CrO_4^{2-}). Therefore, maximum removal of Cr (VI) from aqueous solution was achieved at pH 3.0 and all the further studies were carried out by maintaining the solution at pH 3.0.

Effect of agitation speed

Effect of agitation speed on removal of Cr (VI) ion by MSP was studied using 50 ml of 50mg/l ion concentration with shaking rate of 50 - 200 rpm. It is shown that the ion uptake was found to increase with an increase in agitation rate from 50 to 150 rpm and then remained constant for higher agitation rate. It is due to the fact that the increase of agitation rate, improves the diffusion of ions towards the surface of the adsorbents and shaking rate of 170 rpm is used to assure the surface binding for ions up-take.

Effect of particle size

The batch adsorption experiments were carried out using four different particle sizes (125-180, 180-250, 250-355, 355-500 μm) of the adsorbent using 50 ml of 50 mg/l ion concentration. Effect of particle size on removal of Cr (VI) by MSP (conditions: adsorbent dose=0.50g; ion concentration=50 mg/l; contact time=45 minute; agitation speed=170 rpm; pH =3; temperature=25°C).

Effect of contact time

The experimental runs measuring the effect of contact time (5-120 minute) on the batch adsorption of Cr (VI) and at initial pH value 3 and initial Cr (VI) concentration of 50 mg/l indicated that increase in contact time from 5 to 45 minute enhanced the percent removal of Cr (VI) significantly. The initial rapid adsorption gives away a very slow approach to equilibrium. The nature of adsorbent and its available sorption sites affected the time needed to reach the equilibrium. For *Moringa olifera* seed powder this time was 45 minute.

Effect of initial ion concentration

The adsorption data of Cr (VI) at different initial concentrations ranging from 50-400 mg/l obtained at optimum values of pH, agitation speed, particle size and adsorbent dose. However, the experimental data were measured at 120 minutes to make sure that full equilibrium was attained. It is well known that by increasing the concentration of metal ions, the adsorbed amount increases.

Adsorption equilibrium study

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations have been used to describe the equilibrium nature of adsorption. Langmuir equation assumes that the surface is homogenous. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor (RL , also called equilibrium parameter)

CONCLUSIONS

The present work shows that *Moringa olifera* seeds, is an efficient sorbent for the removal of Cr (VI) from aqueous solution and it will be an alternative to more costly adsorbents such as activated carbon. Experimental data indicated that the adsorption capacity was dependent of operating variables such as adsorbent dose, particle size, agitation speed, pH, contact time and initial ion concentration. The sorption data of PNP were well fitted with the Langmuir isotherm model. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined to be 40.0 mg/g. The dimensionless separation factor RL revealed the favourability of MSP on Cr(VI) adsorption.

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