

Voltametric trace determination of Vanadium ions and their removal from industrial effluents by using biosorbent

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ABSTRACT

Vanadium is extensively utilized in a variety of industries, including textiles, chemical manufacturing, metal plating, and many more. Pentavalent Vanadium is a highly toxic and carcinogenic substance when present in high concentrations. Therefore, eliminating it from industrial effluents before it can reach any water supply or land is critical. In the present research, the determination of trace V(V) by Differential pulse polarography (DPP) and its removal from industrial effluents by using *Annona squamosa* leaves as biosorbent has been analyzed. The mercury electrode is used as working electrode for DPP analysis. The reference and auxiliary electrodes were Ag/AgCl and platinum wire respectively. The biosorbent capacity of *Annona squamosa* leaves were analyzed by using different parameters like pH, concentration, contact time, biosorbent dosage, and temperature. The V(V) showed a sharp DP peak at -1.19V in presence of Ammonia-Ammonium phosphate buffer. The maximum V(V) adsorption was 8.1mg/g and 85% with respect to contact time and concerning temperature respectively. The present study concluded that the determination of V(V) by DPP are in good agreement with that of results obtained from UV-VIS technique. Further the biosorbent so prepared from *Annona squamosa* leaves is likely to be a cost-effective, economically feasible, and easily available material for removing V(V) from industrial effluents.

Key words : Vanadium, Differential pulse polarography, *Annona squamosa*, and Biosorbent.

Introduction

Industrialization has resulted in a huge increase in the emission of various pollutants into the environment. Heavy metal contamination in wastewater from industrial processes such as mining, smelting, and battery manufacture is one of the world's most critical environmental issues (Gosar, 2004). Heavy metals are one of the most dangerous sorts of pollution in water. Cu, Co, Se, V, Cr, Fe, Ni, Cd, Pb, As, Hg, Zn, and other poisonous metal ions are the most dangerous to humans and other forms of life. Because of their toxicity, bioaccumulation potential, and natural persistence, these heavy metals are of

particular concern (Wang, 2011; Jai *et al.*, 2007; Bailey *et al.*, 1999). Vanadium is abundant in the environment and plays a biological role in most living things. But the existence of Vanadium in the environment above a certain limit is toxic to human health. Vanadium is a persistent environmental pollutant that is released into the environment by numerous industries that work with alloy steel (Stasko *et al.*, 2006; Tang *et al.*, 2008; Gerke *et al.*, 2010 and Liber *et al.*, 2011). They are a serious issue in terms of environmental and human health implications due to their toxicity and build-up in the food chain. The International Agency for Research on Cancer categorized vanadium pentoxide as a probable carcino-

gen. Vanadium is currently on the USEPA's (the United States Environmental Protection Agency) Drinking Water Contaminant Candidate List (CCL3) because of its carcinogenic potential (Naem *et al.*, 2007 and Leiviska *et al.*, 2017). Vanadium concentrations in drinking water can range from 0.2 to 100 µg/l, with normal levels between 1 and 6 µg/l (Ghazvini *et al.*, 2009 and Huang *et al.*, 2015).

The detection of Vanadium ions contamination in wastewater is a critical step in protecting human and environmental health. The need for low-cost, effective methods to remove Vanadium metal ions from wastewater is critical.

Chemical precipitation, ion exchange, chemical oxidation, reduction, reverse osmosis, ultrafiltration, electrodialysis, and adsorption are some of the heavy metal removal processes used (Wang, 2011). Determination of Lanthanum in industrial samples was also achieved by DPP (Sharma *et al.*, 2015). Differential pulse polarography was employed to investigate lead and cadmium in synthetic and natural hair dyes (Majda *et al.*, 2021).

