Removal of Vanadium from Industrial Effluents by Natural Ion Exchanger

Shashikant R. Kuchekar, Haribhau R. Aher, Priti M. Dhage

Abstract—The removal vanadium from aqueous solution using natural exchanger was investigated. The effects of pH, contact time and exchanger dose were studied at ambient temperature (25 ^{0}C ± 2 ^{0}C). The equilibrium process was described by the Langmuir isotherm model with adsorption capacity for vanadium. The natural exchanger i.e. tamarindus seeds powder was treated with formaldehyde and sulpuric acid to increase the adsorptivity of metals. The maximum exchange level was attained as 80.1% at pH 3 with exchanger dose 5 g and contact time 60 min. Method is applied for removal of vanadium from industrial effluents.

Keywords—Industrial effluent, natural ion exchange, *Tamarindus indica,* vanadium.

I. Introduction

RAPID industrialization has affected to rise up disposal of heavy metals in to environment. The exceeding increase in the use of the heavy metals leads to environmental as well as public health problems [1]. Toxic heavy metal ions get discharged in waste water through various industrial activities such as mining, refining of ores and effluents from fertilizer industries, tanneries, batteries, paper industries, pesticides, nuclear power plant and textile industries [2].

Vanadium (V) is found in a few organisms and salts of V have moderate toxicity [3]. Environmental scientists have studied about V poisoning, declared it as a hidden element of plants, and the entire agricultural system. V is present in fossil fuels such as crude petroleum, fuel, oils some coals, and lignite. After burning these fuels, V releases into the air and settles on the surface of soil. There are cases of V poisoning, such as nervous depression, coughing, vomiting, diarrhea, anemia and increased risk of lung cancer that are sometimes fatal [4]. Recently, V has been noticed as the index elements in urban environmental pollution, especially air pollution [5]. An epidemiological evidence suggests that V may also play a beneficial role in the prevention of heart disease [6]. V in environmental samples has been determined by NAA, ICP, and AAS [7]. V is determined by atomic emission spectrometry [8] and spectrophotometers [9]-[21]. V has been determined by solidification of floating organic drop micro extraction (SFODME) [22]-[25], out of all methods spectrophotometric method is the simple and rapid method for the determination of V.

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Different technologies have been developed over the years to remove heavy metals from various sources. The most important technology includes adsorption and coagulation [26], various ion exchange methods [27], electro coagulation [28], adsorption [29], bio sorption [30] and shape selective catalyst having various pore sizes [31]. The natural ion exchangers are attapulgite [32], *Kudzu (Pueraria lobata Ohwi)* [33], activated carbon [34], coconut husk [35], fly ash [36], coffee husk [37], fungal biomass [38], *Tamarindus indica* seed [39], *Tendu (Diospyros melanoxylon)* [40], rise husk [41], *Lactobacillus bulgaricus* [42].

The purpose of present study is to remove V by using natural ion exchanger. In this research different parameters which increase adsorption i.e. pH, natural ion exchanger dose, temperature, contact time were investigated. Method was applied for removal of V from industrial effluents and it gives good results.

II. Experimental

A. Seed Powder

Tamarindus indica seeds were smashed after drying in sunlight at open air for one week. Small size pieces of dried seeds were pounded and pass through the mesh size 150-200 unit. This milled 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 distilled water, exchanger was allowed to dry overnight in open air. Dried powder was used for adsorption studies. The properties of natural exchanger are reported in Table I.

TABLE I
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%

B. Sorbet

For adsorption study stock solution of V (4 mgL^{-1}) was prepared by dissolving 4.968 g of ammonium vanadate in double distilled water (DDW).

C. Method for Separation of V

Aliquot solution containing 1 mg of V was made up to 25 ml. By adjusting the pH 3 it was transferred in conical flask

containing 5 g of the natural ion exchanger. It was shaken after every 15 minutes and at temperature 30 ℃, for 60 min. After 60 min solution was filtered and unadsorbed V was determined by standard spectrophotometric method. The amount of V uptake was calculated by difference in concentration by using mass balance equation, The initial concentration C_o (mg L^{-1}) and metal concentration at various time intervals C_e (mg L^{-1}) were determined and metal uptake q_e (mg L^{-1}) was calculated

$$q_{e\ =\ (c_0\ -c_e)}\frac{v}{m} \tag{1}$$

where, C_o and C_e are the initial and equilibrium concentrations of V 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:

$$\%\ adsorption\ =\ \frac{(C_o-C_e)}{C_o}x100 \tag{2}$$

Freundlich and Langmuir adsorption isotherm was used for adsorption of V on *Tamarindus indica* seed powder. The Langmuir isotherm equation could be written as

$$\frac{q_e}{Q_m}\ =\ \frac{K_L C_e}{1+K_L C_e} \tag{3}$$

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 technique is based on adsorption once the adsorption occurs further adsorption is not possible.

