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Studies on Separation of Heavy Metals from Aqueous Solutions Using Biosorbents

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Man is blessed with an abundance of nature. But in the name of development, the nature is being continuously destroyed by man. As a result, nature is polluted beyond the measure because of an indiscriminate release of heavy metals into the environment. Industrialization and urbanization pose a significant problem to the biosphere. Heavy metal ions do not degrade but harm human body, flora, fauna, and the environment. Biosorption is one of the most effective techniques to remove heavy metals from industrial effluents. The low cost-natural products and waste substances are found to be very effective in the removal of heavy metals from industrial wastewaters. The objective of the present study is to develop inexpensive, eco-friendly and useful metal ion adsorbents that are available in large quantity. As an alternative to existing commercial adsorbents for the removal of different heavy metal ions like chromium, lead and cadmium from synthetic aqueous solutions. In the present work different low cost natural adsorbents such as coconut shell, *tamarindus indica*, *Mangifera indica*, *Moringa oleifera* and waste products such as pineapple peel and soap nut seeds (The Drupe of sapindus plants, containing saponins which are natural surfactants) were used to determine adsorption efficiency in removing chromium, lead and cadmium. All these adsorbents were used without any pre-treatment. The influence of contact time, pH, temperature, adsorbent dose and initial metal ion concentration on the selectivity and sensitivity of the removal process was investigated. The removal of these metal ions from aqueous solutions/industrial effluents was studied using the batch method. It was observed that the rate of adsorption increased with the increase in adsorbent dose. The maximum time for higher adsorption rates was found between 120 to 150 min. The optimum pH for the separation observed was 2. Finally, based on the results obtained, the researcher would like to conclude that the use of low-cost adsorbents for metal ion removal which is feasible and eco-friendly. The results are presented and tabulated.

Key words: Metal ions; biosorption; natural adsorbents; industrial effluents

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The term heavy metal refers to any metallic chemical element that has a relatively high density and toxic or poisonous ingredients at low concentrations. The pollution of heavy metal ions in the environment is a critical problem because of their toxicity and other adverse effects on the receiving waters, soils and living things. They must be removed from wastewater before they are discharged into water bodies. The most common methods of metal ions removal from aqueous systems are chemical precipitation, ion exchange, membrane processes and adsorption. But these conventional methods for the removal of heavy metals from wastewaters had disadvantages like low efficiency at low metal concentrations; particularly in the range of 1–100 mg/l. They generate toxic sludge and the disposal of high sludge. Therefore, among all these methods biosorption has been proved to be a simple, eco-friendly, selective and economical process for the removal of heavy metal ions from aqueous solution. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake. The significant biosorption advantages of over conventional treatment methods include low cost, high efficiency of metal removal from dilute solution, minimization of chemical and or biological sludge, no additional nutrient requirement, and regeneration of biosorbent and the possibility of metal recovery.

Biosorption using dead biological material is easy to maintain, non-toxic and economically feasible. Natural elements that are available in large quantities or specific waste from agricultural operations have been proved to be potential for use as low-cost adsorbents. They are widely available in nature and are eco-friendly. Biosorption depends on many parameters such as ionic metal, solution pH, temperature, ionic strength, initial pollutant concentration, biosorbent dosage, biosorbent size, agitation speed, and also the coexistence of other pollutants. A broad range of biomass types have been tested for their biosorptive capacities under various conditions, but there are no limits to explore new biomass types having low cost and high efficiency. The objective of this study is to develop an inexpensive and effective biosorbent that is readly available in large quantities and feasible economically for multiple metal ions in solution.