Natural biosorbents are made from living tissue and are quite inexpensive. Therefore, while choosing an adsorbent for wastewater remediation, budget analysis is a critical factor to consider. The price of the adsorption process is determined by the adsorbent's price. Commercial activated carbon, for example, costs Rs. 500/kg; however, bio sorbents cost between Rs. 4.4 to Rs. 36.89/kg, which is significantly less than commercialized adsorbents. (Gupta and Babu, 2008). For heavy metal removal, bio-adsorption techniques are widely utilized in wastewater treatment. Biosorbents have the advantages of being inexpensive, readily available, producing no sludge, being regenerated, and having technological feasibility, engineering utility, and affinity for the elimination of toxic metals.

In this study, the determination of Vanadium in the industrial wastewater was achieved by differential pulse polarography, and the results obtained were compared with UV-VIS spectroscopy. The absence of any chelating agent, simplicity, low cost, high sensitivity, sufficient selectivity, precision, and accuracy are the most significant advantages of the suggested method. Further in our investigation *Annona Squamosa* leaves powder has been studied to see if they might be used in useful ways, particularly in wastewater treatment. Their porosity nature makes them an appealing material for use as an adsorbent.

The major goal of this research was to develop a practical voltammetric technology with a straightforward approach for determining vanadium at micro levels and its removal with a cost-effective and pollution-free biosorbent.

Materials and Methods

Instrumentation

Model 174-A polarographic analyser with X-Y recorder (Model RE 0074) and drop timer (Model 174/70). Polarographic recordings were made with (EG&G, USA). The following were the instrumental settings for DPP: The working electrode was a falling mercury electrode (DME). 50 mV pulse duration, 50 mV pulse amplitude Pulse time is 57 milliseconds, and the scan rate is 0.5 seconds. 5mVsec. The reference and auxiliary electrodes were Ag/AgCl and platinum wire, respectively.

The findings of polarographic investigations with a wavelength range of 190-900 nm were compared using a UV-VIS spectrophotometer (Model, 108) from Systronics, India. The light source and detector were a tungsten-halogen deuterium lamp and a broad range photomultiplier, respectively. The resolution spectral bandwidth was 0.5 nm.

For adsorption studies weighing machine, pH meter, Jasco made FT-IR spectrophotometer were used.

Sample Preparation

Industrial effluents samples were gathered from metal and alloy industries in Jodhpur's industrial zones. To separate any suspended particle materials, these were filtered. The water samples were preconcentrated to 1/10 of their original volumes by boiling 100 ml of this aliquot to obtain detectable amounts of metals. The contents were heated until the solution fumed, removing biological and organic matrices. 1 ml of the oxidizing mixture (HNO_3 : H_2SO_4 ; 5ml: 1ml) was added, and the contents were heated until the solution fumed, removing biological and organic matrices.

For the preparation of the biosorbent *Annona Squamosa* leaves were collected from the Udaipur district of Rajasthan. The leaves were washed thoroughly to remove dirt, dried in shade, and grounded with mortar. Approx. 50 g of grounded leaves were treated with 100 ml of HNO_3 and deionized water to prepare the biosorbent.

Chemicals

All the chemicals used were of analytical grade purity. The stock solutions of vanadium were prepared from Vanadium pentoxide (V_2O_5), Batch No.- 10160, Riedel-dehaenag-Seelze-hanmover.

All the sample solutions were made in purified water obtained from Elix (Mili-CT Advantage A 10) of Millipore, SAS, France.

Biosorption studies

The adsorption experiment was carried out at various pH levels, interaction times, initial V (V) concentrations, and biosorbent dosages. Before and after V (V) uptake, the biosorbent was characterized using FTIR. The percentage of V(V) ions removed from industrial effluents were calculated by the given equation: -

$$\text{Percentage removal of V(V) ions} = \frac{C_i - C_f}{C_i} \times 100$$

C_i - initial concentration of biosorbent, C_f -Final concentration of the biosorbents.

The amount of V (V) ion absorbed by biosorbent (q_e) at equilibrium was determined using the given formula-

$$q_e = \frac{(C_i - C_f) \times V}{1000 \times w}$$

where C_i is the initial metal ion concentration (mg/L), C_f is the final concentration at equilibrium (mg/L), and w is the mass of the biosorbent (g), and V is the volume of the solution (L).

