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Removal of Molybdenum(VI) using *Tamarindous Indica* seeds as a natural ion exchanger

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Abstract

In a study, removal of molybdenum from aqueous solution using *Tamarindous Indica* seed powder has been investigated. The effect of contact time, exchanger dose and temperature has been studied at ambient temperature (27^{0}C±2^{o}C). The equilibrium process wasdescribe by the Langmuir isotherm model with adsorption capacity for molybdenum. The *Tamarindous Indica* seeds are subjected to different modification (Formaldehyde and sulphuric acid treatment). The adsorption capacity of *Tamarindous indica* seeds for metal ion was obtained. The maximum exchange level has been attained by 87.94% at acidic pH with exchanger dose 4g and contact time 50 min. Method is applied for removal of molybdenum from industrial effluents. Adsorption of molybdenum(VI) on natural ion exchanger was confirmed by EDX and FTIR

1. Introduction

Water is one of the essential solvent needed for living beings for the survival and growth.The quality of water is if initial concern for mankind since it is directly linked with human welfare [1]. Heavy metal pollution of industrial wastewater represents major problems for the environment as metal ions are non-biodegradable; have a very high toxicity and some of them have proved to be carcinogenic. If the metals are directly discharged in sewers, these are seriously damages the subsequent biological treatments in depuration plants and render the treated sludge unusable for agricultural purposes [2].

Molybdenum metal itself and its compound play an important role in plant, animal health and as catalysis. Hence the separation of molybdenum at trace level is an analytical merit [3]. The study aimed for removal of toxic substances from industrial effluent, water has become increasingly important over the last three decades and have been affected by human activities [4]. The excessive concentration of metal in water can cause various problems, molybdenum causes disease molybdenosa [5]. The aqueous geochemistry of molybdenum makes it a particularly interesting elements for isotopic investigation. As a transition metal of group VIB of the periodic table, molybdenum has a wide range of oxidation states [6]. In natural waters under toxic condition, it occurs as the highly stable molybdate ion (MoO_4^{2-}) [7].

Industries like metal finishing, metal planting, petroleum refining, tanning, wood preserving, mineral smelting, chemical manufacturing textile mills and fertilizer plants contribute high concentration of molybdenum to the environment. The disposal of molybdenum containing industrial wastewater elicits several environmental concerns [8]. Many methods were developed in the past to remove heavy metal ions from waste water [9-13]. The most important technology includes adsorption and coagulation [14], ion exchange [15], electro coagulation [16], adsorption [17], bio-sorption [18] and zeolite [19], but adsorption is one of the possible methods in removal of heavy metals from industrial waste water. The highly porous nature of adsorbent provides large surface area for deposition of adsorbate present in the liquid or gaseous mixture. Wide range of adsorbents are synthesized that show different characteristics depending upon their chemical constituents and the synthesis techniques adopted [20-24]. The removal of molybdenum by using natural ion exchanger treated *Tamarindous indica* seed powder found to be an efficient method.

2. Material and Methods

2.1 Seed powder and its treatment

Tamarindous indica seeds were pulverized after drying in sunlight at open air for one week. Small size pieces of dried seeds were grinded and pass through the mesh size 200 unit. This powder was treated with 39 % formaldehyde and 0.1 mol L^{-1} sulphuric acid at 80^{o} C, for 30 min. After cooling and washing with double distilled water, substrate was allowed to dry for overnight in open air. Dried powder was used for adsorption studies. The properties of *Tamarindous indica* seed powder are reported in Table 1.

Table 1 : Properties of ion exchange resin

Parameters	**Value**
Physical form	Spherical
Bulk density	0.15 $gm.cm^{-3}$
Ash content	10.4%
Moisture content	8.7%
Matter soluble in water	8.4%
Matter soluble in acid	18%
Water holding capacity	80.32%

2.2. Scheme

Seed powder → formaldehyde 700 ml → 0.1N sulphuric acid 10 ml → heat for 30 min at 80^{o} C → cool the substrate → filter →wash with double distilled water and dried at open air and use this substrate as an insoluble natural ion exchange resin.