REVIEW OF LITERATURE

Adsorption using natural adsorbents, an innovative and economical method, has evolved the frontline of defense especially for metals that could not be effectively removed by other techniques. Several natural sorbents from agricultural, aquatic and forest wastes have been utilized as such and in modified forms by various researchers in the sequestration of chromium ion from aqueous solutions and industrial effluents. Javaid *et al.* [1], studied the diversity of an adsorbents like microorganisms (fungi, bacteria, algae and yeast), plant by-products (rice straw and husk, wheat straw and husk, chick pea husk etc.) and waste material (fallen leaves and peels) have been utilized to remove heavy metals from aqueous medium [2], reported that the chromium removal was optimum at pH 2.5–3.0 when sulphuric acid-treated rice husk was used. Ajmal [3] stated the removal of cadmium, zinc, nickel and lead from aqueous solutions by *Mangifera indica* which mainly depend on pH value and contact time and obeyed Freundlich adsorption isotherm. Raj and Raghavan [4] and Suman Mor *et al.* [5], reported that, removal of chromium was maximum at lower pH and at higher dose of activated carbon. Rao *et al.* [6], stated that, the removal of Cr^{6+}, Ni^{2+}, Cu^{2+}, Pb^{2+} ions was more at pH 5.0–8.0, and also stated that, the removal of Cr^{6+}, Ni^{2+}, Cu^{2+}, Pb^{2+} ions was more at pH 5.0–8.0 was more at pH 5.0–8.0 Vasanthy *et al.* [7], stated that, the mixture of adsorbents (fly ash and activated carbon) removed about 90–100% of chromium at pH 2. Car and Malkoc [8], studied about saw dust *Fagus orientalis* L elaborately and examined the removal of Cr(VI). Different structured activated carbons were prepared from *Terminalia arjuna* nuts, an agricultural waste, by chemical activation with zinc chloride for the adsorption of Cr (VI) from dilute aqueous solutions [9]. The most important parameter in chemical activation was found to be the chemical ratio (activating agent/precursor, g/g). The activated carbon developed shows substantial capability to adsorb Cr (VI) from dilute aqueous solutions. Copper adsorption on *Tamarindus indica* was pH dependent at a contact time of 90 min [10]. Abdel Ghani *et al.* [11], used rice husks, maize cobs and sawdust as adsorbent. They found that rice husks was the most effective adsorbent for many metals for which the removal reached 98.15% of lead at room temperature. Zinc adsorption on *Shorea robusta* was totally dependent on carbon dose, contact time and pH [12].

Gupta *et al.* [13], stated Cadmium removal from modified bagasse dust depend on pH 6.0, temperature 25°C, agitation time 5 h, sorbent dose of 5 g/l and 150 rpm. Human hair adsorption of nickel (II) and chromium (VI) were maximum at pH 6 and 4, respectively [14]. Hence, the adsorption was pH dependent. Kannan and Veemaraj [15], reported about the nickel (II) ions removal by lemon peel and pomegranate shell carbon, depending on particle size, initial concentration, contact time, dose and pH. Das [16] investigated dried biomass of *Oscillatoria laete-virens* and found it possess the potential to remove heavy metals like Cr(VI) and Ni(II) from polluted water.

Abraham *et al.* [17], studied cadmium adsorption on montmorillonite and reported at lower pH and with increasing concentration of humic acid, the metal ion does not adsorb.

Chakrapani *et al.* [18], stated that methylene blue by maize shell carbon depends on pH 6.5, agitation time, and a dose of the adsorbent. Kannan and Balamurugan [19], stated that, copper ions adsorption depends on the dose of adsorbent and contact time. Bamboo dust had higher adsorption capacity for dyes compared to ground nut-shell, coconut shell, rice husk and straw [20]. Chandra Sekhar [21] stated that removal of lead by coconut shell carbon obeyed first-order reversible kinetic reaction and sorption isotherm followed Freundlich isotherm. Babu *et al.* [22] studied the adsorption of Cr (VI) using activated neem leaves. Baisakh and Patnaik [23] stated, that at ambient temperature condition, the removal efficiency of chromium was more (70%) by charcoal. Gupta *et al.* [24] stated that *Prosopis cineraria* leaf powder removes copper ions maximum in 240 min contact time and at increasing adsorbent amount, pH 5.5, fitting Langmuir and pseudo-second-order equation. Nageeb *et al.* [25] found that fruit stones were good adsorbents for the removal of lead ion from polluted water. Joshi and Srivastava [26] stated pipal bark after chemically carbonized adsorbs 76.04 %, at pH 2. Kobya [27] has studied adsorption kinetics and equilibrium studies of Cr (VI) by hazelnut shell activated carbon. Latika [28] reported that cyanobacterium adsorption on cadmium depends on contact time. Low *et al.* [29], stated about the sorption of Cd (II) and Pb (II) from aqueous solutions by spent grain.Madhava Krishnan *et al*. [30] reported that *Ricinus communis* pericarp carbon removes iron (II), with optimum pH, concentration and dose by obeying Langmuir and Frendlich isotherms. Chaudhuri [31] reported that coconut coir carbon removed red F-3B and remazole blue at pH 3.0, dose 10 g/l and increased contact time to remove 96% for remazol blue and 84% for remazol red F-3B, obeying Langmuir and Freundlich adsorption isotherms.

In this present work, the suitability of various low-cost natural adsorbents is tested for the removal of metal ions from wastewaters.

