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Removal of chromium (VI) and iron (III) from aqueous solution using agricultural byproducts

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ABSTRACT

Heavy metal contamination in drinking water has become a more serious environmental problem in the last several decades as a result of its toxicity and insusceptibility to the environment. Adsorption process has been overlooked as one of the best water treatment technologies around the world. Use of waste materials as low-cost adsorbents is attractive due to their contribution in the reduction of costs for waste disposal, therefore contributing to environmental protection. The primary objective of this study is to identify the most appropriate agricultural byproduct among Strychnos potatorum (nirmali) and Azadirachta indica (neem) seeds for the removal of Chromium (VI) and Iron (III) from water and to compare their removal efficiency. The parameter investigated includes the effect of contact time, metal ion concentration, temperature and pH. Strychnos potatorum shows better removal efficiency of 69% of Chromium (VI) and 58% of Iron (III) at acidic pH and 0.1 mg L^{-1} of initial metal ion concentration. Optimal conditions were obtained with an increase in temperature at an exposure time of 24 hours. The adsorption of the metal ion species on Strychnos potatorum seed is characterized by X-Ray Diffraction analysis. This method is studied and proved for its eco-friendly feasibility and simple technology for water treatment thus providing quality of life for underdeveloped communities.

Key words: *Strychnos potatorum*, *Azadirachta indica*, Chromium (VI), Iron (III), X-Ray Diffraction.

INTRODUCTION

Pollution of water with toxic substances is of major concern for human health as well as for the environmental quality [1]. According to recent surveys, the most common contaminants reported in groundwater are heavy metals [2]. Cr, Cd, Pb, Hg, Zn, Ni and Fe are the most common heavy metals discharged into water streams from large industrial sectors [3, 4]. These heavy metal ions and their complexes exhibit a wide range of toxicity to the organism that ranges from sublethal to lethal depending on the time of exposure and amount of dose [5]. Chromium (Cr) typically occurs in two oxidation states namely trivalent, Cr (III) and hexavalent, Cr (VI) in the natural environment, water treatment processes and water distribution systems. Recent studies, shows that no deleterious effects from low Cr (III) in the diet and there is no known biological mechanistic function for Cr (III) in cells [6]. The Cr (VI) compounds are known to be toxic and mutagenic for most living organisms. When Chromium enters the gastric system, epigastric pain, nausea, and vomiting, severe diarrhoea, corrosion of skin, respiratory tract and lung carcinoma were noticed [7]. Iron exists in two forms, soluble ferrous ion (Fe^{2+}) and insoluble ferric particulate ion (Fe^{3+}). Iron in water is generally present in the ferric state. Iron typically enters water bodies in the form of ferrous ion (Fe^{2+}), which can be oxidized to ferric ion (Fe^{3+}) by the oxygen dissolved in water [8]. There are many problems that result from iron toxicity. These include anorexia, oligura, diarrhoea, hypothermia, diphasic shock, metabolic acidosis and even death.

Since the past few decades, various conventional technologies for the removal of heavy metal ions from aqueous solutions such as chemical precipitation [9], ion exchange [10], membrane separation [11], reverse osmosis and electrochemical treatments [12] have been reported [13, 14]. These methods generally are either expensive or inefficient, especially when the concentrations of heavy metal ions are less than 10mg / L [1]. The development of an efficient and environmental friendly method is thus needed to reduce heavy metal content in polluted environments.

Adsorption processes for removal of metals have been found cheaper and more effective than the conventional technologies [15]. Numerous by products of agro – industrial productions and agricultural by- products have been studied for potential use as inexpensive sorbents [16]. A variety of plant biomaterials *viz. Pinus sylvestris* [17], *Cajanus cajan* husk [4], Hazelnut shell [18], *Cicer arientinum* husk [8], *Azadirachta indica* leaf [7], *Caesalpinia bonducella* seed powder [19], *Psidium guajava* leaf powder [20] etc., have been reported to be useful for heavy metal removal.

