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A NEW EFFECTIVE ADSORBENT DERIVED FROM THE BARKS OF *Ziziphus mauritiana* PLANT FOR THE REMOVAL OF CHROMATE FROM POLLUTED WATER

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ABSTRACT

An adsorbent prepared from *Ziziphus mauritiana* barks powder (ZMBP) is found to adsorb Chromate ions from water. The extractions conditions for the maximum removal of Chromate ions from water are optimized. 94.0% of Chromate is removed from water having 20 mg/L of Chromate ions at pH = 2, agitation time: 90 min, adsorbent dosage: 0.5 g/500mL, rpm: 250 and temp.: 30°C ± 1°C. The adsorption capacity is 18.8 mg/g. Co-ions are less interfered. Spent adsorbents can be regenerated and reused up to three cycles. The procedure is applied to polluted water/industrial effluents samples.

Key Words: *Ziziphus mauritiana* barks, Chromate removal, Applications.

INTRODUCTION

The toxicity of Chromium species to aquatic life is well known[1-5] and its source of contamination of natural water is the disposal of untreated or ill-treated sewages from different industries such as leather, paint, textile, rubber, metallurgical, ceramics, photographic, fungicides and ink [1-9].

Of the various conventional methods developed involving chemical precipitation[10], ion exchange[11,12], electrocoagulation process[8], Nanofiltration[13] and Electrolytic process[14], adsorption methods are found to be simple and economical. The recent past witnesses a growing research trend in developing bio-adsorbents from plant materials having an affinity towards Chromate ions. These non-conventional adsorbents are proving to be effective and economical and are suitable especially in agricultural countries like India[15-28].

Our research group is investigating these aspects of pollution control methods and found some successful adsorbents for various toxic ions[25-35]. In our initial search among the various bio-materials, bark powder of *Ziziphus mauritiana* plant is found to adsorb Chromate ions from water. The adsorption nature of the Chromate ions is investigated in this work with respect to the gradual change in the various physicochemical parameters The optimum conditions for the possible maximum removal of Chromate ions are investigated. The procedure developed is validated using polluted water/ industrial effluent samples.

EXPERIMENTAL

Adsorbent

Ziziphus mauritiana, is an evergreen shrub grows to a height of 15 meters and its trunk has the diameter of 40 cm. It grows widely in the Indian subcontinent. It is a fast-growing tree with medium lifespan and it belongs to the *Rhamnaceae* family in the plant kingdom. The tree barks are cut into pieces, air dried and crushed to powder and meshed to the size of 75µm. The powder is then oven-dried at 105^{0}C for about 1 h and then it was stored. Thus prepared adsorbent from *Ziziphus mauritiana* barks powder is named as ZMBP.

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Fig.-1: Ziziphus mauritiana Plant Showing An Affinity towards Chromate Ions

Reagents and Chemicals

A.R. grade chemicals and distilled (double) water were used. Diphenyl carbazide solution (0.25%) in 50% acetone and 6 N H_2SO_4 were used. 500 mg/L Chromate stock solution was prepared and it was diluted as per the need.

Method

Batch methods were adopted.[6,36,37] Known amounts of ZMBP were added to definite volumes of known concentrations of Chromate solutions in stoppered bottles of 250 ml. capacity . Initial pHs were adjusted either by addition of drops of dil. HCl or by dil. NaOH or both and monitoring the pH changes with pH meter (Sytronics-make). Then the solutions were agitated in mechanical shakers at 250 rpm. After a certain time of equilibration, the shaking was stopped and the solutions were filtered and the concentration of Chromium was assessed by Diphenyl Carbazide" method [38].

The adsorption of Chromate by *ZMBP* was investigated by gradually varying the various parameters and the results were depicted in Fig.-2 to 6.

The interference caused by common co-ions (in five folds) on the % removal of Chromate from waters was investigated and the findings are presented in Fig.-7 The adsorbent developed was used to extract Chromium (VI) from the sewage samples collected at the tannery and Chrome plating industries and also samples from /polluted lakes. The findings are noted Table-1.

RESULTS AND DISCUSSIONS

Initial pH of Equilibrium System

The adsorption is pH dependent as is detailed in Fig.-2. % of extraction is progressively increased with the decrease in initial pH of the extraction system. At low pH values, the extraction is marked; it is 94.0% at pH: 2, 85.5% at pH: 4, 65.0% at pH:6, 52.0% at pH: 8, 45.0% at pH: 10 and only 25.0% at pH:12 at ZMBP dosage: 0.5g/500mL, agitation time: 90 min; rpm: 250 and temp.: 30°C±1°C .