MATERIALS AND METHODS

Preparation of Adsorbents

Various agricultural waste biosorbents (Figure 1) such as, coconut shell, pineapple peel, tamarindus nuts, moringa seeds, mangifera bark, neem leaves, soap nut seeds, guava leaves, sweet lime peel, pumpkin seeds, custard apple leaves and seeds, and papaya peel were collected in ample quantities. The seeds were sun dried to remove moisture content. Dried biomass was ground into a powder and sieved through a 150 mesh screen, and 125 – 250 μm fine substances were obtained.

Preparation of Solutions

Analytical grade chemicals were used for determination of Cr, Pb and Cd metal ions. The wastewater containing Cr, Pb and Cd were prepared in the laboratory by dissolving a known amount of Cr, Pb and Cd in distilled water. All the three solutions were prepared at different concentrations. Standard methods were followed.

Adsorption Experiments

The experiments were carried out in 125 ml Borosil conical flasks by agitating a pre-weighed amount of adsorbent powder with 10 – 100 ml of the aqueous metal solutions for a predetermined period at 20–40°C. The biosorbent doses were maintained at 1–5 g/l for different experiments. Several solutions with different initial concentrations of chromium stock solution were prepared. The required pH was adjusted (between 1–6) using NaOH and HCl. All experiments were carried out at room temperature (30°C) by adding different amounts of adsorbents to different concentrations of 100 ml of heavy metal ion solution. The agitation rate for all experiments was 200 rpm. The effects of several parameters, such as contact time, initial concentration, adsorbent dose, temperature and pH on the adsorption of metal ions versus adsorbents were studied. The equilibrium concentration of free chromium (VI) ions at different experimental conditions with a suitable time interval in the solution was determined by filtering the adsorbent loaded with hexavalent chromium through Whitman filter paper, and the samples were analyzed by using an atomic absorption spectrophotometer with an air-acetylene flame.

Figure 1. Different low cost natural adsorbents.

RESULTS AND DISCUSSION

Effect of pH on the Uptake of Chromium

The results show (Figure 2) that as pH value increase the removal rate of chromium decrease, but at PH 2 it observed that maximum removal of metal ions takes place. The pH of the solution is an important variable which controls the adsorption of the metal ions at the solid-water interface. Hence, the influence of pH on the adsorption of Cr (VI) ions are tamarind seeds, *moringa oleifera*, *mangifera Indica*, and soap nut seeds were examined in the pH range of 1–6. These results were shown in the graph and observed that the adsorption capacities of Cr (VI) ions of those adsorbents increased significantly, till pH value 2 and then decreased and the maximum removals of Cr (VI) ions by all 4 adsorbents for contact time (120 min) were carried out at pH (2.0). The maximum percentage removal of chromium ions observed with *moringa oleifera* seeds (MOS) at pH (2.0) was 80.2. *Tamarindus indica* seeds (TIS), *Mangifera Indica* Bank (MIB), and soap nut seeds (SNS) are shown maximum adsorption of chromium at pH (2.0) were 75.2%, 61.5% and 73%, respectively. The same type of trend was observed for lead and other metals.

Effect of Adsorbent Dosage on Uptake of Chromium

Figure 3 shows that as absorbent concentration increases the rate removal of chromium which is almost constant and a maximum is observed for 1.5 g/l for MIB, MOS, TIS. However it is observed that the rate of removal of chromium decreases as the absorbent concentration increases for SNS.The adsorbent dose of TIS, MIB, *Moringa oleifera* and soap nut seeds powder was varied and the percentage removal of Cr (VI) metal ion was plotted in the graph. The adsorbent doses were varied as 0.5, 1, 1.5, 2.0 and 2.5 g/l., and maintained at pH 2.0, temperature 25°C, contact time 120 min and initial Cr (VI) ions concentration of 10 mg/l constant. The results showed that with the increase in adsorbent doses of each adsorbent, the percentage adsorption of Cr (VI) was increased. Maximum removal of Cr (VI) ions was observed with adsorbent dose of 2 g/l for TIS powder and 2.5 g/l for *M. oleifera* seeds powder. The biosorption of Cr (VI) was observed to be maximum 87% with 2 g of tamarindus seeds powder and 85% with 2.5 g of moringa seeds powder.