Strychnos potatorum L. (Loganiaceae) is a moderate sized tree found in Southern and central parts of India, Srilanka and Burma. Seeds are widely used in Ayurvedic and traditional medicine. Apart from its medicinal properties the seed powder is being used for clearing muddy water by the rural community. They are reported to be very effective as coagulant aids. This property is attributed because of the presence of polyelectrolyte, proteins, lipids, carbohydrates and alkaloids containing the –COOH and free –OH surface groups in the seed. Properties of the *S. potatorum* seeds there has been a recent interest in the metal binding property [21].

Azadirachta indica (Neem) is a plant originated from India. Cr (VI) has been removed by neem leaves powder [7]. Certain study reports the biosorption kinetics and the biosorption equilibrium of Zinc by Neem leaves and stem bark powder [22]. Neem bark powder (NBP) has also been used as an adsorbent for the removal of hexavalent chromium from aqueous solutions [23]. The potentiality of Neem has been widely explored for solving various problems related to agriculture, public health, population control and environmental pollution [22].

The effect of metal ions adsorbed on the seed can be determined using XRD analysis. X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. As a method, X-ray diffractometry is attractive because of its speed and ease of performance, and because it requires only small amounts of material, is nondestructive, and can be used to perform semi-quantitative analyses of poly-mineralic mixtures [24]. The present investigation is aimed to compare the removal efficiency of Chromium (VI) and Iron (III), from aqueous solutions using the seeds of *Azadirachta indica* (Neem) and *Strychnos potatorum* (Nirmali) as natural adsorbents (biosorbents) and utilize as alternatives to high cost adsorbent materials.

EXPERIMENTAL SECTION

Sample collection

Azadirachta indica (Neem) seeds and *Strychnos potatorum* (Nirmali) seeds were collected from Kayamkulam, Kerala. Both the seeds were washed extensively in running tap water to remove dirt and other particulate matter. Subsequently the seeds were sun dried for 3 days, and used for biosorption studies in the original piece size.

Preparation of adsorbate solutions

Stock solution of Cr (VI) and Fe (III) (1 mg/ L) was prepared by dissolving required quantity of Potassium dicomate and Ferrous ammonium sulphate respectively(analytical reagent grade) in double-distilled water. Experimental Cr (VI) and Fe (III) solutions of different concentrations were prepared by diluting the stock solution with suitable volume of double-distilled water.

Batch adsorption experiments

Batch mode adsorption studies for individual metal compounds were carried out to investigate the effect of different parameters such as adsorbate concentration, contact time, temperature and pH. The synthetic metal ion solutions were prepared by measuring various concentrations (0.1, 1 mg/L) in 100ml distilled water and was subjected to various pH levels (4, 7 & 10). pH was adjusted using 0.1N HCl and 2N NaOH. Each samples were treated with pre weighed 1g seeds of *Azadirachta indica* and *Strychnos potatorum* subjected to three different temperatures (291 K, 301 K & 311 K) and sampling was carried out at different exposure times (0, 8, 16 & 24 hrs). The initial and final concentrations of the metal ions in the solution were measured using UV- Vis Double beam Spectrophotometer (Infra IR513D) at 540 nm for Cr (VI) [25] and 510 nm for Fe (III) [26] and adsorption capacities of the adsorbents were calculated.

The extent of biosorption in percentage was calculated using the following equation: [2]

$$\%\, removal = \left(\frac{Ci - Ce}{Ci}\right) * 100$$

Where, C_i and C_e are initial and equilibrium metal ion concentration (mg / L) respectively.

Desorption study

After adsorption, the maximum adsorbate – loaded adsorbents were separated from the metal ion solution. These adsorbed seeds were then suspended in 100ml of distilled water at varying pH and temperature. At different time interval (0, 8, 16, 24 hrs) the desorbed adsorbate in the water was analyzed. The extent of desorption can be calculated using the following equation: [2].

$$\text{Desorption rate} = \frac{\text{Amount of metal ions desorbed to the distilled water}}{\text{Amount of metal ions adsorbed on seeds}} * 100$$

XRD Analysis

X-ray diffraction spectroscopy (XRD) analyses were carried out with PANalytical X-ray, Philips Analytical. The dried sample of the produced material was ground using an agate mortar and pestle and tested at 40kV and 40mA.