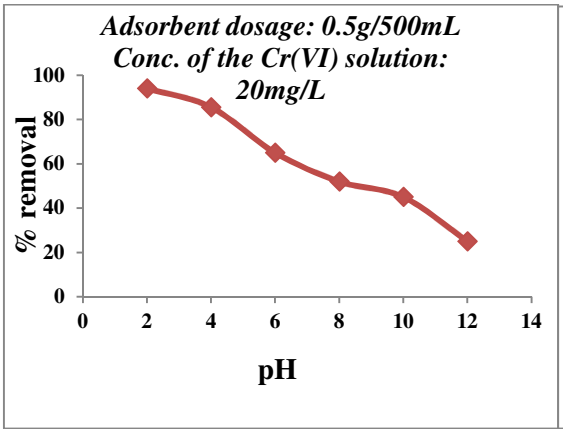

Fig.-2 : pH Vs % Removal of Cr(VI)

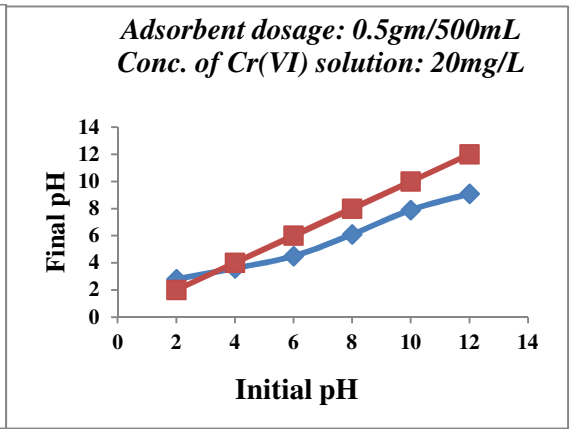

Fig.-3: pH $_{ZPC}$ of ZMBP

The less affinity of ZMBP surface towards Chromate ion at high pHs, may be viewed from the pHzpc point of view. The pHzpc is 3.6 (Fig.-3) and so, the surface acquires negative charge above this pH value and it is attributed to the dissociation of functional groups namely hydroxide, carboxyl etc. that are naturally present. At low pHs, the ionization of these groups are less favored and even protonated. Hence, the conducive pH of the equilibration mixture for the adsorption of Chromate anions is low pHs.

Agitation Time

Percentage removal is time-dependent. The influence of agitation time on the extent of extraction of Chromium (VI) is depicted in Fig.-4.

Percentage removal of the Chromate ion is 34.0% at 15 min, 56.0% at 30 min, 75.0% at 45 min, 84.0% at 60 min, 88.0% at 75 min, 94.0% at and above 90 min. An equilibrium state is reached above 90 min.

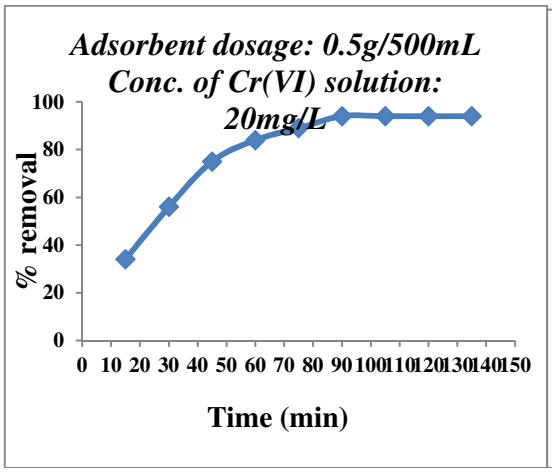

Fig.-4: Agitation time Vs % Removal of Chromate

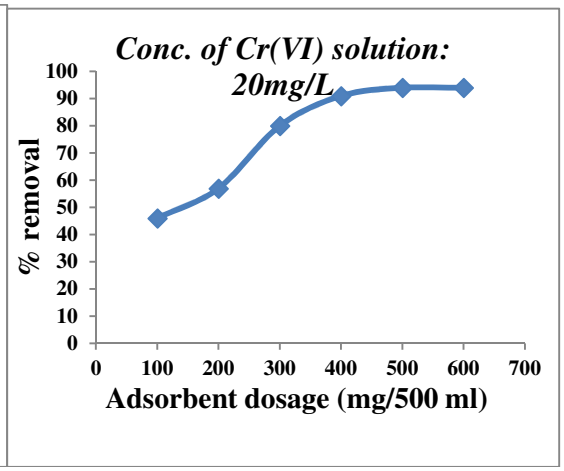

Fig.-5 : ZMBP Dosage Vs % Removal of Chromate

ZMBP Concentration

As the concentration of ZMBP is varied from 100 mg/500ml to 600 mg/500 ml, while keeping the other conditions at optimum levels, the % removal of Chromate is fast initially and slowdown at higher concentrations. Maximum removal of 94.0% is attained with 500 mg/500 ml (Fig.-5). The adsorption capacity is 18.8 mg/g