Freundlich equation also written in the logarithmic form as:

$$q_{e\ =\ K_F C_e}{}^{1/n} \tag{4}$$

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 adsorption isotherm can be described by using heterogeneous surface, this expression is empirical and 1/n factor, reflecting the curve in the isotherm, may represent the energy distribution of adsorption sites.

The equation of Freundlich sorption isotherm is

$$\ln q_{e\ =\ \ln K_F+\frac{1}{n}\ln C_e} \tag{5}$$

By plotting $\ln q_e$ versus $\ln C_e$, K_F and n can be calculated by using straight line. This experiment deals with study of some important parameters like pH, contact time, resin amount, metal concentration and temperature for the removal of V by natural ion exchanger, experiments were conducted at room temperature.

D. Effect of pH on Ion Exchange Process

In order to establish the effect of pH on the ion exchange of

V ion on natural ion exchanger, the batch equilibrium studies at different pH values were carried out in the range of 1.0 - 6.0 for a constant weight of ion exchanger (5 g) and initial metal concentration of 2 mg ml^{-1} at 298 K (Fig. 1). The high values of pH were not studied because of precipitation of metal ion. Fig. 1 shows the change in metal uptake by natural ion exchanger at different pH levels. The pH of the aqueous solution is important to control the ion exchange process. The percentage removal of metal increased with increase in pH and maximum binding was at pH 3. At this pH, 92% removal of V was observed.
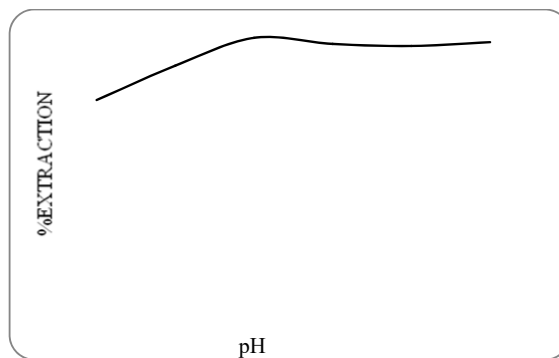

Fig. 1 Effect of pH

E. Effect of Initial Metal Concentration on Ion Exchange Process

To study the effect of metal concentration 25 ml of solution containing V having different concentrations ranging from 1 to 10 mg ml^{-1} with 5 gm of natural ion exchanger was stirred with ambient temperature (298K) for a contact period of 60 min. The result obtained is shown in Fig. 2.
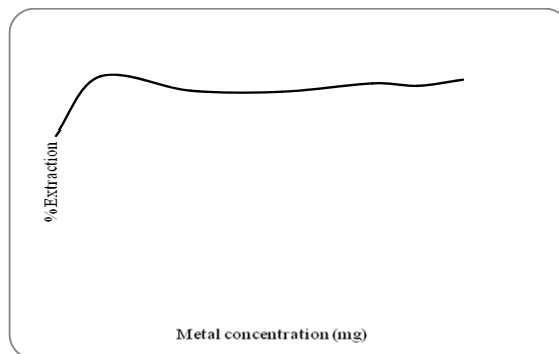

Fig. 2 Effect of Metal concentration

It was also realized that the capacity of metal removed by natural ion exchanger at the equilibrium increases with the initial concentration of metal but the percent removal decreased with the increase in initial metal concentration. Apparently, the initial metal ion concentration played an important role in affecting the capacity of metal exchange on natural ion exchanger. The higher the metal concentration, stronger the driving forces of the concentration gradient and therefore the higher the adsorption capacity.