RESULTS AND DISCUSSION

Batch adsorption experiments

Effect of pH

Figure I – IV shows that both Chromium and Iron has maximum removal at acidic pH. At pH 4, the seeds become positively charged due to protonation of the amino groups , while the dichromate ions, exist mostly as anions ($Cr_2O_7^{2-}$, $HCr_2O_7^-$, $HCrO_4^-$ andCrO_4^{2-}) leading to electrostatic attraction between sorbent and sorbate. In case of ferric ions, it remains as cations, the concentration of proton existing in the solution will be decreased (when compared to very low pH) and hence will not give a chance to compete with Iron ions on the adsorption sites of seeds thus facilitating greater Fe (III) ions uptake.

Figure-I: Effect of pH on Chromium (VI) biosorption (%) by the seeds of *Azadirachta indica*

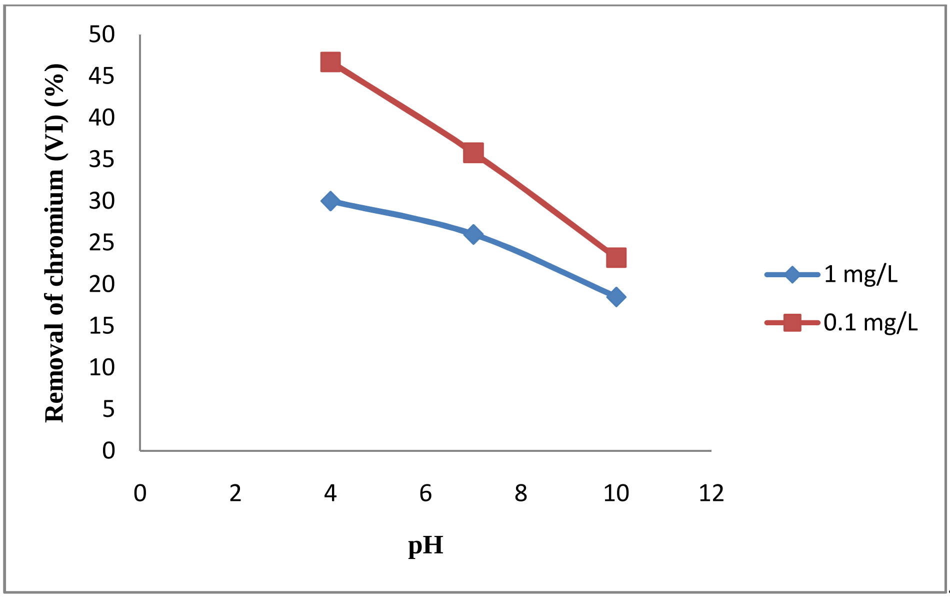


Figure-II: Effect of pH on Chromium (VI) biosorption (%) by the seeds of *Strychnos potatorum*

