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TREATMENT OF Cr (VI) CONTAMINATED WASTE WATER USING BIOSORBENT *PRUNUS AMYGDALUS* (ALMOND) NUT SHELL CARBON

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ABSTRACT

Increase in population coupled with mining, extraction and use of various metals as different industrial and household materials, the load of toxic metal pollution in the environment is increasing. The waste from metallurgical/mining sectors, in general, creates destabilization in the ecosystem, as most of the heavy metal ions are toxic to the living organisms. The demand of chromium has been increasing globally because of its extensive use in various metallurgical, chemical and leather tanning industries due to its various physico-chemical properties. The present paper deals with the adsorption of Cr (VI) using a *Prunus Amygdalus* (Almond nutshell). The uptake capacity of the present adsorbent was studied as a function of contact time, pH, adsorbate concentration and adsorbent dose. From the time variation experiments, the equilibrium contact time was found to be 6 hr. Cr (VI) uptake capacity of the adsorbent increased with decrease in pH. The maximum uptake capacity of the adsorbent was observed at pH 1.8. The adsorption capacity of the adsorbent was found to increase with increase in adsorbate concentration, whereas it decreased with increasing in adsorbent dose.

Key words: Adsorption, Hexavalent chromium Cr (VI), Wastewater treatment.

INTRODUCTION

Heavy metals are major pollutants of environment in most parts of the world that may be generated during industrialization processes. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products[1]. In the last few decades, industrialization in many regions has increased the discharge of heavy metals in the environment and aquatic ecosystems[2]. Toxic metals can seriously affect plants and animals and have been involved in causing a large number of afflictions[3]. Therefore, eliminating heavy metals from environment is one of the

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most important issues. Chromium exists in natural water in two main oxidation states, hexavalent chromium [Cr (VI)], and trivalent chromium [Cr (III)]. Cr (VI) is more hazardous, carcinogenic, and mutagenic to living organisms. Cr (VI) is included in the priority list of hazardous substances because it is threatening to both; human and environment[2]. Cr (VI) is widely used in manufacturing and processing plants. The main industrial sources of chromium pollution are tanneries, electroplating, metal processing, wood preservatives, paint and pigments, textile, dyeing, steel fabrication, canning industry. The tolerance limits for Cr (VI) are 0.05 and 0.1 mg/L in drinking water and inland surface waters, respectively[4].

Several methods utilized to remove Cr (VI) from aqueous solutions/wastewater include: reduction followed by electrochemical precipitation, chemical precipitation, chemical oxidation–reduction, ultra-filtration, ion exchange, reverse osmosis, solvent extraction, electro-dialysis, electrochemical, coagulation, evaporation and adsorption[5]. Most of these methods suffer from drawbacks such as high capital and operational costs and problems in the disposal of the residual metal sludge's. The high cost of activated carbon sometimes limits its applicability for heavy metal removal. Therefore, the interest of researchers is increasing using alternative materials, which are quite low cost, easily available and extremely effective adsorbents. Many studies have been conducted on the agricultural wastes as cheap and environmentally friendly natural materials, as well as certain waste from agricultural operations that are available in large quantities[6].

Adsorption techniques

Adsorption is the process where molecules are concentrated on the surface of the sorbent. The molecules go from the bulk phase to being adsorbed in the pores in a semi liquid state. The driving force for adsorption is the ratio of the concentration to the solubility of the compound. Adsorption is used widely to remove chromium metals from waters and industrial wastewaters. Suzuki[7] described and investigated adsorption phenomenon with more details including adsorption equilibrium and kinetics and influences of parameters such as pH, temperature, surface area, etc. Adsorption offers significant advantages like low cost, availability, profitability, easy of operation and efficiency, in comparison with conventional methods (such as membrane filtration or ion exchange) especially from economical and environmental points of view[4,5]. A variety of natural and synthetic materials has been used as Cr (VI) sorbents, including activated carbons, biological materials, zeolites, chitosan, and industrial wastes.

Biosorbents

Biosorption of chromium from aqueous solutions is relatively a new process that has proven very promising in the removal of contaminants from aqueous effluents. Adsorbent materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of chromium ions from wastewater streams. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials[7].