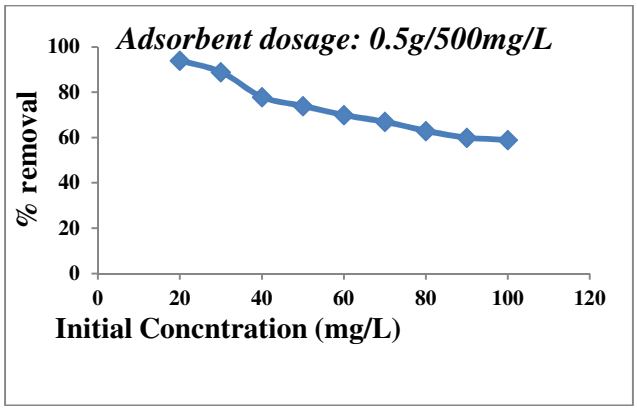

Fig.-6: Initial Concentration of Chromate Vs % Removal of Chromate

Initial Concentration

By gradually changing the Chromate initial concentration from 20 mg/L to 100 mg/L, % removal of Chromate is investigated while keeping other extraction conditions at optimum levels namely, pH = 2, agitation time : 90 min, ZMBP dosage: Findings are shown in Fig 6. % removal is observed to be

decreasing from 94.0% to 60.0% as Chromate initial concentration varies from 20 mg/L to 100 mg/L (Fig. 6). The ratio of Chromate ions to the active sites on ZMBP is high at low concentration of Chromate and hence more removal. But as the concentration of Chromate increases for a fixed dosage of ZMBP, the ratio: Chromate/active site is less and so decrease in % removal. In other words, at elevated concentrations of Chromate, the demand for the adsorption (active) sites is high but as the adsorbent concentration is fixed, the demand is not fully been met and hence, the fall in % removal Chromate ions.

Interference of Co-ions

The interference caused by fivefold excess of Co-ions on the extraction of Chromate is investigated and the findings are presented in Fig.-7(a) and 7 (b).

Co-anions are interfered in the decreasing order: $PO_4^{3-} > SO_4^{2-} > Cl^- > HCO_3^- > NO_3^-$. The order of interference of Co- cations is: $Zn^{2+} > Cu^{2+} > Mg^{2+} > Ca^{2+} > Fe^{3+}$.