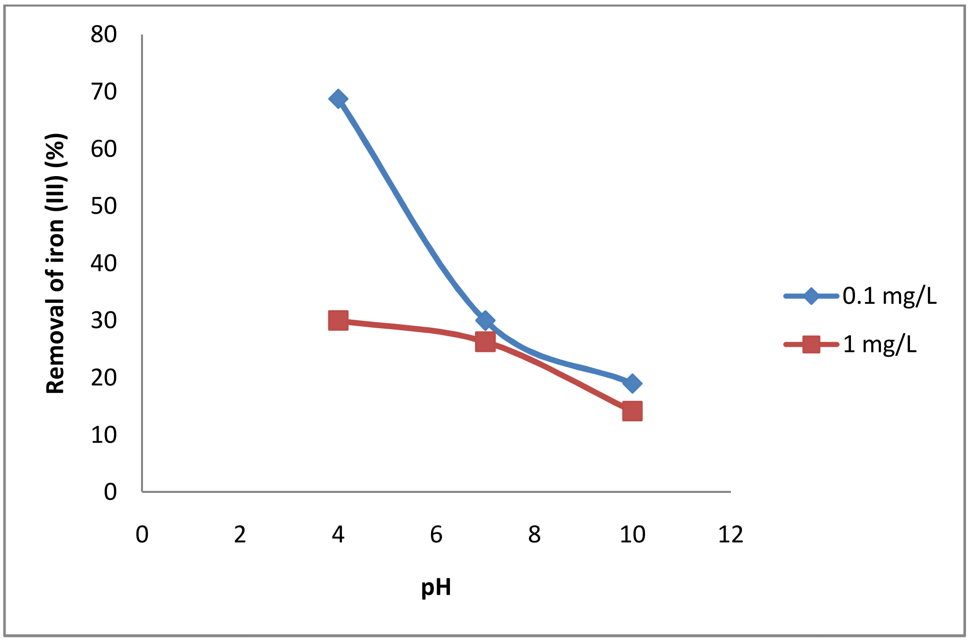


Figure-III: Effect of pH on Iron (III) biosorption (%) by the seeds