F. Effect of Solution Temperature on Ion Exchange Process

The effect of solution temperature on adsorption of V by natural ion exchanger is shown in Fig. 3
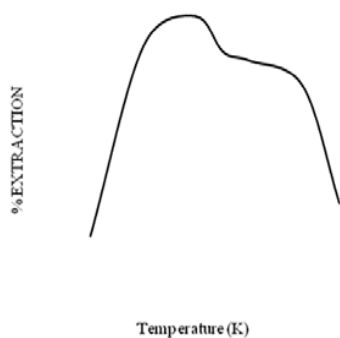

Fig. 3 Effect of temperature

As temperature increases from 283 K to 323 K the removal of metal ion increases (Fig. 3). When natural ion exchanger is used for V removal with an increase in temperature from 283 K to 323 K, the ion exchange capacity increased from 86.32% to 94% with initial metal concentration.

G. Effect of Natural Ion Exchanger Dose on Ion Exchange Process
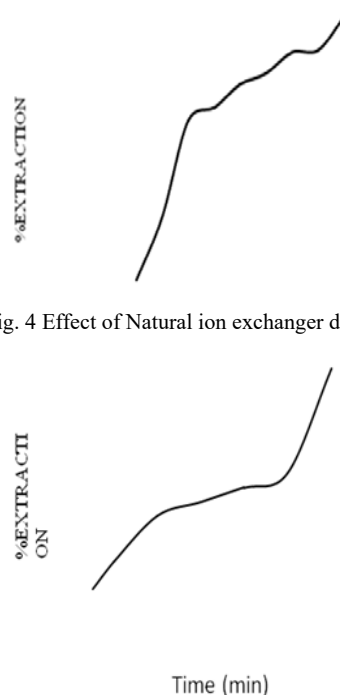
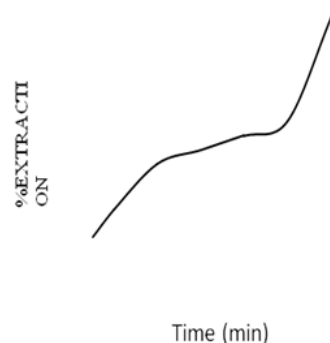Fig. 4 Effect of Natural ion exchanger dose

Fig. 5 Effect of contact time

The percentage adsorption efficiency of V at different doses of natural ion exchanger was shown in Fig. 4. The percentage removal efficiency increases as the natural ion exchanger dose was increased. It might be concluded that by increasing the natural ion exchanger dose, the removal efficiency of V

increases. When increased resin dosage from 0.5 g to 5 g, removal efficiency increased from 83.97% to 96.63% for V.
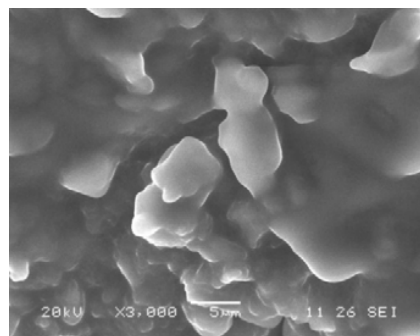

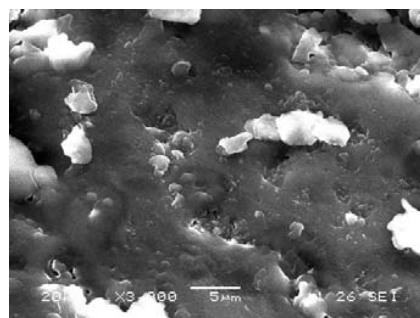
Fig. 6 (a) SEM photograph of raw seed powder

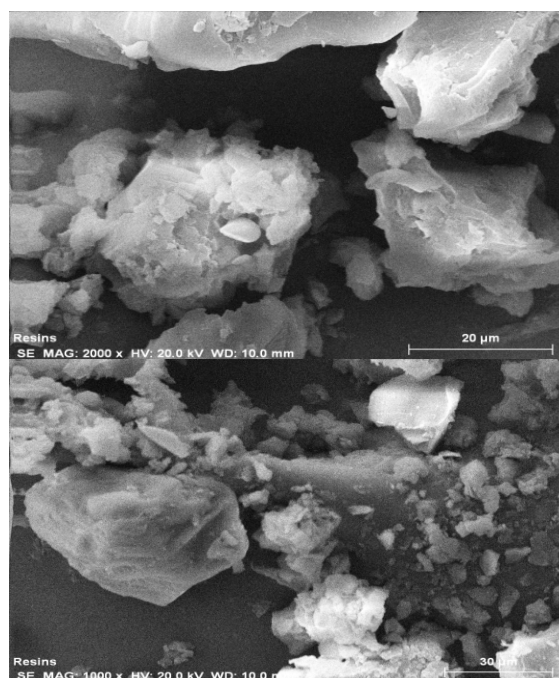Fig. 6 (b) SEM photograph of phenol-formaldehyde resin

Fig. 6 (c) Phenol formaldehyde resin after adsorption, V

With increase in contact time the removal efficiency increases. By keeping *p*H, adsorption dose and temperature of solution constant, it can be seen that V removal efficiency

increased from 85.08% to 91%, when contact time increased from 5 min to 60 min (Fig. 5).