2.3. Sorbets

For adsorption study stock solution of molybdenum was prepared by dissolving 0.075g of MoO_3 in double distilled water (DDW). The various concentrations were then obtained by diluting the stock solution with double distilled water.

2.4. Method for Separation of Molybdenum

An aliquot solution containing 20 µg of molybdenum(VI) was taken in 25 ml flask. By adjusting the acidic pH it was transferred in conical flask containing 4g of the natural ion exchanger. It was shaken after every 15 min and at temperature 30°C for 50 min. After 50 min solution was filtered and unadsorbed molybdenum was determine by the thiocyanate-stannous chloride method [25]. The amount of molybdenum uptake was calculated by difference in concentration. The initial concentration C_0 (mg L^{-1}) and metal concentration at various time interval C_e (mg L^{-1}) were determined and metal uptake q_e(mg L^{-1}) was calculated from the mass balance equation as:

$$q_e = (C_0 - C_e)\frac{v}{m} \qquad (1)$$

Where, C_o and C_e are the initial and equilibrium concentration of molybdenum solution (mg l^{-1}), v is the solution volume (ml), and m is the adsorbent weight (g). The adsorption percent (%) was calculated using the equation.

$$\%\,adsorption = \frac{(C_o - C_e)}{C_o} \text{x } 100 \qquad (2)$$

The sorption equilibrium data for vanadium on *Tamarindous indica* seed powder was analyzed in terms of the Freundlich and Langmuir isotherm models. The Langmuir isotherm equation could be written as:

$$\frac{q_e}{Q_m} = \frac{K_{LC_e}}{1+K_{LC_e}} \qquad (3)$$

Where

q_e = the equilibrium concentration on adsorbent (mg g^{-1})
C_e = equilibrium concentration in solution (mg L^{-1})
Q_m = maximum adsorption capacity (mg L^{-1})
K_L = adsorption equilibrium constant (mg L^{-1})

This method is based on the assumption that the forces of interaction between sorbed molecules are negligible and once a molecule occupies a site no further sorption take place.

Also, the logarithmic form of Freundlich equation may be written as:

$$q_e = K_F C_e{}^{1/n} \qquad (4)$$

Where,

q_e = the equilibrium concentration on adsorbent (mg g^{-1})
C_e = equilibrium concentration in solution (mg L^{-1})
K_F = adsorption capacity
n = reaction energy

The Freundlich equation can be described by assuming heterogeneous surface with adsorption on each class of sites. Although this expression is empirical, 1/n reflects the curvature in the isotherm and may represent the energy distribution of adsorption sites.

The liberalized form of Freundlich sorption isotherm is:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (5)$$

By plotting $\ln q_e$ versus $\ln C_{e,}K_F$ and n can be determined, if a straight line is obtained.

To study the effect of important parameters like contact time, resin amount, pH, initial metal concentration and temperature on the removal of Mo(VI) by natural ion exchanger, experiment were conducted at room temperature except those in which the effect of temperature.

3. Results and discussion

3.1. Effect of contact time

In this study, contact time of natural ion exchanger with molybdenum(VI) solution is vary from 5min to 50 min. It is observed from result that with increase in contact time adsorption of molybdenum(VI) increase from 86% to 97% (Figure 1) 50 min contact time is fixed for further study.