The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical and/or biological sludge regeneration of biosorbent, no additional nutrient requirement, and the possibility of metal recovery. At low concentrations of heavy metals, the conventional techniques such as chemical precipitation, membrane filtration, electrolysis, ion exchange, carbon adsorption are not cost-effective and suitable. Low-cost biosorbents are much suitable for high concentrations of metals. Various biosorbents have been widely used for the treatment of chromium containing wastewaters. Table 1 gives the agricultural by-products or wastes used in Cr (VI) uptake[7,8].

Table 1: Agricultural by-products absorbents used in Cr (VI) uptake

Biosorbent	Cr (VI) removal (%)	Adsorption system	Wastewater	pH
Hazlenut shell	99.4	Batch	Synthetic	1.0
	98.9			2.0
	97.8			3.0
Wool	69.3	Batch	Synthetic	2.0
	5.8			5.0
Olive cake	47.1	Batch	Synthetic	2.0
	8.4			5.0
Sawdust	53.5	Batch	Synthetic	2.0
	13.8			5.0
Almond shell	90.2	Batch	Synthetic	2.0
(*Prunus Amygdalus*)	55.2			5.0
Coal	19.8	Batch	Synthetic	2.0
	8.2			5.0
Walnut shell	85.3	Batch	Synthetic	3.5

EXPERIMENTAL

Material and methods

Material preparation and characterizations

A stock synthetic standard solution having Cr (VI) concentration l000 mg/L was prepared using required amount of potassium dichromate (E. Merck, GR grade). Adsorbate solutions of required strength were prepared by diluting this 1000 mg/L solution. The raw material used was *Prunus Amygdalus* (almond nutshells), which were obtained from the local market. The collected almond nutshells was washed with tap water followed by distilled water and sun-dried. The weed was then dried at 60°C for 1 hr in an oven to remove the adhering moisture. The dried material was crushed to powder form. The powder weed thus produced was sieved to different size fractions. The smallest size fraction, was used for adsorption studies.

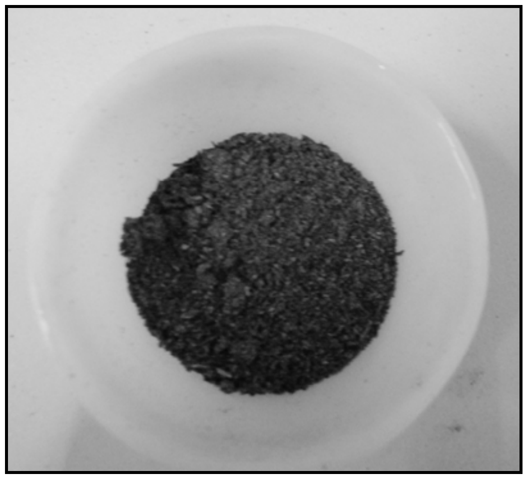

Fig. 1: Dry *prunus amygdalus* (almond nutshells)

Experimental set-up

The set-up of the experiment is shown in Fig. 2. For the development of the culture, a five-litre beaker, one stirrer and one aqua pump was used. For biological treatment a one-litre beaker, one stirrer and one aqua pump will be used for one set-up. Industrial effluent water in the beaker and measured amount of biological culture will be added and aerated. Fig. 2 gives the schematic diagram of the set-up, which is used for treatment of wastewater.

Adsorption experiments

Adsorption experiments were carried out in 500 mL beaker using 250 mL Cr (VI) solution with required amount of adsorbent. The flasks were continuously stirred for the required time period in Rime make mechanical stirrer. The mixture was filtered through Whatman No. 42 filter paper. The residual Cr (VI) concentration after filtration was determined Perkin-Elmer made LAMBDA 35 UV-Vis spectrophotometer.