Optimum contact time for V removal was found to be 60 min.

H.SEM and EDX Analysis

The morphological analysis of phenol formaldehyde treated seed powder was performed by SEM as shown in Figs. 6 (a)-(c).

Many small pores and particles > 20 μm diameter are observed on the surface of resin. Absorption of V on natural ion exchanger was observed from pores size of exchanger. EDX spectrum from Fig. 7 (b) also showed a peak at 0.5 Kev, which confirmed that V was adsorbed on phenol formaldehyde resin, which was absent in Fig. 7 (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.
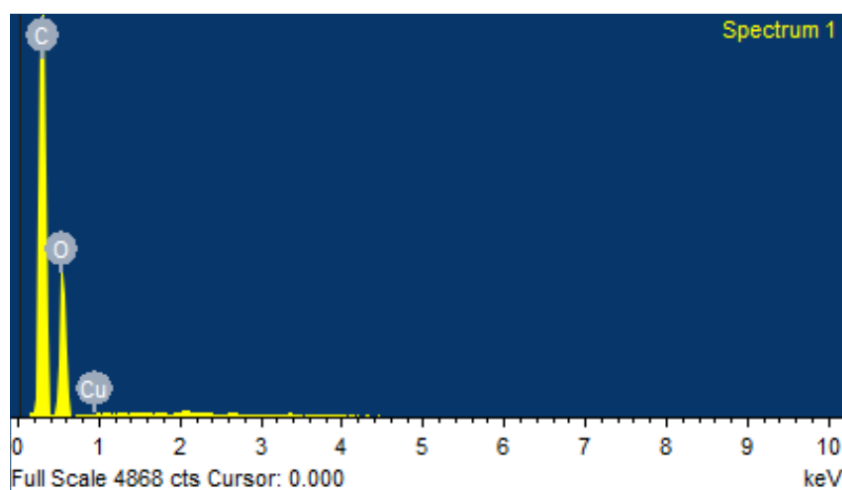

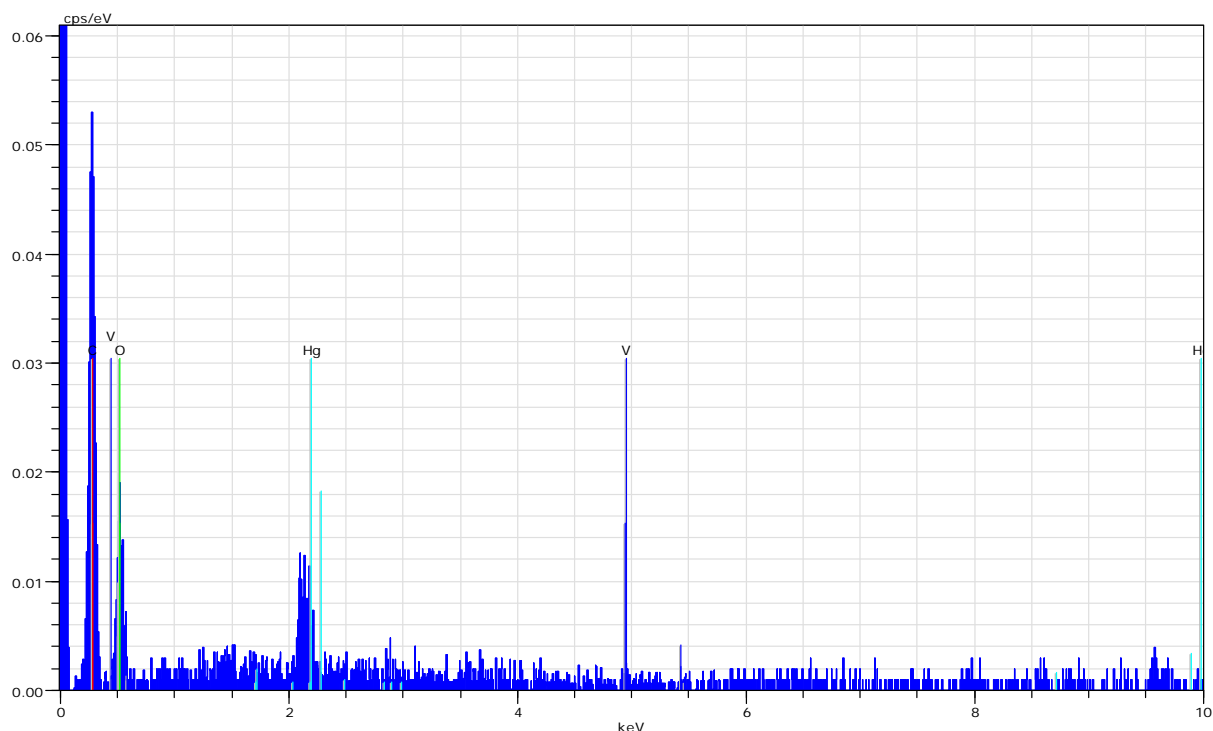Fig. 7 (a) EDX spectra of phenol-formaldehyde resin