of *Azadirachta indica*

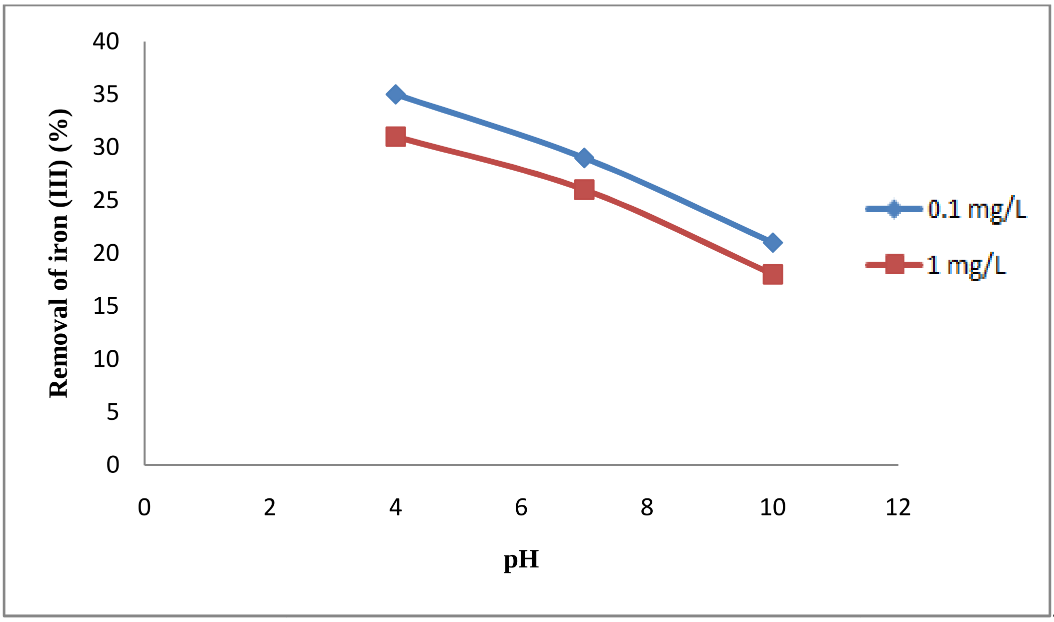
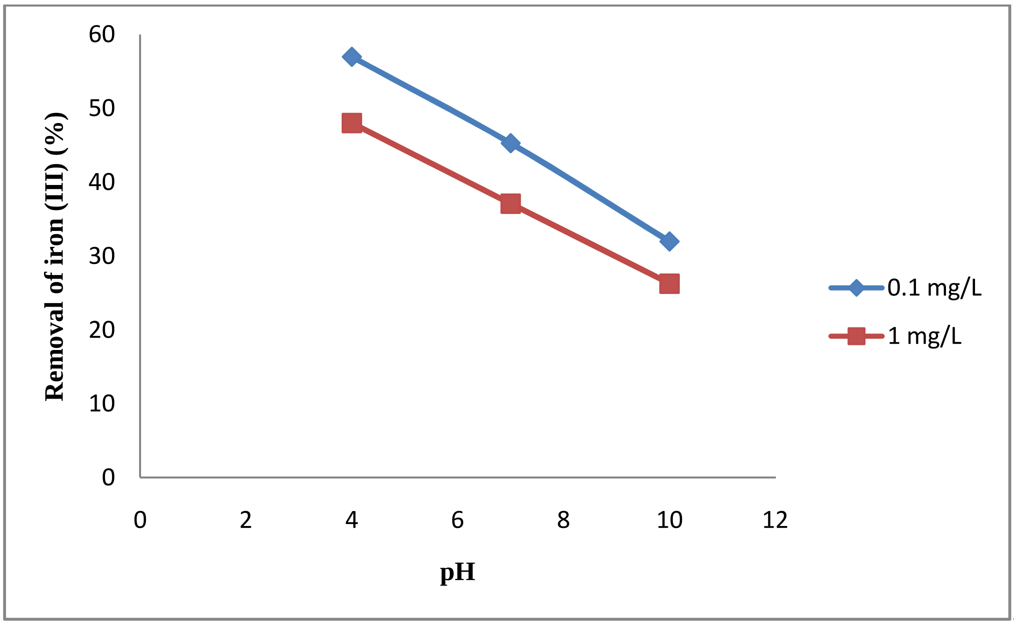


