Effective Removal of Hexavalent Chromium from Polluted Water using *Phoenix sylvestris* Seed Powder as Adsorbent

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Phoenix sylvestris seed powder (PSSP) was investigated as an adsorbent for the removal of chromium(VI) ions from water using batch extraction method. The conditions for the maximum extraction were optimized. The adsorption capacity was found to be 22.5 mg/g at pH = 2, contact time: 60 min, PSSP dosage: 0.40 g/500mL, rpm: 300 and temp.: 28 ± 2 ºC and found to be more suitable adsorbant than compared to other reported adsorbents in the literature. Co-ions even in five-fold excess were less interfered. Regeneration studies revealed that *Phoenix sylvestris* seed powder can be used up to three cycles. The method developed was successfully applied to polluted water/industrial effluents samples.

Keywords: *Phoenix sylvestris* seed powder, Hexavalent Chromium, Adsorption.

INTRODUCTION

The removal of chromium ions from water is one of the important aspects of pollution control research as the species are highly toxic [1-6]. The contamination of water with the chromium species mainly arises due to the ill-treated or untreated disposal of effluents from chromium based industries [1-8].

Besides the various conventional methods [7-10], growing interest is seen in adopting unconventional adsorbents for the extraction of chromium species from water in view of economy and effectiveness. Various biomaterials such as active carbons [11-13], fly ash [14], bone charcoal [15], microbes [16], modified zeolites [17,18], coconut fiber [19], bioaccumulation [20], maple sawdust [21], eucalyptus bark [22], waste tea leaves and rice husk [23], *Hevea brasilinesis* sawdust [24] and neem sawdust [25] are investigated for the removal of chromium ions from water. Spent coffee grounds [26], *Nerium odorum* and *Calotropis zygantia* [27], *Chenopodium album* and *Eclipta prostrate* [28], *Anogeissus latifolia* and *Hardwickia binata* [29], *Justicia adhatoda*, *Cissus quadrangularis* and *Soapnut acacia* [30], *Salvadora persico* and *Caesalpinia bonduc* plants [31]. *Croton tiglium* and *Cassia occidentalis* [32], and *Azadirachta indica*, *Syzygium cumini* and *Acacia arabica* [33] were also investigated as adsorbents.

Our research group is working on these same outlines and found some successful methods for the removal of various toxic ions using biomaterials as adsorbents [34-40]. While searching various plant materials for their possible use as adsorbents in the removal of various toxic ions, it is noticed that there is a strong affinity between the seeds powders of *Phoenix sylvestris* plant and chromium(VI) ions. Hence, *Phoenix sylvestris* seed powder (PSSP) is investigated as adsorbent in the present work for the removal of chromium(VI) from wastewaters by optimizing the various physico-chemical parameters. The procedure developed is applied to real polluted waters/industrial effluents.

EXPERIMENTAL

All the chemical used were of analytical grade. Double distilled water was used for the preparation of solutions. Stock solution (500 mg/L) was prepared and suitably diluted as per the need. Diphenyl carbazide (0.25 %) in 50 % of acetone and 6 N H_2SO_4 was used as colour developing agent.

Adsorbent: *Phoenix Sylvestris* tree (wild palm tree) is common in India and grows even in shades (absence of proper sunlight) to a height of 1 to 12 meters. It belongs to Arecaceae family in plant kingdom. The fruits of the tree form on about
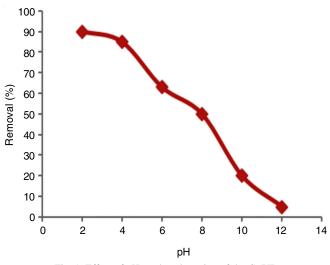
1 meter long pendulous stem having a number of bunches. The fruits were collected, washed, sun-dried and their skins were peeled off. The seed obtained were oven dried at 105 ºC for about 2 h and then crushed to powder of less than 75 μ in size.