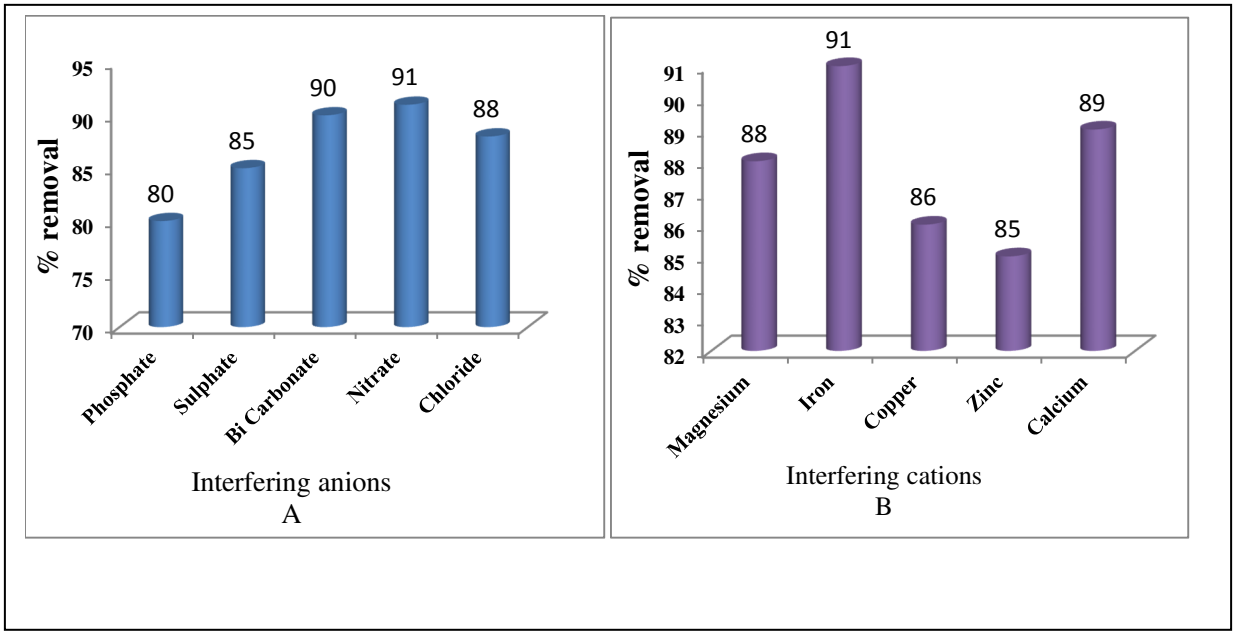

Fig.-7: (a): Interference of Co- anions on % Removal of Chromate (b): Interference of Co-cations on % removal of Chromate

Applications

The validity of the procedure developed in the present investigation was assessed by applying it to the Tannery/ Chrome plating industries/ polluted lake samples as detailed in Table 1. It may be noted that the adsorbent investigated is effective as it removes substantial amounts of Chromate ions.

Table-1: Removal of Chromate from Samples Collected from Various Sources
(pH:2, ZMBP Dosage: 0.5gm/500 mL, Agitation Time: 90 min, rpm:250 and Temperature 30°C±1°C)

Samples	Initial Cr(VI) conc.	Cr(VI) conc. after extraction	% removal
Tannery Industries			
1 2 3	10.5 mg/L 13.3 mg/L 19.0 mg/L	1.7 mg/L 1.5 mg/L 1.9 mg/L	83.8% 88.7% 90.0%
Chromate Plating Industries			

1 2 3	15.5 mg/L 18.4 mg/L 20.0 mg/L	2.1 mg/L 2.6 mg/L 2.8 mg/L	86.5% 85.9% 86.0%
Lake Samples(containing known Chromate concentrations)			
1 2 3	12.2 mg/L 16.4 mg/L 18.5 mg/L	1.9 mg/L 2.0 mg/L 1.8 mg/L	84.4% 87.8% 90.3%

Regeneration and Reuse

The spent adsorbent**,** ZMBP, was tried for regeneration using various eluents. 0.1 M NaOH was observed to be effective. Thus regenerated adsorbent was again used in the extraction process. This regeneration process was repeated. The loss of adsorption capacity with the increase in regenerations was assessed by plotting a graph between % removal Vs No of regeneration as depicted in Fig. 8. It can be noted that the adsorbent ZMBP, is retaining its capacity up to three generations with a marginal loss of adsorption capacity.

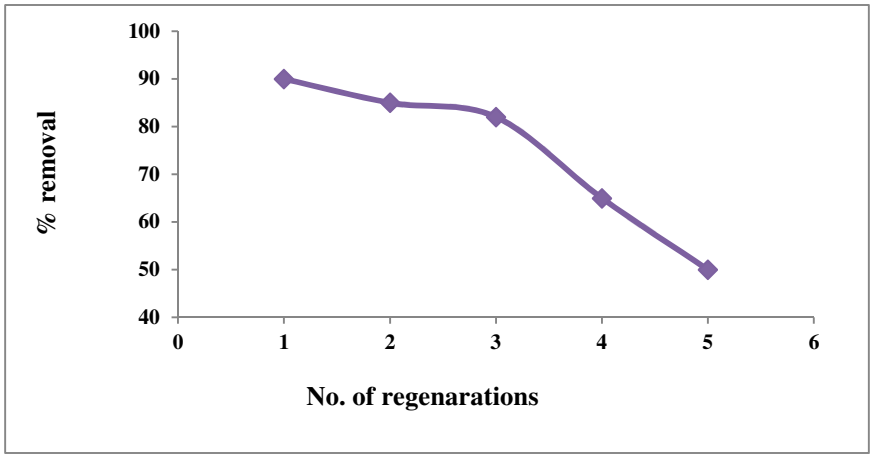

Fig.-8: Effect of Regenerations on Percentage Removal

CONCLUSION

A sorbent prepared from *Ziziphus mauritiana* barks powder (ZMBP) is investigated as an adsorbent to remove Chromate ions from polluted water. Various conditions are investigated and optimized for the maximum extraction of Chromate ions. % of extraction is observed to be 94.0% at pH = 2, agitation time: 90 min, Chromate conc.: 20 mg/L, ZMBP dosage: 0.5 g/500mL, rpm: 250 and temp.: 30°C ± 1°C. The adsorption capacity is 18.8 mg/g.

The spent ZMBP is regenerated with 0.1 M NaOH for subsequent re-use as an adsorbent. It is noted that the adsorption capacity is marginally lost up to three re-generations. The adsorbent developed is successfully applied to polluted waters/effluents.

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