Results and Discussion

Differential pulse polarographic studies

Choice of Supporting Electrolyte

Preliminary experiments on vanadium (V) electroreduction on DME suggested that an ammonia-ammonium phosphate buffer medium might be

Table 1. Polarographic characteristics of vanadium (V)

S. No.	Supporting electrolyte	$-E_{1/2}$ (V)	I_d (μ A)
1.	1M hydrochloric acid	1.45	1.3
2.	1M sulphuric acid	0.91	0.5
3.	1M ammonia	1.35	2.4
4.	Sodium citrate buffer (pH = 8.1)	1.37	2.9
5.	Ammonium oxalate buffer (pH = 9.2)	1.79	2.6
6.	Ammonia-ammonium chloride buffer (pH = 8.4)	1.28	1.4
7.	0.5 M ammonia-ammonium acetate buffer	1.35	2.2
8.	Ammonia-ammonium phosphate buffer (pH= 3.2)	1.19	3.1

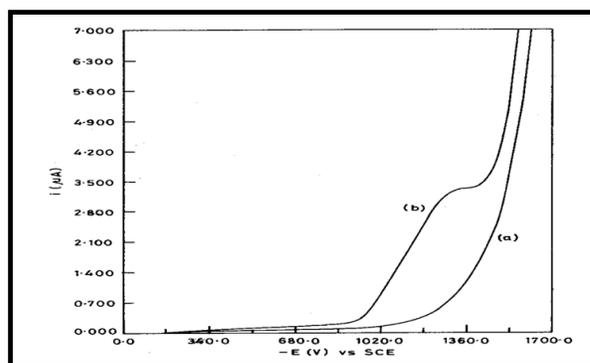


Fig. 1. DC Polarogram of vanadium (V)

- (a) Blank solution of ammonia-ammonium phosphate buffer (pH 3.2)
 (b) 1.0×10^{-5} M V (V) in ammonia-ammonium phosphate buffer (pH 3.2)

suitable. With a half-wave potential of -1.19 V, a single DC polarographic wave was obtained (Fig. 1.1). Table 1 shows the polarographic features of vanadium (V).

Vanadium (V) showed a sharp DP peak at -1.19 V in the presence of an ammonia-ammonium phosphate buffer, according to DPP experiments. Figure 2 depicts the situation. Peak current versus vanadium concentration was found to be linear between 0.008 and 35 ppm.

Figure 3 shows DP polarograms recorded at various vanadium (V) concentrations. Figure 4 shows a calibration curve.

Calibration curve characteristics:

Slope	=	0.0624
Intercept	=	0.0837
Coefficient of correlation (r)	=	1.0775

Limit of Quantification

Under these conditions, the minimum concentration of vanadium (V) that could be calculated was 0.008 g/ml.

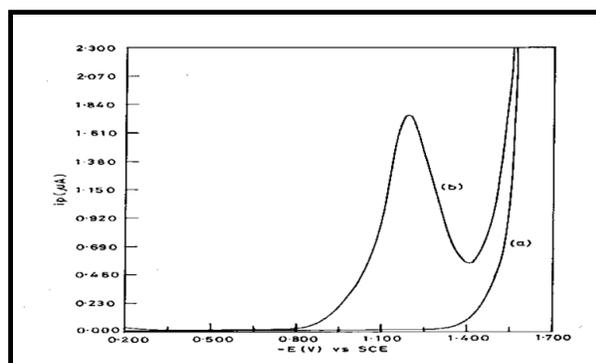


Fig. 2. DP Polarogram V (V)
 (a) Blank solution of ammonia-ammonium phosphate buffer (pH 3.3)
 (b) 24.5 ppm vanadium (V) in ammonia-ammonium phosphate buffer (pH 3.3)