Effect of Contact Time on Chromium Uptake

The following results (Figure 4) showed the effect of contact time on the treatment of chromium ions from aqueous solutions. It was observed that the percentage removal of Cr (VI) metal ions increased for *Mangifera Indica* Bank (MIB), *moringa oleifera* seeds (MOS), *Tamarindus indica* seeds (TIS), and soap nut seeds (SNS) with increasing the contact time. The percentage removal was 70% for moringa seeds powder and 78% for tamarind seed powder at 120 min. It was clear that at the beginning, percentage

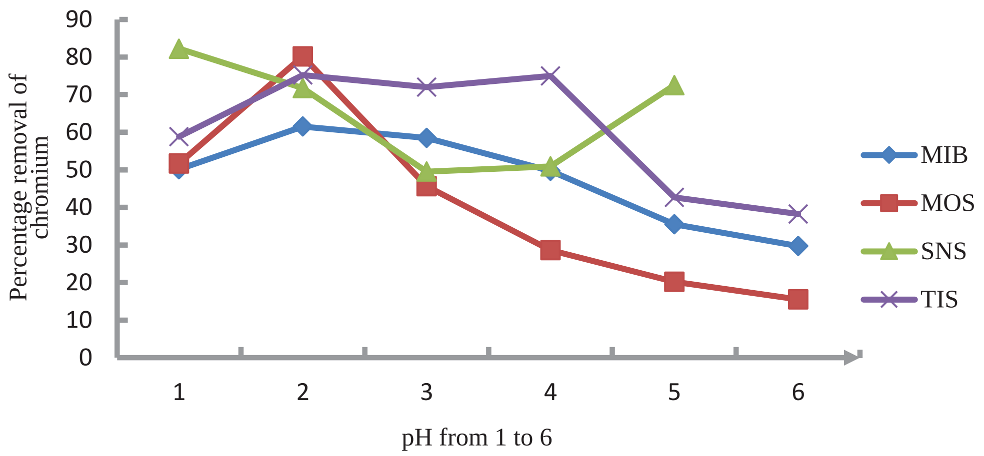

Figure 2. Effect of PH on the removal of chromium for various biosorbents.

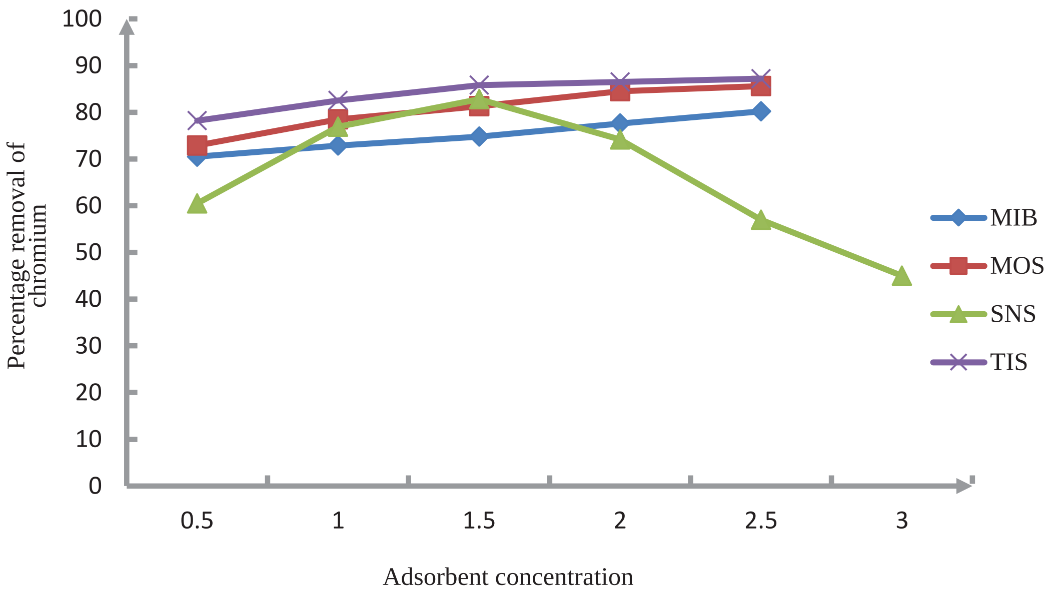

Figure 3. Effect of adsorbent concentration on removal of chromium for various biosorbents.