Method: Procedures based on batch methods were adopted [7-9]. Known quantities of *Phoenix sylvestris* seed powder were taken into 1 L/500 mL stopper bottles containing 500 mL/250 mL of potassium dichromate solution of known concentrations. Initial pHs of the solutions were adjusted with dil. HCl/dil. NaOH using pH meter. The samples were agitated in mechanical shakers for a desired time and filtered. The residual amounts of Cr(VI) were determined adopting diphenyl carbazide method [41].

The effect of various parameters such as equilibration time, initial pH, sorbent dosage, *etc*. on the extraction of Cr(VI) onto the surface of *Phoenix sylvestris* seed powder were investigated. Interference caused by five-fold excess of co-ions (naturally existing) on the removal of chromium(VI) was also investigated. The methodology developed was applied to real polluted water samples namely, effluents of tannery and chrome plating industries.
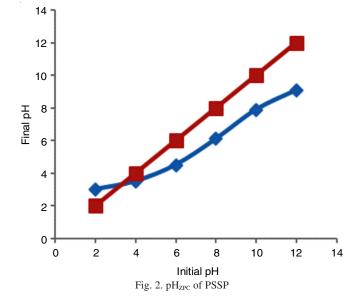
RESULTS AND DISCUSSION

Initial pH of equilibrium system: pH of agitating solution is found to effect the removal percentage profoundly. With the increase in pH, the extraction percentage is decreased (Fig. 1). The removal % is found to be 90 % at pH: 2; 85 % at pH 4; 63 at pH: 6; 50 % at pH: 8; 20 % at pH: 10 and 5 % at pH:12, at other optimum extraction conditions namely, *Phoenix sylvestris* seed powder (PSSP) dosage: 0.8 g/L, rpm: 300, equilibration period: 60 min and temp.: 28 ± 1 ºC.

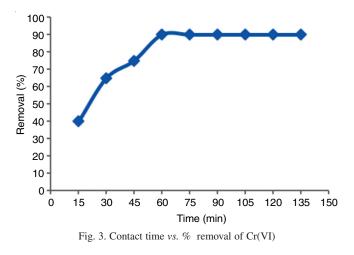Fig. 1. Effect of pH on the adsorption of the Cr(VI)

The adsorption behaviour may be understood from the view point of pH of zero point of charge (pHzpc). The pHzpc for *Phoenix sylvestris* seed powder (PSSP) is found to be 3.5 (Fig. 2). So above this pH, the surface of adsorbent possesses negative charge due to the dissociation of functional groups (-OH, -COOH, *etc*.) present on the surface of adsorbent and below this pHzpc, the dissociation is less favoured and moreover protination also may occur at sufficiently low pHs. Thus
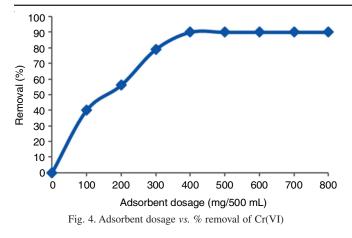
Fig. 2. pH$_{ZPC}$ of PSSP

the surface of adsorbent shows different thrusts towards cations or anions depending upon the pH conditions of the equilibrium mixture. At low pH solutions (≈ 2), adsorption of chromate, an anion is favoured because the surface of adsorbent is positively charged while at higher pHs, the adsorption is less favoured as the inter-surface is negatively charged. Hence, the removal percentage is more with decrease in pH of the extraction mixture.
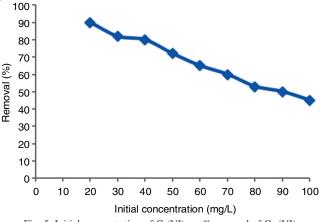
Agitation time: As the time of equilibration between the adsorbent, *Phoenix sylvestris* seed powder (PSSP) and the adsorbate (chromate) solution is varied, the extraction percentage is also changed (Fig. 3). The removal % is found to be 40 % at 15 min, 65 % at 30 min, 75 % at 45 min, 90 % at 60 min and above. A steady state is reached after 60 min of equilibration time.