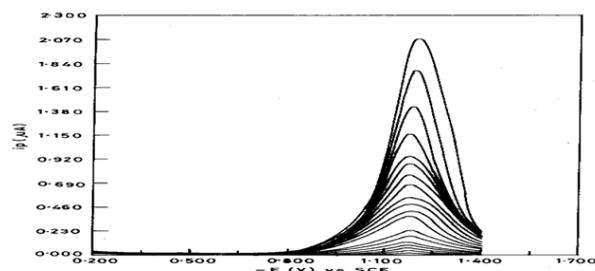


Fig. 3. DP Polarograms of vanadium (V) at different concentrations in ammonia-ammonium phosphate buffer (pH 3.3)

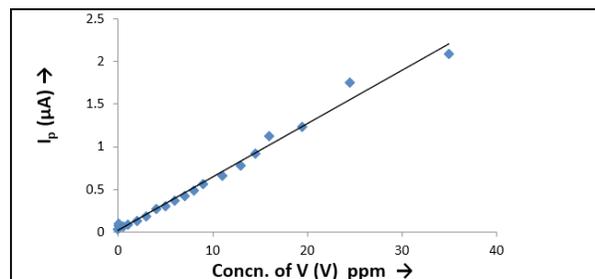


Fig. 4. Calibration curve of vanadium (V) concentration Vs. peak height

Interferences

During the DPP determination of vanadium, the interference of copper, lead, cadmium, and zinc was observed. Industrial wastewaters are more likely to contain these metal ions. In an ammonia-ammonium phosphate buffer, Cu (II), Pb (II), Cd (II), and Zn (II) produced distinct DP peaks. As a result, these metal ions had no effect. Figure 1.5 depicts the situation. Table 2 shows the peak potentials.

Table 2. Peak potential of metal ions in ammonia-ammonium phosphate buffer (pH 3.3)

S.No.	Interfering ion	-Ep (V) vs SCE
1.	Copper (II)	0.03
2.	Lead (II)	0.47
3.	Cadmium (II)	0.66
4.	Zinc (II)	1.14
5.	Vanadium (V)	1.25

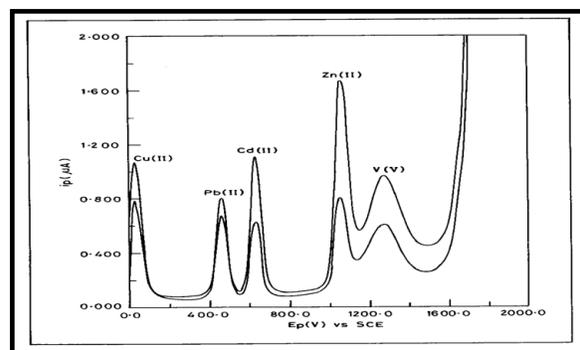


Fig. 5. DP Polarogram of V (V) in presence of Cu (II), Pb (II), Cd (II), and Zn (II) in ammonia-ammonium phosphate buffer (pH 3.3)
 Cu (II)= 11 ppm; Pb (II)= 6 ppm; Cd (II)= 8 ppm;
 Zn (II)= 11 ppm and V (V)= 16 ppm.

Precision and Accuracy

By evaluating vanadium (V) in ammonia-ammonium phosphate buffer (pH 3.3), where its concentration was preserved at 0.5 ppm, DPP observations were examined for precision and accuracy in the form of standard variance. Table 3 summarizes the findings.

Determination of Vanadium in Diverse Matrices

The vanadium concentration in industrial waste streams and dietary supplements was determined by DP polarographic reduction of vanadium (V) in ammonia-ammonium phosphate buffer (pH 3.3).