Fig. 7 (b) EDX spectra of phenol-formaldehyde resin after adsorption of V

I. FTIR Analysis

The FTIR spectrum of raw seeds powder, formaldehyde treated seed powder and V adsorbed seed powder are presented in Figs. 8, 9 respectively. The 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 resins. The IR bonds in the region of 1149-1066 cm^{-1} indicate C–O bond in raw seed powder. One characteristic peak at 1739-743 cm^{-1} indicates presence of ester group in both seed powder. Some peaks in the region of 1670-1612 cm^{-1} olefinic bonds are present in raw and treated resin. The stretching IR frequency of –CH$_2$– group in alkane is at 2924 cm^{-1}. IR absorption at 2022 cm^{-1} in treated seed powder also suggests presence of –CH$_2$– group in between two phenolic rings which is lower frequency than that of raw seeds powder.
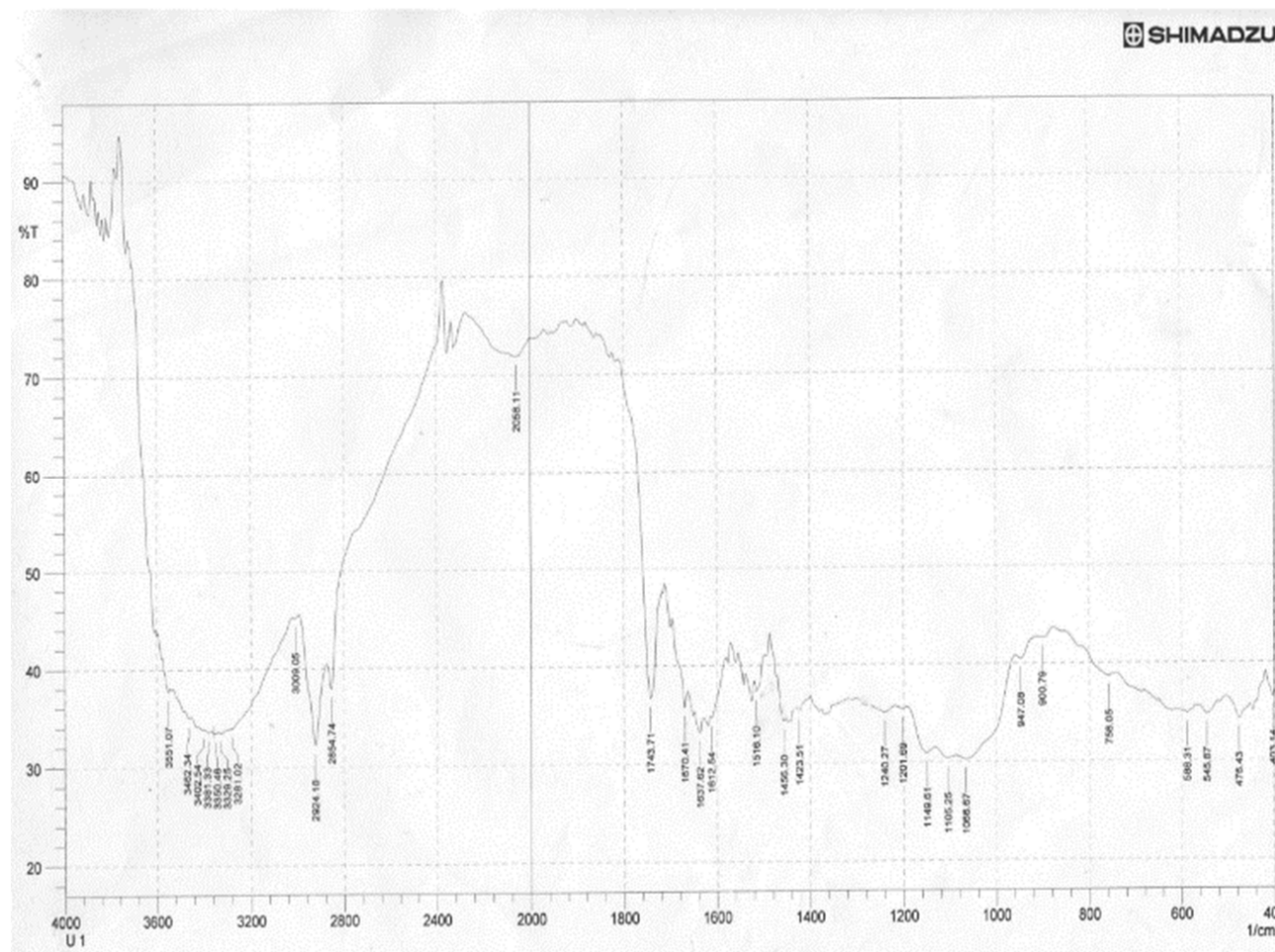