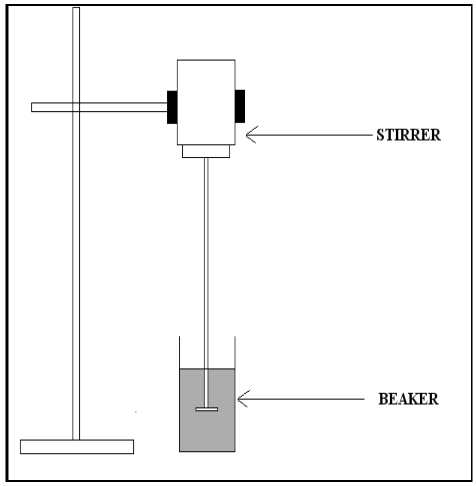

Fig. 2: Experimental setup

RESULTS AND DISCUSSION

Effect of adsorbent dose

Adsorption experiments were carried out by varying the adsorbent dose to find out its effect on the % adsorption as well as Cr (VI) uptake capacity of the adsorbent (Fig. 3 and 4). During the experiments, adsorbate concentration and pH were kept constant at 100 mg/L and 3.0 respectively. The percentage adsorption increased from 55.1 to 90.2 when the adsorbent dose increased from 0.8 to 2.4 g/L as shown in Fig. 3.

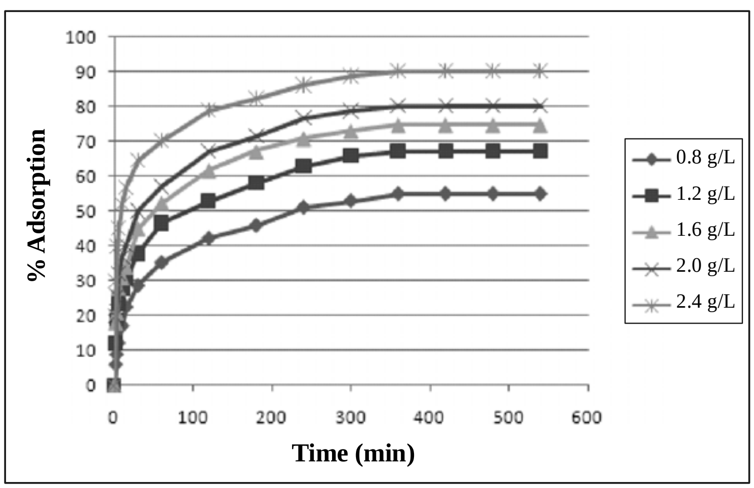

Fig. 3: Effect of adsorbent dose on % of adsorption

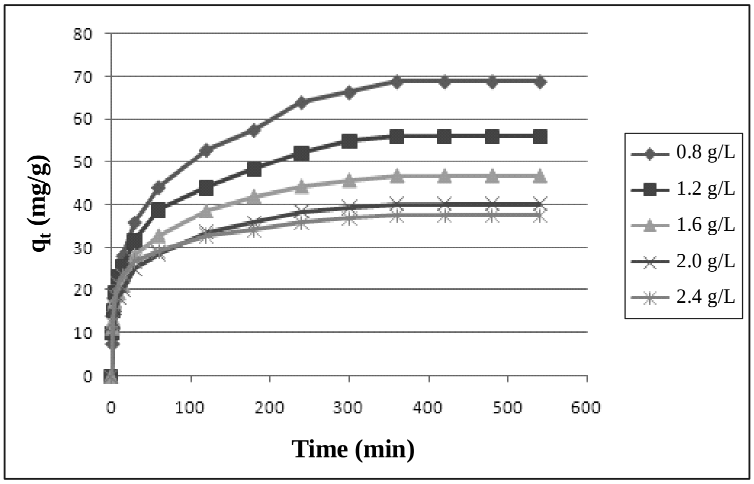

Fig. 4: Effect of adsorbent dose on loading

Whereas, the Cr (VI) uptake was decreased from 68.9 to 37.6 mg/g when the adsorbent dose increased from 0.8 to 2.4 g/L. Higher percentage of adsorption with the increase of adsorbent concentration may be due to the availability of more surface area. The slope of the line is < 1 implies that adsorption is not directly proportional to adsorbent concentration.