Table 3. Precision and accuracy of vanadium (V) determination by DPP

S. No.	V (V) concn. (ppm)	S.D.(±)	R.S.D.	Percent-
	Present	Determined	(%)	Error
				age
				(%)
1.	0.5	0.481	0.0077	1.578
2.	0.5	0.489		2.44
3.	0.5	0.493		
4.	0.5	0.497		
5.	0.5	0.479		

Table 4. Concentration of vanadium in industrial wastewater

Sampling sites	Vanadium content.($\mu\text{g}/\text{ml}$)			S.D.(\pm)	C.V.(%)
	Min	Max	Ave.		
Textile industry 1	1.63	1.68	1.65	0.03	1.82
Textile industry 2	1.15	1.24	1.19	0.06	5.04
Alloy industry	1.95	2.02	1.98	0.05	2.52

N = 5, Number of samples
= Jodhpur industrial area

The corresponding data were shown in Table 4 and 5.

Table 5. Concentration of vanadium in the mineral supplement

S. No.	Vanadium concentration ($\mu\text{g}/\text{ml}$)*	Ave.	S.D.(\pm)	R.S.D. (%)	Error (%)
1.	3.64	3.69	0.04	1.08	± 2.5
2.	3.71				
3.	3.69				
4.	3.73				
5.	3.66				

*cited value 3.6 $\mu\text{g}/\text{ml}$ vanadium

Comparison

To demonstrate the validity of DPP measurements, the findings of vanadium (V) determination were compared using UV-VIS spectrophotometry. Table 6 provides comparative data.

Biosorption studies of V(V) ions

Effect of pH on removal of V(V) ions

The pH value is a key component in influencing the adsorption process, as the surface charge of the adsorbents, the degree of ionization, and the species of the adsorbate are all affected by pH. The electrostatic interaction, or attraction between adsorbent and adsorbate, is the primary driving force behind

Table 6. Determination of vanadium by DPP and UV-VIS spectrophotometric method

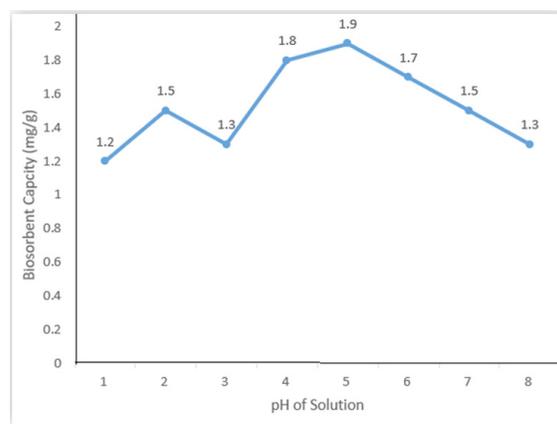
S. No.	Sample	Vanadium conc.($\mu\text{g}/\text{ml}$)	
		DPP	UV-VIS
1.	Wastewater		
	Textile industry 1	1.65	1.54
	Textile industry 2	1.19	1.13
	Alloy industry	1.98	1.86
2.	Mineral Supplement	3.69	3.59

metal ion adsorption. Heavy metal adsorption was shown to be higher when the interaction was high (Krishnaand Sreeb, 2013).

In a pH range of 1-8, the influence of pH solution was investigated using 5 ml V (V) 15 mg/l, 0.25 g biosorbent, and an interaction period of 10 minutes with a stirrer speed of 150 rpm. Figure 6 shows the outcome. With increasing pH and pressure, adsorption capacity increased from 1.2 mg/g to 1.9 mg/g. Then it reduced. Since pH affects metal ion adsorption, it's one of the most important factors to consider that directly influences metal solubility or the degree of dissociation of organic functional groups on the sorbent's membrane. Normally alkaline circumstances will reduce the rate of adsorption of metal because a higher pH produces fewer protons, which reduces the competition between proton and heavy metal ions (Homaidan *et al.*, 2014). At low pH, there is a partial increase in the metal adsorption rate due to competition between H^+ ions with metal ions for exchange sites available on the surface of the biosorbent (Khan *et al.*, 2013).