Fig. 8 FT-IR spectrum of raw seed powder

III. APPLICATION

Removal of V from Industrial Effluents

For removal of V from industrial effluent by using natural ion exchanger, an experiment was carried out after adjusting the pH to 3 at which the maximum adsorption of V can be achieved. Developed method is applied for removal of V, from various industrial effluents. The concentration of V from these effluents was determined before treatment and after treatment with natural ion exchanger. It is observed that more than 99% of V was removed from effluents. The results are reported in Table II.

TABLE II
PERCENT REMOVAL OF VANADIUM FROM EFFLUENTS

Sample No.	Effluent	Added quantity of V (mg)	Concentration before treatment mg	Concentration after treatment mg	%Removal
1	25	2	1.99	0.70	64.8
2	25	2	1.98	0.43	78.28
3	25	2	1.99	0.41	80.1

IV. CONCLUSION

In this work, we studied about the removal of V from effluents through by natural exchanger. The data reported, show that *Tamarindus indica* seed powder is an effective

adsorbent for removing V from effluent. It could be planned to use natural ion exchanger for water treatment economically.
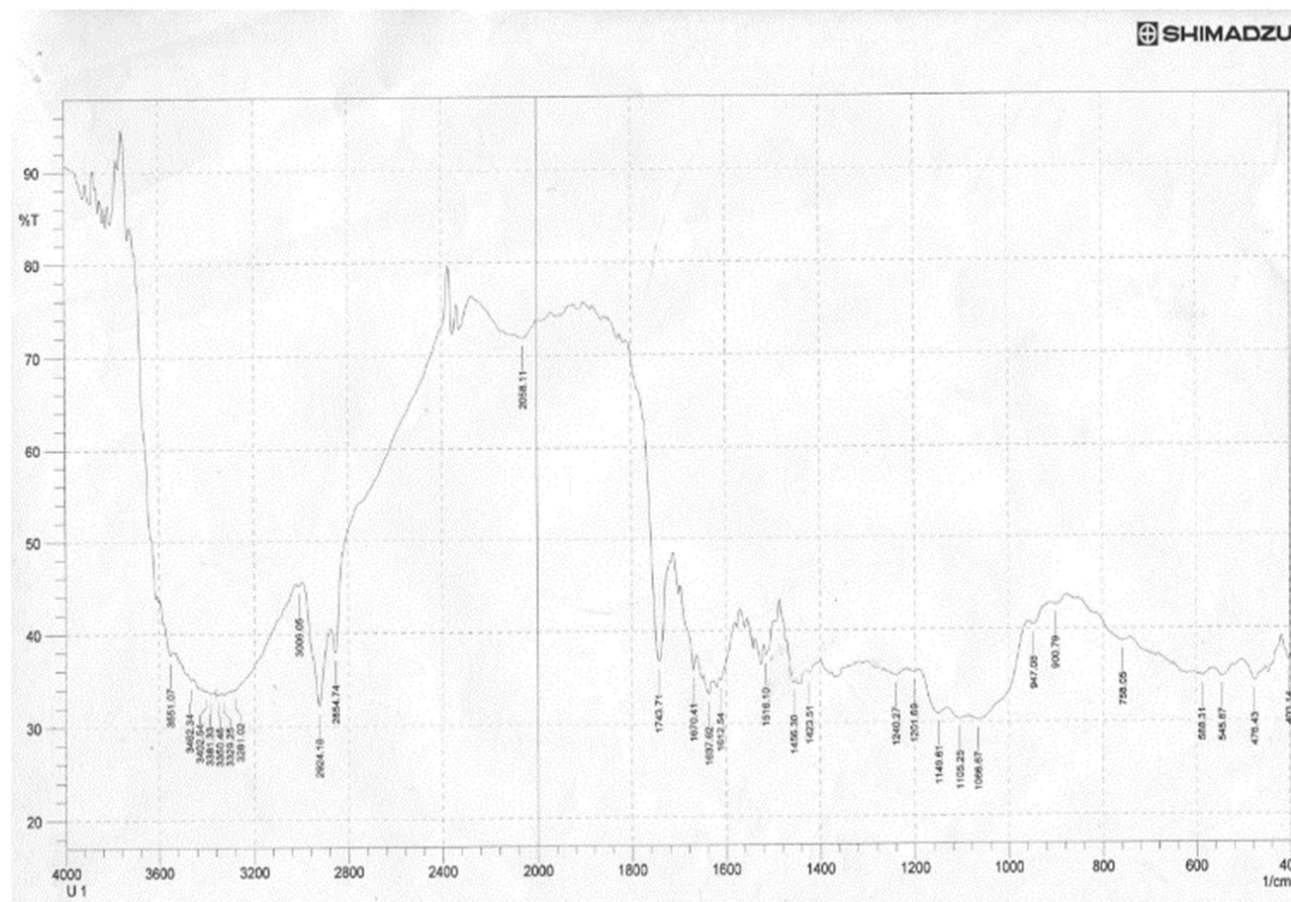