Fig. 3. Contact time *vs.* % removal of Cr(VI)

Phoenix sylvestris seed powder (PSSP) dosage: The effect of PSSP concentration on the removal percentage of chromium (VI) is shown in Fig. 4. The concentration is varied from 100 mg/500 mL to 800 mg/500 mL. With the increase in the PSSP concentration, the removal precentage is progressively increased and the maximum of 90 % extraction of chromium(VI) is observed at and above 400 mg/500 mL adsorbent concentration. The adsorption capacity is 22.5 mg/g and found to be excellent adsorbant as compared to several adsorbents reported in the literature [42-48] .

Fig. 4. Adsorbent dosage *vs.* % removal of Cr(VI)

Fig. 5. Initial concentration of Cr(VI) *vs.* % removal of Cr (VI)

Initial concentration: The effect of initial concentration of chromium(VI) on the percentage removal of Cr^{6+} is investigated by varying the initial concentration from 20 mg/L to 100 mg/L while keeping the other extraction conditions at optimum levels *viz.*, pH: 2 agitation time: 60 min, PSSP dosage: 0.4 g/500 mL; rpm: 300 and temp.: 28 ± 2 °C. As the initial concentration increases, the removal percentage is also decreased (Fig. 5) means 90 % at 20 mg/L; 82 % at 30 mg/L; 80 % at 40 mg/L; 72 % at 50 mg/L; 65 % at 60 mg/L; 60 % at 70 mg/L; 53% at 80 mg/L; 50 % at 90 mg/L; 45 % at 100 mg/L. At low concentration of chromium(VI), the availability of active sites on the adsorbent (PSSP) is more and hence greater removal. As the concentration of chromium(VI) is progressively increased, the demand for active sites increased but for the fixed adsorbent concentration (0.4 g/500 mL), the availability is less and hence, the removal percentage is decreased with the increase in the initial concentration of adsorbate (chromate).

Interference of co-ions: The removal percentage of chromate is investigated in the presence of five-fold excess of co-cations and anions while keeping other extraction conditions at optimum levels. The results obtained are shown in Fig. 6. It is interesting to note that substantial amounts of chromium(VI) are removed and the interference of co-ions is less. Co-anions are interfered

in the order: $PO_4^{3-} > SO_4^{2-} > Cl^- > HCO_3^- > NO_3^-$ while co-cations in the order: $Zn^{2+} > Cu^{2+} > Ca^{2+} > Mg^{2+} >> Fe^{2+}$. In any case, the percentage removal has not come down below 75 % indicating that effectiveness of the adsorbent towards highly toxic chromium(VI) ions.

Applications: The adoptability of present adsorbent (PSSP) for removing chromium (VI) from polluted waters *viz.*, effluents from tannery, chrome plating industries and lake water were investigated and the results are presented in Table-1. As is evident from the data that substantial amounts of chromate is removed and hence, the adsorbent can be used in the treatment of wastewater/industrial effluents.

Regeneration and reuse: If the spent adsorbent is regenerated and reused, the cost of procedure is effectively decreased. So, the regeneration of spent PSSP is investigated using various eluting agents. It is found that 0.1 M NaOH is successful but with decrease in efficiency (Fig. 7). With 1st, 2nd, 3rd, 4th and 5th regenerations, the removal percentage of chromate is found to be 90 , 86, 82, 75 and 50 %, respectively. Hence, the spent adsorbent can be regenerated until three cycles.