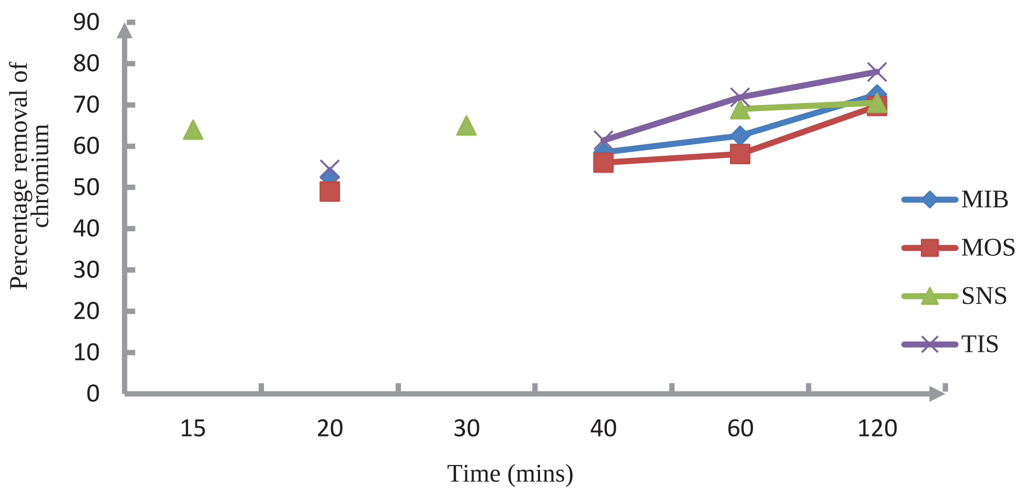

Figure 4. Effect of contact time on removal of chromium ion for various biosorbents.

removal increased in few minutes, by increasing the contact time; the percentage removal increased slowly till it reached the maximum value. These results indicated that the MIS and MOS had a good capacity for adsorption of Cr (VI) ions in solutions.

Effect of Initial Chromium(VI) ion Concentration

It was observed that the removal of chromium ion was different for different absorbents concerning absorbents dosage (Figure 5). The concentration of metal ion varied, and percentage removal of Cr (VI) metal ion was plotted in the graph (Figure 5). The concentrations of Cr (VI) metal were varied at 20, 40, 60, 80, 100 mg/l, maintained pH (2.0), temperature (25°C), contact time (120 minutes) and adsorbents concentration (2 g/l each) constant. The results showed that the percentage Cr(VI) ions adsorption was increased till the surface of adsorbents reached optimal concentration, and later decreased with increasing initial concentration. The maximum percentage removal of chromium metal ion 86% observed at initial concentration was 20 mg/l by TIS and 73% by moringa seeds.

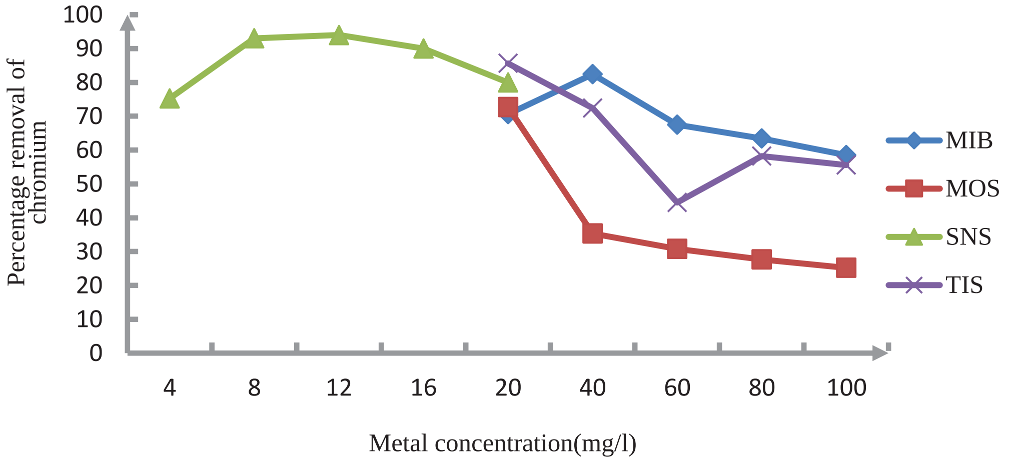

Figure 5. Effect of metal concentration on the removal of chromium ion for various biosorbents.

Effect of Temperature on Chromium Uptake

All the experiments were carried out at 30°C where the maximum removal was observed. The following graph (Figure 6) indicates the effect of temperature on the removal efficiency of Cr (VI) ions from wastewater using tamarind seeds, MOS and MIB. Five different temperatures were considered in this study (20, 25, 30, 35 and 40°C). The graph showed that the removal efficiency increased by increasing the temperature till 25°C, and then decreased in case of three adsorbents. But the maximum adsorption (82.5%) is achieved at 25°C in case of tamarind seeds. The adsorption process does not usually operate at high temperature (more than 40°C) and this may be due to the damage of active binding sites and because of high operational cost, so experiments were performed at the temperature range (20–40°C). MOS and MIB showed maximum percentage adsorption of chromium ions at 25°C as 78.8 and 76.6, respectively. However, a slight decrease was observed as the temperature increased, for all the adsorbents.