Figure-IV: Effect of pH on Iron (III) biosorption (%) by the seeds of *Strychnos potatorum*



Effect of temperature

Figure V and VI shows the effect of temperature on the adsorption phenomenon. It can be observed that removal of metal ions increases with increase in temperature. This is mainly due to the availability of more binding sites.

Figure-V: Effect of temperature (K) on Chromium (VI) biosorption (%) by the seeds of *Strychnos potatorum* and *Azadirachta indica* (concentration of metal ion = 0.1 mg/L, pH = 4)

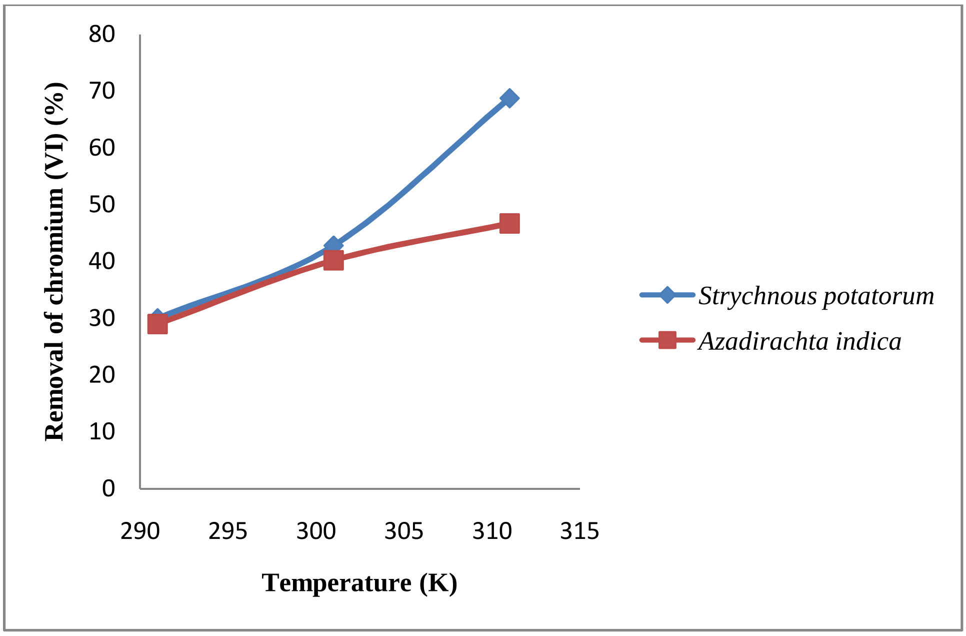
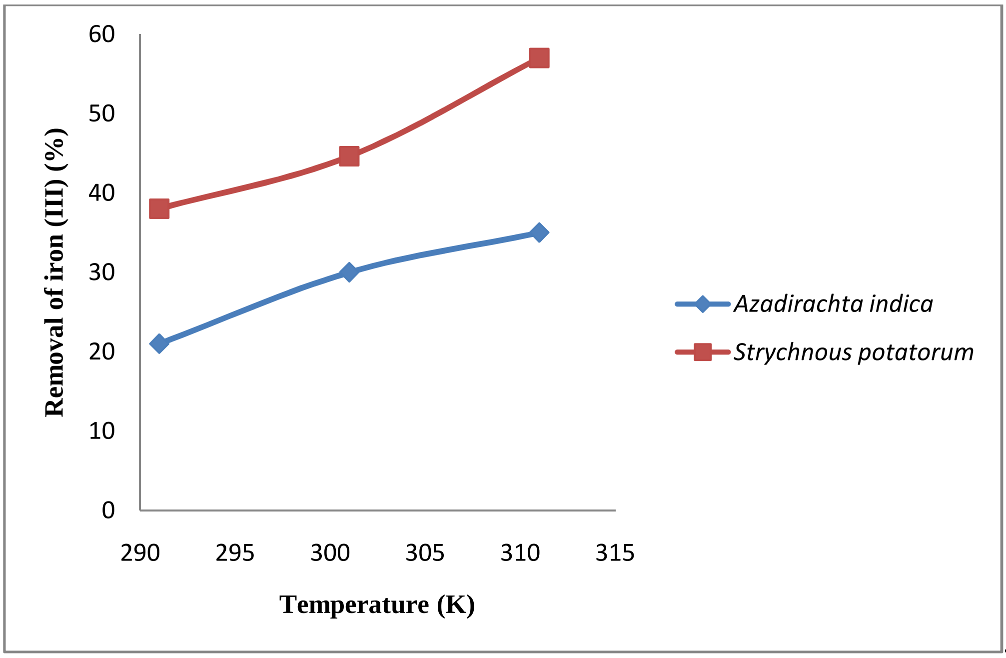