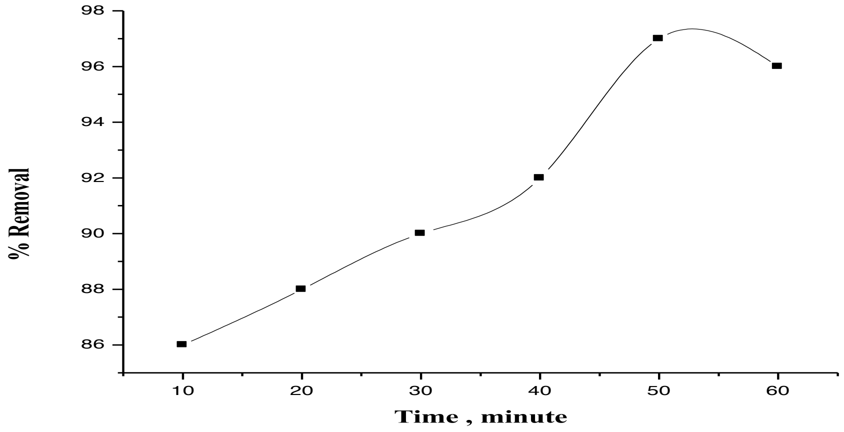

Figure 1 : Effect of time

3.2. Effect of pH

In order to established the effect of pH on adsorption of molybdenum(VI) on natural exchanger, at different pH values were carried out at acidic pH with 4g exchanger was stirred with temperature 30^0C for a contact time 50 min. The high values of pH were not studied because of precipitation and turbidity of metal ion take place. It is observed from result at acidic pH,96% molybdenum(VI) is removed.

3.3. Effect of initial metal concentration

To study the effect of initial metal concentration at optimum conditions (4g natural ion exchanger pH, contact time 50 min) the different concentration ranging from 0.2 mg to 2 mg were studied. At optimum condition maximum removal of metal increases with increase in concentration. (Figure 2). The higher the heavy metal concentration, stronger the driving forces of the concentration gradient and therefore the higher the adsorption capacity [26].

3.4. Effect of solution temperature

To study the effect of solubility temperature on removal molybdenum(VI) at optimum condition, the temperature is increased from 10^0C to 40^0C.It is observed from result, at 30^0C,91% molybdenum is removed (Figure 3).

3.5. Effect of natural ion exchanger dose

In a study of effect of natural ion exchanger dose on adsorption of molybdenum(VI), natural ion exchanger dose was varying from 0.5g to 4.5g by keeping all other condition constant. The result shows that by increase in dose of natural ion exchanger adsorption of molybdenum (VI) increases from 66% to 92% (Figure 4).