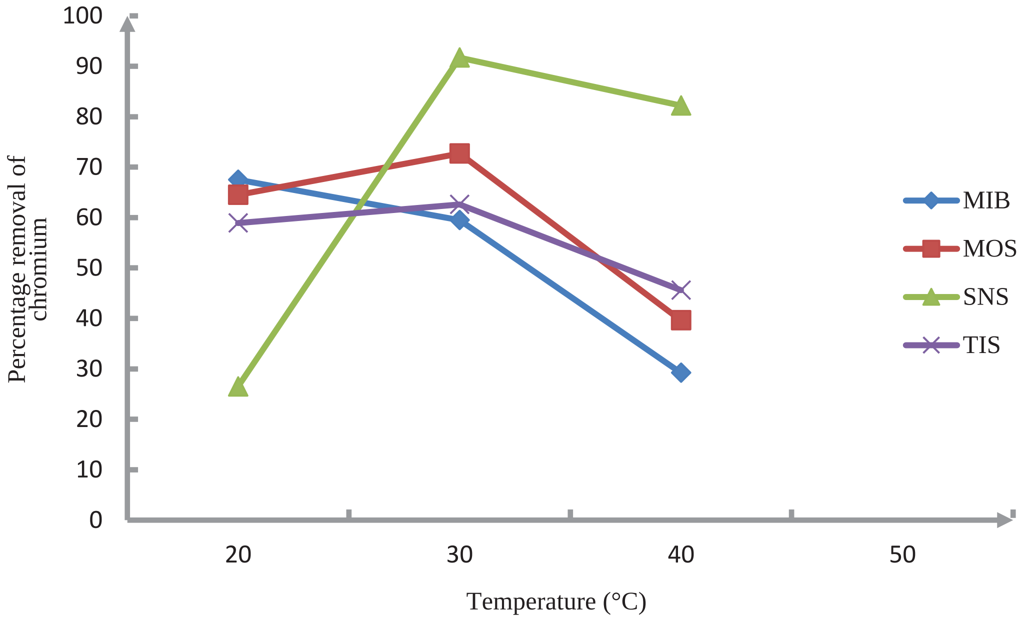

Figure 6. Effect of temperature on the removal of chromium ion for various biosorbents.

Uptake of Chromium Ion by All the Adsorbents

The following graph (Figure 7) shows that the uptake of Cr (VI) from various biosorbents. It is apparent from the figure that soap nut seeds have the highest (81.5%) uptake capacity for Cr(VI) ions followed by custard fruit seeds (77.5%). The lowest percentage of removal of Cr (VI) ions was observed in guava (10%) whereas biosorbents like sweet lime peel powder (55%), custard fruit leaves (30%), pumpkin seeds (75%), papaya peel (10.5%) and neem leaves (25%) gave intermediate values. From our study on the screening of various biosorbents for their chromium removal property it was found that soap nut seeds exhibited maximum removal of chromiun; it was observed for soapnut seed powder and hence soapnut seed powder was used as biosorbent.

CONCLUSIONS

The effectiveness of MIS, TIS, MOS, and SNS as biosorbent for the removal of chromium, lead and cadmium ions werw studied. The adsorption efficiencies of MIS, TIS, MOS, SNS seeds in the separation of chromium from aqueous solution were also determined. Various biosorbents like sweet lime peel, custard apple leaves, pumpkin seeds, papaya peel, guava leaf, soap nut seed, custard apple seed and neem leaves were tested for their efficiency for Cr (VI), lead and cadmium removal. The effect of various parameters like pH, temperature, initial metal ion concentration, and adsorbent dosage was also studied in the removal of chromium, lead and cadmium from aqueous solutions. Studies were also conducted using cadmium and lead solutions and it was found that parameters like pH, initial ion concentration, adsorbent dosage, contact time and temperature followed the same trend as that of the removal of chromium.

REFERENCES

1. Javaid, A., Bajwa, R. and Javaid, A. (2010) Biosorption of heavy metals using a dead macro fungus *Schizophyllum commune* (Fries), *Pakistan Journal of Botany*, **42(3)**, 2105–2118.