Figure-VI: Effect of temperature on Iron (III) biosorption (%) by the seeds of (concentration of metal ion = 0.1 mg/L, pH = 4)



Effect of contact time

Fig. VII and VIII illustrate the relationship between exposure time and the amount of Cr (VI) and Fe (III) ions adsorbed onto the seeds of *Azadirachta indica* and *Strychnos potatorum*. The rate of adsorption is very fast initially and maximum removal occurs at 24 hours. The initial fast sorption may be due to the uptake of Cr (VI) and Fe (III) through physical adsorption since adsorption phenomenon characteristically tends to attain instantaneous equilibrium. The number of active sites in the system is fixed and each active site can adsorb only one ion in a monolayer therefore metal uptake by the sorbent surface is rapid initially and then decreases as the availability of active sites decreases thus slowing down the transfer of metal ion from solution to adsorbent surface.

Figure-VII: Effect of contact time (h) on Chromium (VI) biosorption (%) by *Strychnos potatorum* and *Azadirachta indica* seeds (concentration of metal ion = 0.1 mg/L, pH = 4, Temperature = 311 K)

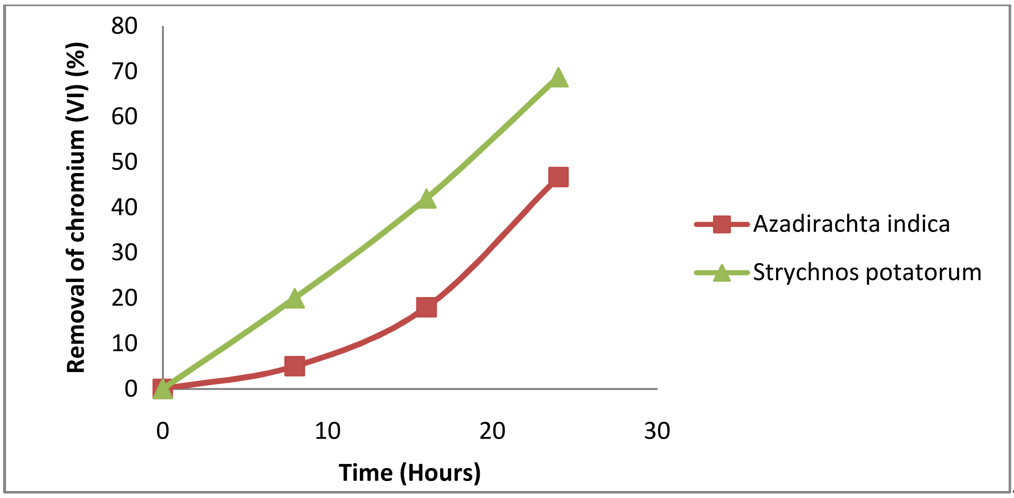
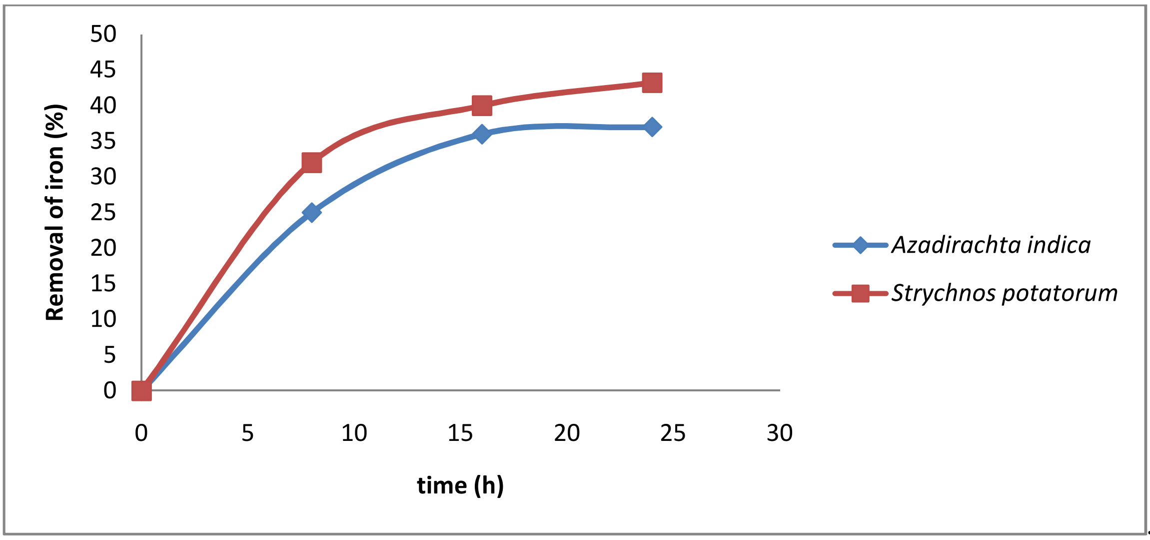


Figure-VIII: Effect of contact time (h) on Iron (III) biosorption (%) by *Strychnos potatorum* and *Azadirachta indica* seeds (concentration of metal ion = 0.1 mg/L, pH = 4, Temperature = 311 K)



Desorption studies

Desorption of Cr (VI) and Fe (III) from Chromium and Iron loaded biosorbents (seeds) respectively increased with increase in the initial pH. At pH 10, 28.6% of Cr (VI) was desorbed from *Azadirachta indica* seeds and followed by *Strychnos potatorum* seeds. Iron (III) was desorbed maximally at an initial pH of 10.

Table I: Effect of contact time (h) on Cr (VI) desorption (%) by the seeds of *Azadirachta indica* and *Strychnos potatorum* (concentration of metal ion = 0.1 mg/L, pH = 10, Temperature = 311 K)

Time (hrs)	Desorption (%) of Cr (VI) from the seeds of *Azadirachta indica*	Desorption (%) of Cr (VI) from the seeds of *Strychnos potatorum*
0	0	0
8	5.5	3
16	11	7
24	28.6	15