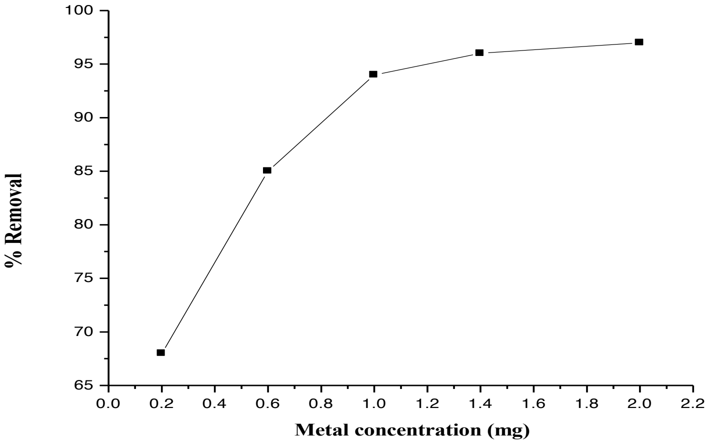

Figure 2: Effect of metal concentration

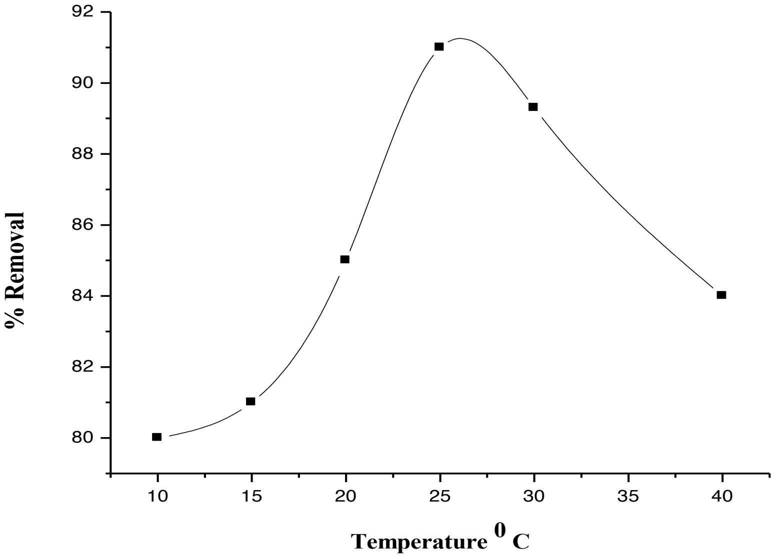

Figure 3: Effect of temperature

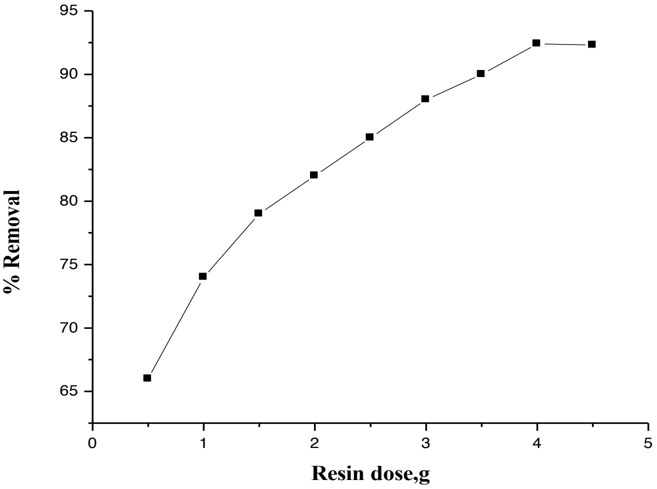

Figure 4: Effect of resin dose

3.6. SEM and EDX Analysis

The morphological analysis of phenol formaldehyde treated seed powder was performed by SEM as shown in Figure 5(a) - (c). Many small pores and particles >20µm diameter are observed on the surface of natural ion exchanger. Pores are does not observed. It clearly indicates that biosorption of molybdenum on phenol formaldehyde natural ion exchanger. EDX spectrum from Figure 6 (b) also showed a peak at 2 Kev, which confirmed that Mo was adsorbed on phenol formaldehyde resin, which was absent in Figure 6(a). It supports that the reaction of metal ion and phenolic –OH group on phenol formaldehyde treated seed powder surface may be partly ion exchange or complexation.