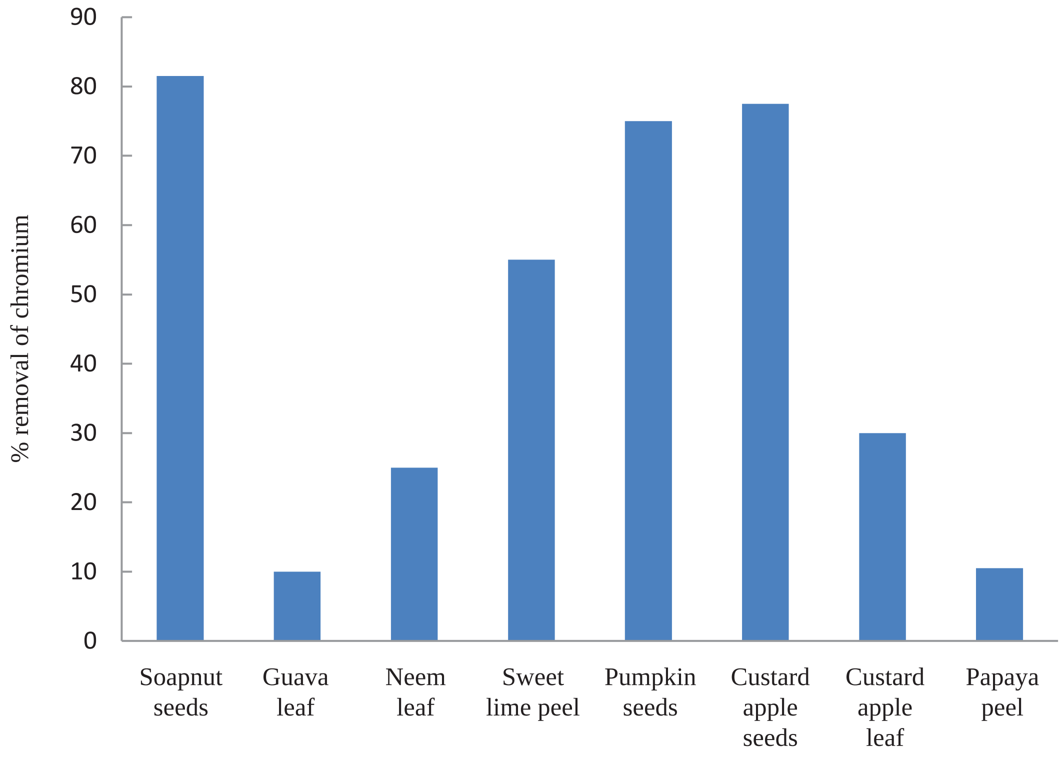

Figure 7. Effect of the uptake of Cr (VI) ion by various biosorbents.

2. Srinivasan K., Balasubramanian, N. and Ramakrishnan, T.V. (1988) Studies on chromium removal by rice husk carbon, *Ind. J. Environ. Health*, **30**, 376–387.

3. Ajmal, A. M., Rehana, Y. and Anus, A. (1998). Adsorption behaviour of cadmium, zinc, nickel and lead from aqueous solutions by *Mangifera indica* seed shell, *Indian Journal of Environmental health*, **40(1)**, 1–5.

4. Amal, R. S. and Srinivasa, R. R. (2002) Removal of chromium on synthetic effluent by adsorption on activated carbon, *Indian J. Environmental Protection*, **22(1)**, 69–72.

5. Mor, S. R. and Bishnoi, N. R. (2002) Adsorption of chromium using activated baggase carbon as adsorbent, *Indian Journal of Environmental Protection*, **22(5)**, 564–568.

6. Rao, M., Parwate, A.V. and Bhole, A.G. (2003) Heavy metals removal by adsorption using bagasse and modification to Helfferich Model, *J. Environ. Pollu. Control*, **6(4)**, 6–13.

7. Vasanthy, M., Sangeetha, M. and Kavitha, C. (2003) Solutions using a mixture of fly ash and activated carbon, *J. Indian Journal of Environmental Protection*, **23(12)**, 1321–1325.

8. Acar, F. N. and Eren, Z. (2006) Removal of Pb (II) ions by activated poplar sawdust (Samsun clone) from aqueous solutions, *Journal of Hazard Materials*, **137**, 909–914.

9. Kaustubha Mohanthy, K. (2005) Removal of chromium (VI) from aquesous solutions by activated carbon developed from Terminalia arjuna nuts activated with zinc chloride, 60(11) 3049–3059.

10. Gharde, B. D., Gholse, S. B. and Patil, P.V. (2006). Removal of copper (II) from aqueous solution using *Tamarindus indica* fruit shell substrate, *J. Poll. Res.*, **25(2)**, 449–450.

11. Abdel-Ghani, Nour El-Din, T., Ghadir, A. and Chaghaby, El-1. (2008) The use of low cost and environment friendly materials for the removal of heavy metals from aqueous solutions, *J. Current World Environment*, **3(1)**, 31–38.