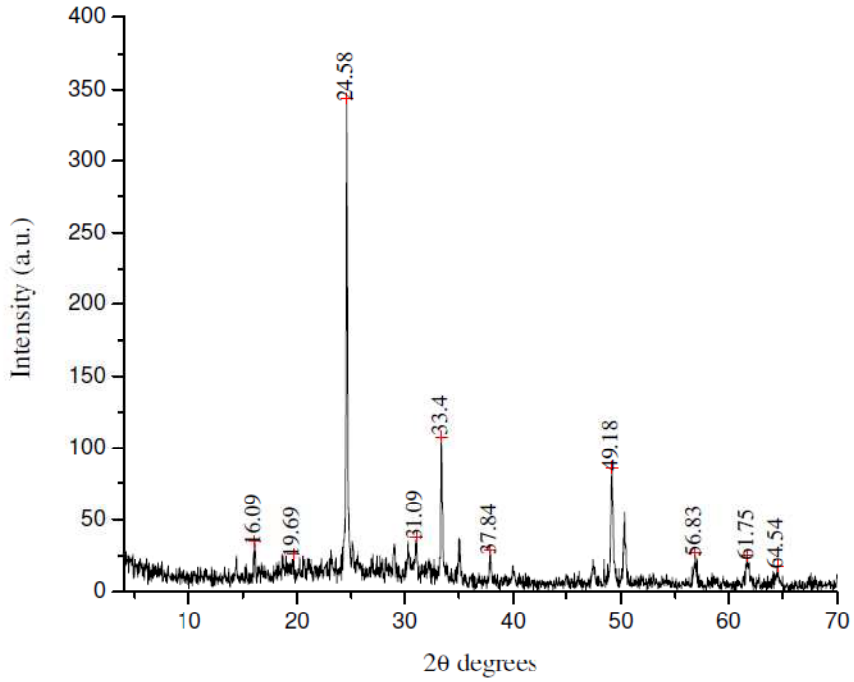
Table-II: Effect of contact time (h) on Fe (III) desorption (%) by the seeds of *Azadirachta indica* and *Strychnos potatorum* (concentration of metal ion = 0.1 mg/L, pH = 10, Temperature = 311 K)

Time (hrs)	Desorption (%) of Fe (III) from the seeds of *Azadirachta indica*	Desorption (%) of Fe (III) from the seeds of *Strychnos potatorum*
0	0	0
8	6	4.12
16	10	7
24	20.35	13.56

XRD Analysis

Strychnos potatorum seeds showed the maximum removal of Cr (VI) from solutions. Therefore the influences of the metal ions to the seeds were studied by XRD analysis. The results showed that the amorphous seed sample subjected to Chromium (VI) adsorption showed the formation of peaks. This shows that there are more vacant sites for adsorption on the adsorbent surface.

Figure-IX: XRD spectra of *Strychnos potatorum* seed powder after adsorption process



CONCLUSION

The current investigation shows that the seeds of *Strychnos potatorum* (Nirmali) and *Azadirachta indica* (Neem) are of low cost, abundantly available and can be used as an effective biosorbent for removal of Cr (VI) and Fe (III) ions in aqueous solution. The adsorption process is a function of the metal ion concentrations, pH, time and temperature. The maximum percentage removal of Cr (VI) and Fe (III) ions from aqueous solution is found to be 57.6 % and 35% for *Azadirachta indica* and 68.75 % and 46.7% for *Strychnos potatorum* respectively. The effective pH for both metal ion removal is at acidic (pH - 4) and temperature is at 301 K. Equilibrium was achieved practically in 24 hours. Desorption studies showed prominent datas for the regeneration of the biosorbents. The adsorption of the metal ion species on *Strychnos potatorum* seed was characterized by X-Ray Diffraction analysis, the peak showed the extent of adsorption and presence of more active sites.

This study helps in reducing the Cr (VI) and Fe (III) ion concentration in aqueous solution by using (*Azadirachta indica* and *Strychnos potatorum*) seeds. It can be concluded that, when compared to the seeds of *Azadirachta indica*, *Strychnos potatorum* showed better removal efficiency. Thus, this method is studied and proved for its eco-friendly feasibility and simple technology for water treatment.

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