Effect of contact time

Adsorption experiments were carried out over different contact time for varying pH of Cr (VI) solution (Fig. 5). From the time variation experiments, it was observed that the percentage of Cr (VI) adsorption increased with increase in contact time upto 6 hr. Beyond that there is no further increase in percentage adsorption. So it can be concluded that the equilibrium time for the process is 6 hr. Further it can be observed from Fig.5 that the rate of adsorption was very fast at the initial stage of adsorption and it increases with further increase in time. Therefore the adsorption process can be divided into two parts i.e. initial faster rate followed by slower one. The faster rate was continued upto 60 min. and account for more than 60% of total adsorption.

Effect of pH

pH is an important parameter affecting the adsorption of Cr (VI) on the adsorbent surface. Therefore adsorption studies were carried out by varying the pH from 1.8 to 5 to find out its effect on percentage adsorption as well as uptake capacity. Fig. 6 shows the effect of pH on Cr (VI) adsorption. It is evident from the figure that the percentage adsorption is higher at lower pH and decreases with the increase in pH. The percentage adsorption decreased from 100 to 29.8 when the pH increased from 1.8 to 5. Similarly the Cr (VI) uptake capacity of the adsorbent decreased from 50 to 14.9 mg/g when the pH increased from 1.8 to 5. The effect of pH on the adsorption capacity of weed may be attributed to the combined effect of the nature of surface and the presence of acid and base used to adjust the pH of the solution. To explain the observed behavior of Cr (VI) adsorption with varying pH, it is necessary to examine various mechanisms such as electrostatic attraction/repulsion, chemical interaction and ion exchange, which are responsible for adsorption on sorbent surfaces.

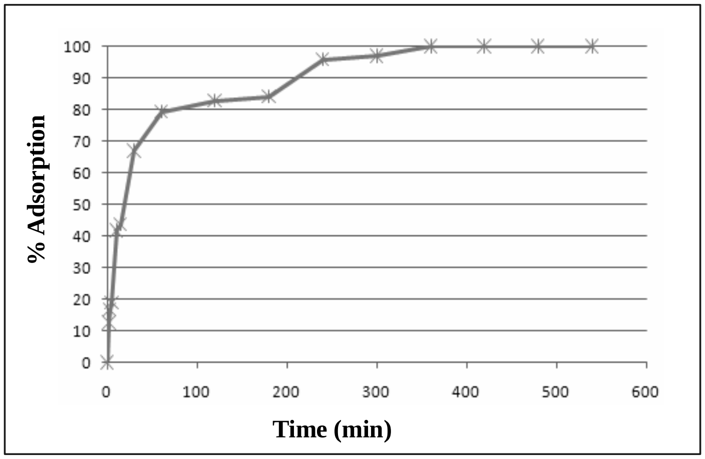

Fig. 5: Effect of contact time
(Conditions: Adsorbate conc. 100 mg/L, adsorbent dose 0.8 g/L)

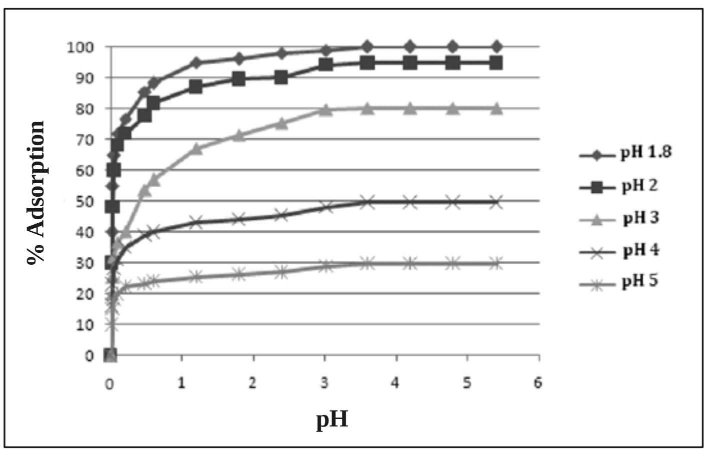

Fig. 6: Effect of pH on percentage of adsorption
(Conditions: 100 ppm, 0.5 g, 250 mL, temp. -27^{o}C)

Effect of initial adsorbate concentration

Fig. 7 and 8 shows the effect of initial adsobate concentration on percentage adsorption vis-a-vis the adsorption efficiency. It was observed that the percentage of adsorption decreased with the increase of adsorbate concentration whereas the reverse trend was observed in case of Cr (VI) uptake. The percentage of adsorption decreased from 80.1 to 47.1 when the adsorbate concentration increased from 50 to 250 mg/L.