Fig. 9 FT-IR spectrum of phenol formaldehyde resin

REFERENCES

[1] R. W. Gaikwad, R S Sapkal, V. S. Sapkal, *J. Water Resource and Protection,* vol.2 2010, pp.984-989.
[2] M. Gholipour, H. H. Rafsanjani, A. S. Goharrizi, *ResJApplSci, EngTechnol*, vol.3(9), 2011, pp.880-886.
[3] G.D. Clayton, F.E. Clayton (Eds.), Patty's Industrial Hygiene and Toxicology, vol.2A 3rded., Wiley, Newyork, 1981, 2013.
[4] B. Venugopal, T.D. Luckey, Metal toxicity in Mammals,vol.2, Plenum Press, New York 1979, pp.220.
[5] S. Langard, T. Norseth, in: L. Friberg, G.F. Nordberg, V.B. Vouk (Eds), Handbook on the Toxicology of metals, Elsevier, Amsterdam, 1986, pp.20.
[6] M. Mracova, D. Jirova, H. Janci, J.Lener,Sci. TotalEnviron., part 1, 1993, pp.633-633.
[7] C.F. Wang, T.T. Miau, J.Y. Perng, S.J. Yeh, P.C. Chiang, H.T. Tsai, M.H. Yang, Analyst, vol.114, 1989, pp.1067-1067.
[8] M. Jamaluddi Ahmed, Arpan Kanti Banerjee, Analyst, Vol.120, 1989, pp.2019-2023.
[9] T. Yamshige, M. Yamaoto, H. Sunahara, Analyst, vol.114 1989, pp.1071- 1077.
[10] A.R.S. Chauhan, L.R. Kakkar, Chem.Ana, vol.39, 1994, pp.585-589.
[11] Rezaie Behrooz, A.K. Goswai, D.N. Purohit, ActaCienc. IndicChem. vol.19, 1993, pp.101-101.
[12] A.E. Arifen, J. Chem, vol.4, 1992, pp.804-811.
[13] M.J.C. Taylor, J.F. Van Staden, Analyst, vol.119, 1994, pp. 1263-1276.
[14] G. Chakrapani, D.S.R. Murty, B.K. Balaji, R. Rangaswamy, Talanta, vol.40, 1993, pp.541-544.
[15] J. Miura, Anal.chem. vol.62, 1990, pp.1424-1428.
[16] Y. Anjaneyulu, C.G. Kavipurapu, R.R. Manda, C.M. Pillutla, Anal.Chem, vol.58, 1987, pp. 1451-1451.
[17] C. Anastasia, C.G. Papadopoulos, Analyst, vol.115, 1990, pp.323-327.
[18] E. Kavlentis, Anal.Lett, vol.22, 1989, pp. 2083-2089.
[19] I. Mori, Y. Fujita, K. Fujita, T. Tanaka, Y. Nakahashi, A. Yoshu, Anal.Lett, vol.20, 1982, pp. 747-760.
[20] S.P. Bag, A.B. Chatterjee, A.K. Chakrabarti, P.R. Chakaraborty, Talanta, vol.29, 1982, pp.526-528.
[21] E. Arnold, Greenberg, S. Lenore, Clesceri, D. Andrew, Eaton (Eds), Standard Methods for the Examination of water and Wastewater, 18thed., American Public Health Association, Washington DC, vol.3, 1992, pp.98.
[22] M.L. Jackson, Soil Chemical Analysis, Prentice-Hall, Englewoodcliffs, 1965, pp.326-330.
[23] Khalili Zanjani, M.R. Yamini, Y. Shariati, S. J"onsson, J.A. Anal.Chim.Acta 2007, vol.585, 2007, pp.286-293.
[24] S. Dadfarnia, A.M. Haji Shabani, E. Kamranzadeh, Talanta, vol.79, 2009 , pp.1061-1065.
[25] S Dadfarnia, A.M .Haji Shabani, Salmanzadeh, A.M. Anal.Chim.Acta, vol.623, 2008, pp.163-167.