12. Dash, S. N. and Sagar, P. N. S. (2008) Adsorption of Zn metal from paper mills waste water by activated carbon prepared from Shorea robusta leaf litter, *J. Nature Environment and Pollution Technology*, **7(1)**, 117–122.

13. Gupta, V., Gupta, R., Vashishtha, S. and Robusta and Singh R. P. (2009) Removal of cadmium by modified bagasse dust and fly ash, *Journal of Ecotoxicology & Environmental Monitoring*, **19(1)**, 79–83.

14. Malliga, D., Jeyanthi, G. P. and Bhuvaneswari, V. (2010) Adsorption of nickel (II) and chromium (VI) from synthetic metal solutions using powdered human hair as adsorbent, *Journal of Ecotoxicology & Environmental Monitoring*, **20(1)**, 39–50.

15. Kannan, N. and Veemaraj, T. (2011) Detoxification of nickel (II) ions by adsorption onto carbons prepared from agricultural materials — A comparative study, *Indian Journal of Environmental protection*, **31(4)**, 338–344.

16. Das, S. (2012) Biosorption of chromium and nickel by dried biomass of cyanobac-terium Oscillatoria-laete virens, *Int. J. Environ. Sci.*, **3(1)**, 341–352.

17. Abraham, B. T. and Anirudhan, T. S. (1998) Influence of humic acid and pH on cadmium (II) adsorption on montmorillonite, *Indian Journal of Environmental protection*, **19(5)**, 363–366.

18. Ch. Chakrapani, R. M., Rao, K.S., Babu, S., Rao, V. C. V. and Rao, V.S. (2008) Removal of methylene blue by maize shell carbon, *Indian Journal of Environmental Protection*, **28(6)**, 547–553.

19. Kannan, N. and Balamuragan, J. (2004) Removal of copper ions by adsorption on to coconut shell and dates nut carbons—A comparative study, *Indian Journal of Environmental protection*, **24(5)**, 371–378.

20. Kannan, N. and Sundaram, M. (2002) Kinetics of adsorption of dyes on activated carbon: A comparative study, *Indian Journal of Environmental Protection*, **22(1)**, 9–16.

21. Shekar, C.M. (2008) Removal of Lead from aqueous effluents by adsorption on coconut shell carbon, *Journal of Environmental Science and Engineering*, **50(2)**, 137–140.

22. Babu, B.V. and Gupta, S. (2008) Adsorption of Cr (VI) using activated neem leaves: kinetics studies, *Adsorption*, **14(1)**, 85–92.

23. Baisakh, P.C. and Patnaik, S.N. (2002) Removal of hexavalent chromium from aqueous solutions by adsorption on coal char, *Indian J. Environ. Health*, **4(3)**, 189–196.

24. Gupta, V. and Sharma, M. (2010) Adsorption analysis of chromium (VI) by Natural polymer tamarind kernel powder (TKP) in aqueous medium, *Research Journal of Chemistry and Environment*, **14(1)**, 41–45.

25. Rashed, N.M. (2005) Fruit stones as adsorbents for the removal of lead ion from polluted water, Chemistry Department, Faculty of Science, 152872, Aswan, Egypt.

26. Joshi, M. and Srivastava, R. K. (2005) Chromium (VI) removal from waste water by using carbonized pipal bark adsorbent, *Indian J. Environmental Protection*, **25(1)**, 57–60.

27. Kobya, M. (2004) Adsorption kinetics and equilibrium studies of Cr (VI) by hazelnut shell activated carbon, *Adsorption Science Technology*, **22**, 51–64.

28. Latika, S., Bharati, R. and Sinha, M. P. (2008) Biosorption of cadmium from aqueous medium by cyanobacterium Nostoc carneum Agardh, *The Ecoscan*, **2(1)**, 125–127.

29. Low, K.S., Lee, C.K., and Liew, S.C. (2000), Sorption of Cd (II) and Pb (II) from aqueous solutions by spent grain, *Process Biochemistry*, **36**, 59–64.

30. Madhavakrishnan, S., Manickavasagam, K., Mohanraj, R., Kadirvelu, K. and Pattabhi, S. (2008) Removal of mercury (II) from aqueous solution by adsorption onto *Ricinus communis* pericarp activated carbon, *Indian J. Environmental Protection*, **28(11)**, 967–972.

31. Chaudhuri, M., Elmolla, E.S. and Othman, R. (2011) Adsorption of reactive dyes Remazol Red F-3B and Remazol blue from aqueous solution by coconut coir activated carbon, *J. Nature Environment and Pollution Technology*, **10(2)**, 193–196.