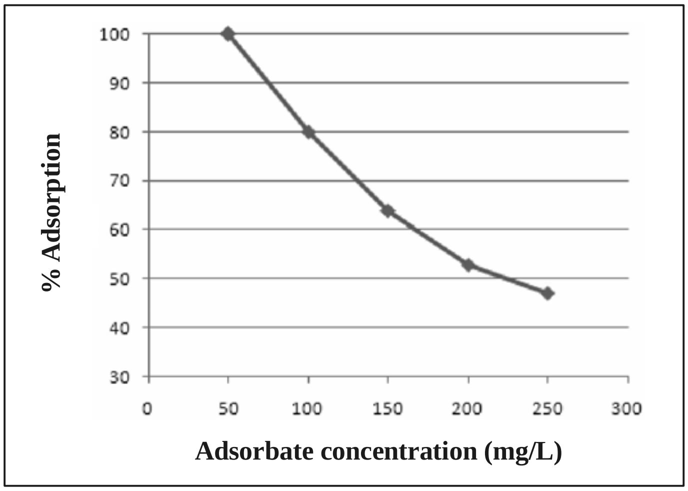

Fig. 7: Effect of adsorbate concentration on % of adsorption

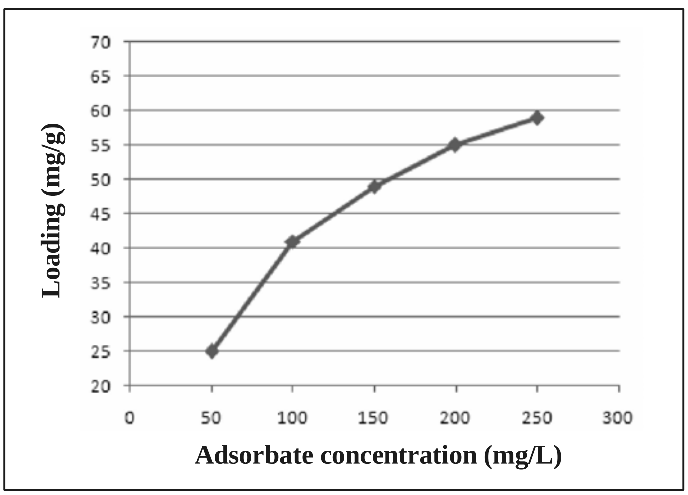

Fig. 8: Effect of adsorbate concentration on loading

Similarly the Cr (VI) uptake capacity of the adsorbent increased from 25 to 58.9 mg/g when the adsorbate concentration increased from 50 to 250 mg/L. This may be due to the fact that at a fixed adsorbent dose, the number of active adsorption sites to accommodate the adsorbate ion remains unchanged, while with higher adsorbate concentrations, the adsorbate ions to be accommodated increase. Thus, the loading is faster with higher initial concentrations of adsorbate.

CONCLUSION

From the above discussion, it can be concluded that the adsorbent can be used efficiently to treat Cr (VI) contaminated wastewater. Adsorption method was used for the treatment of Cr (VI) contaminated waste water. This paper deals with the adsorption of Cr (VI) using a *Prunus Amygdalus* (Almond nutshell). The uptake capacity of the present adsorbent was studied as a function of contact time, pH, and adsorbate concentration and adsorbent dose. The maximum uptake capacity of the adsorbent was observed at pH 1.8. The percentage adsorption as well as uptake capacity of the adsorbent increased with decrease in pH. The percentage adsorption was found to be increased with increase in adsorbent dose whereas; it decreased with increase in adsorbate concentration. Similarly the Cr (VI) uptake capacity of the adsorbent decrease with increase in adsorbent dose whereas, it shows reverse trend with increase in adsorbate concentration.

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