Comparative study with the reported adsorbents: The adsorption capacity of the present developed adsorbent PSSP
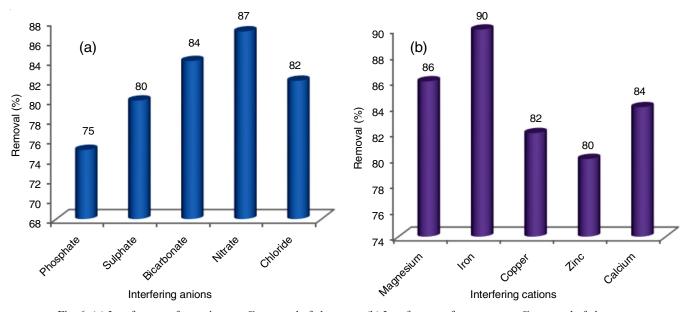

Fig. 6. (a) Interference of co-anions on % removal of chromate; (b) Interference of co-catons on % removal of chromate
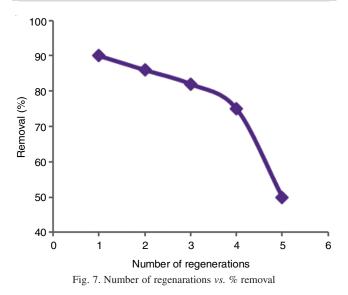
TABLE-2
COMPARISON OF CHROMIUM(VI) ADSORPTION CAPACITIES OF VARIOUS ADSORBENTS REPORTED IN LITERATURE WITH *Phoenix sylvestris* SEED POWDER (PSSP)

S. No.	Adsorbent	pH	Initial conc. Cr(VI) (mg/L)	Adsorption capacity towards Cr(VI) (mg/g)	Ref.
1	Coconut tree sawdust	3	20	3.6	[42]
3	Coconut shell carbon	4	25	20	[43]
2	Beech sawdust	1	200	16.10	[48]
5	Hazelnut shell	-	-	17.70	[47]
7	Red mud modified by lanthanum	2	50	17.35	[44]
4	Sugarcane bagasse	2	500	13.40	[45]
6	Treated sawdust of Indian rosewood	3	10	10.0	[46]
8	*Phoenix sylvestris* seeds powder (PSSP)	2	20	22.5 mg/g	Present work

TABLE-1
REMOVAL OF CHROMIUM(VI) FROM SAMPLES COLLECTED FROM VARIOUS SOURCES

Samples	Initial Cr(VI) conc. (mg/L)	Cr(VI) conc. after extraction (mg/L)	Removal (%)
Tannery industries			
1	10.0	1.2	88.0
2	8.3	1.0	88.0
3	9.0	1.3	85.5
Chromate plating industries			
1	12.5	1.5	88.0
2	14.5	2.0	86.2
3	16.0	2.5	84.4
Natural lake samples (fed with known amounts of chromates)			
1	15.0	1.8	88.0
2	20.0	2.9	85.5
3	25.0	2.8	88.8

(pH: 2, PSSP dosage: 0.4 g/500 mL, time of equilibration: 60 min, rpm: 300 and temperature 28 ± 2 °C).

Fig. 7. Number of regenarations *vs.* % removal

is compared with the reported adsorbents in the literature (Table-2). It can be inferred that PSSP has more adsorption capacity towards chromate than other reported adsorbents.

Conclusion

An adsorbent derived from *Phoenix sylvestris* seeds powder (PSSP) is investigated for its adsorption nature towards chromate ions from water using simulated waters. By varying various physico-chemical parameters such as pH, sorbent dosage, time of equilibration, initial concentration of chromium

(VI), *etc.*, the optimum conditions for the maximum extraction of chromate ions are optimized. Extraction of chromium(VI) is 90 % at pH = 2 , 60 min of agitation time, 300 rpm, PSSP dosage: 0.4 g/500 mL and initial concentration of chromium (VI): 20 mg/L. Substantial adsorption capacity of 22.5 mg/g is observed towards chromium(VI). The interference caused by the presence of five-fold excess of co-ions which are naturally present in water caused marginal interference. The spent PSSP can be regenerated with 0.1 M NaOH and reused until three cycles.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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