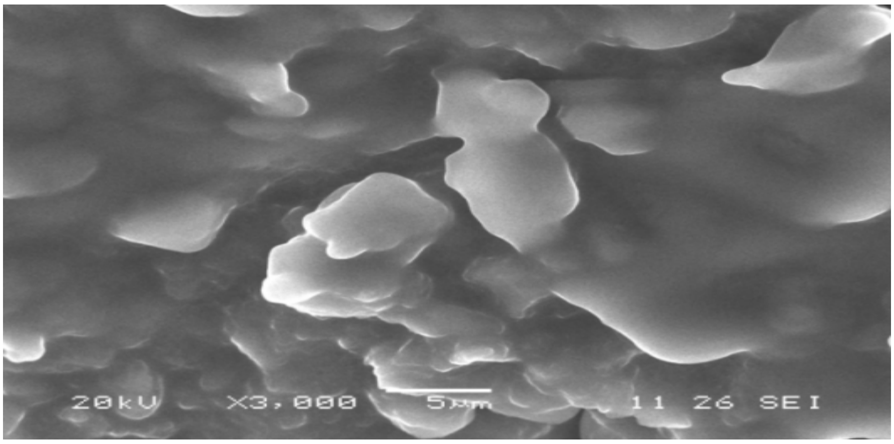

Figure 5a: SEM photograph of raw seed powder

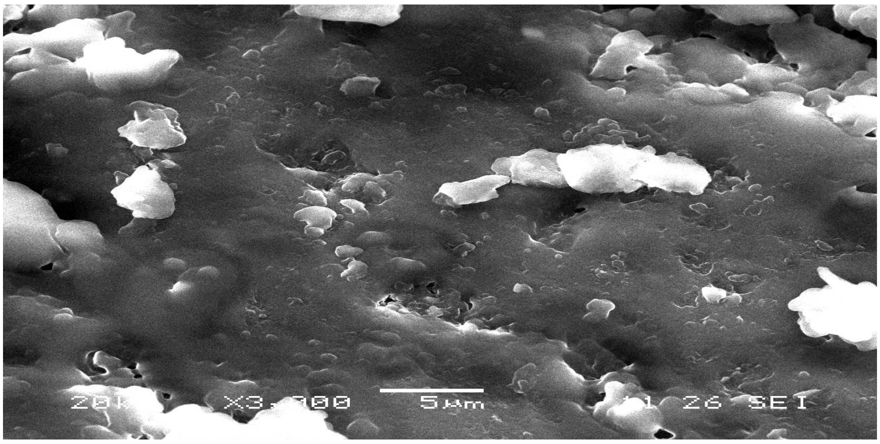

Figure 5b: SEM photograph of phenol-formaldehyde resin

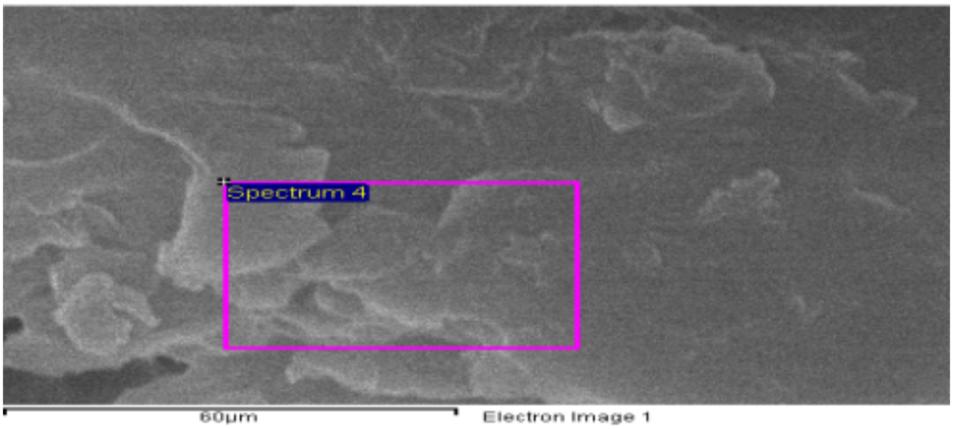

Figure 5c: Phenol adsorption formaldehyde resin after Mo(VI)