[26] S. Rangaraj, Y. Kim, C. K. Joo, K. Choi, J. Yi, *Korean J.ofChem.Eng*, vol.21, (2004), pp.187-194 .

[27] S. Rangaraj, J. Yeon, Y. Kim, Y. Jung, Y. Ha, W. Kim, *Journal of Hazardous Materials*, vol.143,2007, pp.469-477.

[28] K. Dermentzis, A. Christoforidis, E. Valsamidou, *International Journal of Environmental Science*, vol.1, 2011, pp.697-710.

[29] R. G. Talla, S. U. Gaikwad, S. D. Pawar, *Indian Journal of Chemical Technology*, vol.17, 2010, pp. 436-440.

[30] P. C. Mane, P. C. Bhosle, P. D. Deshmukh, C.M. Jangam, *Pelagia Research Library*, *Advances in Applied Science Research*, vol.1, 2010, pp. 22-28.

[31] M. Kragovic, A Dakovic, Z. Sekulic, M. Tgor, M. Ugrina, J. Peric, G.D. Gatta, Appl Surf Sci, vol.258, 2012, pp.3667-3673.

[32] J. Zhang, S. Xie, Y. Ho, *Journal of Hazardous Materials*, Vol.165, 2009, pp. 218-222.

[33] B. J. Brown, *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management,* vol.4, 2000, pp.82-87.

[34] E. S. Ghazy, S. M. El-Morsy, *African Journal of Biotechnology*, vol.8, 2009, pp.4140-4148.

[35] P.N. Dave, N. Pandey, H Thomas, *Indian Journal of Chemical Technology*, vol.19, 2012, pp.111-117.

[36] N. Ozturk, N. Kavak, *Journal of Hazardous Materials*, 127 2005, pp.81-88.

[37] D. Kratochvil, P. Pimentel, B. Volesky, *Environ. Sci.Technol*, vol.32, 1998, pp.2693-2698.

[38] M. X. Loukidou, K. A. Matis, A. I. Zouboulis, M. L. Kyriakidou, *Water Research*, vol.37,2003,pp. 4544-4552.

[39] S. R. Kuchekar, V. B. Gaikwad, D. V. Sonawane, S. P. Lawande, *Pelegia Research Library, Der Chemica Sinica*, Vol.2, 2011, pp. 281-287.

[40] A. G. Deviprasad, M. A. Abdullah, *BioResources*, vol.5, 2010, pp. 838-853.

[41] K. Gopalakrishnan, J. Jeyadoss, *IndJ.ChemTechnol*, Vol.18, 2011, pp. 61-66.

[42] M. Ghasemi, M. Rahimnejad, G. D. Najafpour, M. Sedighi, M. Asadi, B. Hashemiyeh, *Nigerian Society for Experimental Biology, Biokemistri*, vol.20, 2008, pp. 41-46.