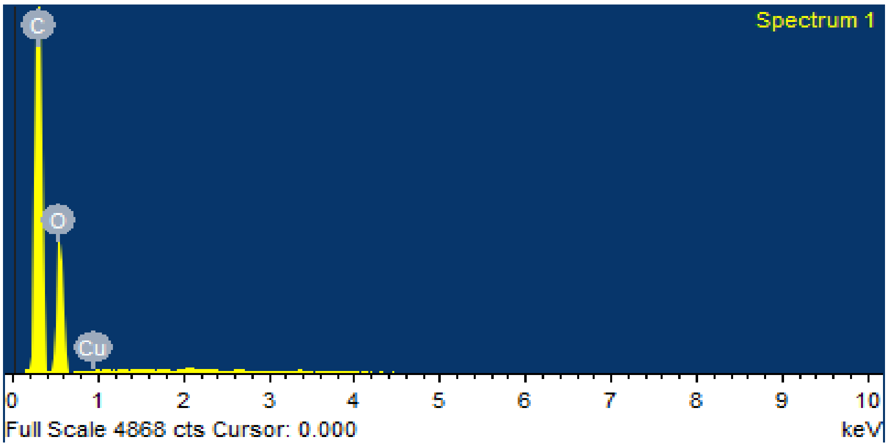

Figure 6a: EDX spectra of phenol-formaldehyde resin

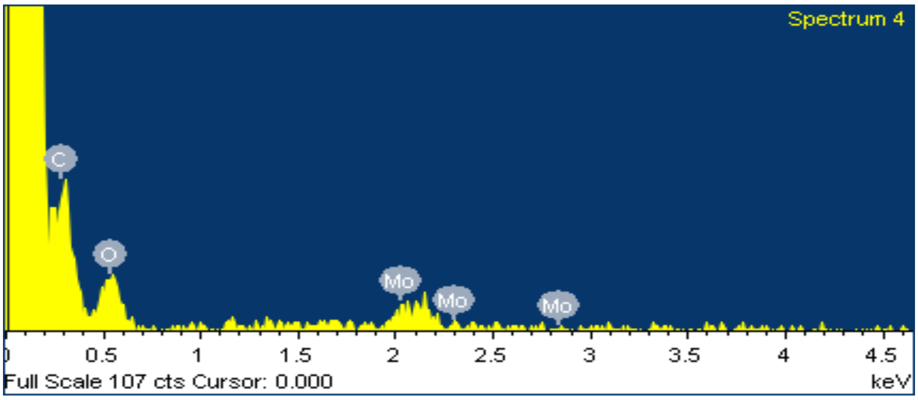

Figure 6b: EDX spectra of phenol-formaldehyde resin after adsorption of molybdenum

3.7. FTIR Analysis

The FTIR spectrum of raw seeds powder, formaldehyde treated seed powder and Molybdenum(VI) adsorbed seed powder are presented in Figure 7-8 respectively. The fact that, broad peak in between 3462 and 3281 cm $^{-1}$ indicates presence of phenolic – OH group in both resin. IR absorption at 2924 cm^{-1} also indicates presence of = C – H group on the benzene ring. The 1600 – 1500 cm^{-1} absorption peak clearly indicates the presence of aromatic double bonds in both resin.

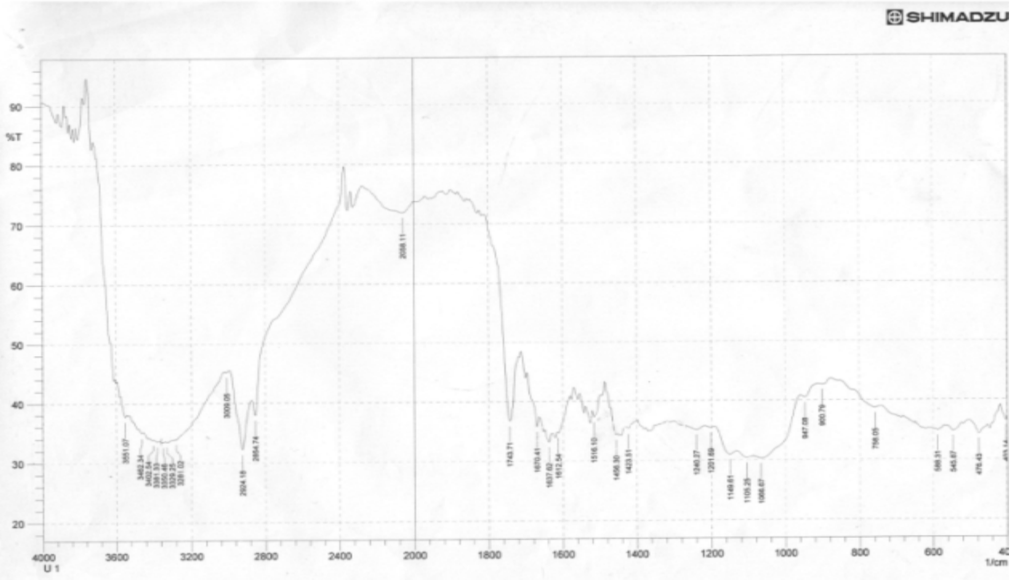

Figure 7: FT-IR spectrum of raw seed powder

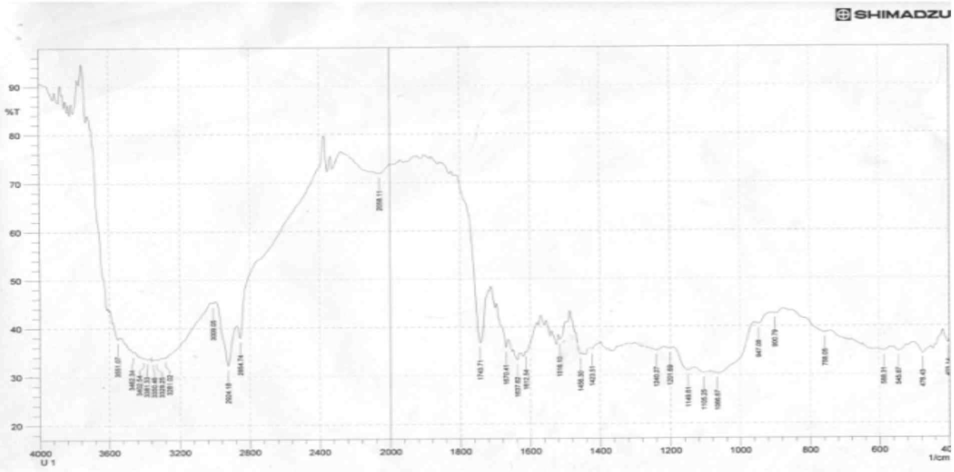

Figure 8: FT-IR spectrum of phenol formaldehyde resin

The IR bonds in the region of 1149 – 1066 cm^{-1} indicate C – O bond in raw seed powder. One characteristic peak at 1739 – 1743 cm^{-1} indicates presence of ester group in both seed powder. Some peaks in the region of 1670 – 1612 cm^{-1} also are due to olefinic bonds in raw and treated natural ion exchanger. The IR frequency at 2924 cm^{-1} is due to stretching vibration of $– CH_2 –$ group in alkane. IR absorption at 2022 cm^{-1} in treated seed powder also suggest presence of $– CH_2 –$ group in between two phenolic rings which is lower frequency than that of raw seeds powder

4. Application

4.1. Removal of Molybdenum from industrial effluents

In order to assess the practical performance of natural ion exchanger for removal of molybdenum from industrial effluent, an experiment was carried out after adjusting the *acidic pH.* At which the maximum adsorption of molybdenum can be achieved. Developed method is applied for removal of molybdenum, from various industrial effluents. The concentration of molybdenum from these effluents was determined before treatment and after treatment with natural ion exchanger. It is observed that more than 87.94% of molybdenum was removed from effluents. The results are reported in Table 2.

Table 2: Separation of Molybdenum from effluents

Sample No.	Effluent	Added quantity of Molybdenum (mg)	Concentration before treatment (mg)	Concentration after treatment(mg)	%Removal
1	25	1	1.99	0.46	76.88
2	25	1	1.98	0.30	84.84
3	25	1	1.99	0.24	87.94

Conclusion

The purpose of this work was to study the possibility of removing molybdenum from effluent through sorption by modified natural ion exchanger. The data reported, show that *Tamarindous indica* seed powder is an effective sorbent for removing molybdenum from effluent. The sorption capacity of natural adsorbent was higher than the reported value of other adsorbents. The equilibrium data have been analyzed using Langmuir and Freundlich isotherm models, and results showed that the sorption of molybdenum occur at *acidic pH*, which is fit better to Freundlich isotherm model. It could be planned to use natural ion exchanger for water treatment economically.

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