Effect of initial concentration of V (V) ions

At pH 7, the effect of V (V) concentration was tested

**Fig. 6.** Effect of pH on biosorption of V(V) by *Annona squamosa* biosorbent.

at various doses ranging from 100 to 500 mg/l and keeping the biosorbent concentration fixed. The optimum adsorption capacity of the *Annona Squamosa* biosorbent was attained at V(V) 400 mg/l with a value of 6.9 mg/g, as shown in Fig. 7. With the increase in the concentration of V(V) ions the Biosorption capacity has increased and then reduced after attaining the equilibrium. It was found that with the increase in V(V) ion concentration, V(V) adsorption by the biosorbent increases. All V(V) ions interact with the binding sites at lower concentrations, resulting in maximal adsorption at low concentrations. However, at higher concentrations, V(V) ions will seek out free binding sites available on the biosorbent, but adsorption will decrease due to a lack of binding sites for complexation. (Jevaseelaand Gupta, 2016). The percentage biosorption of V(V) ions decreases with increasing concentration after attaining equilibrium is shown in Fig. 7.

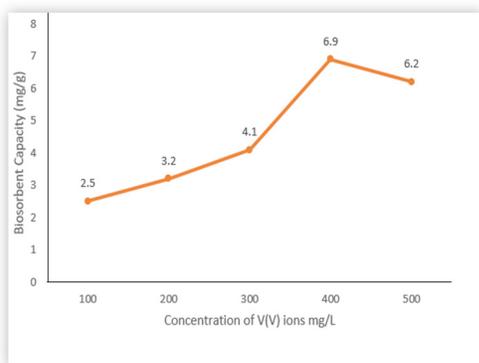


Fig. 7. Effect of initial concentration on biosorption of V(V) by *Annona squamosa* biosorbent.

Effect of biosorbent dosage on removal of V(V) ions

The amount of *Annona squamosa* biosorbent utilized in this investigation ranged between 0.2 and 1 g. Figure 8 depicts the outcome. The biosorption capacity was improved at V(V) low doses of biosorbent mass. With a biosorbent dose of 0.4 g, the optimum sorption capacity for *Annona Squamosa* L leaves powder was 6.5 mg/g. As the biosorbent dosage was increased, the sorption capacity of the biosorbent dropped. This could be explained by the fact that the lower the biosorbent concentration, the higher the metal and biosorbent ratio and the metal retained by a sorbent at a fixed concentration in suspension (Homaidan *et al.*, 2014). The absorption of metal ions increases as the concentration of biosorbent de-

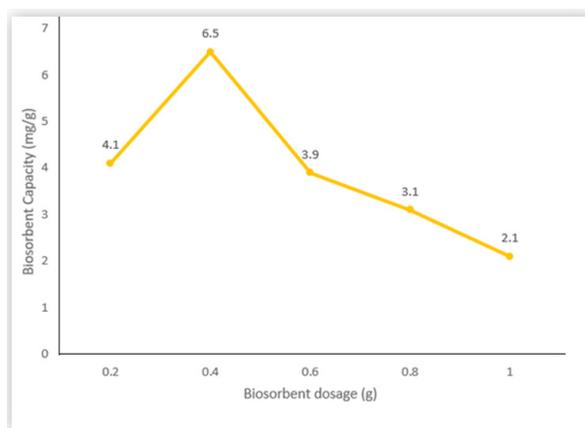


Fig. 8. Effect of biosorbent (*Annona squamosa*) dosage on biosorption of V(V).

creases (Raoand Prabhakar, 2011).

Effect of contact time on the removal of V(V) ion-

The effect of contact time on V(V) biosorption by *Annona squamosa* biosorbent was investigated with contact times ranging from 30 to 150 minutes. The maximum biosorption capacity of *Annona Squamosa* biosorbent was observed at contact time 90 min with a value of 8.1 mg/g, as shown in Fig. 9. Biosorption capacity increased for the first 90 minutes of contact time and thereafter declined. The contact time is a critical parameter for the efficient elimination of metal ions in an aqueous environment. The decrease in the coefficient of mass transfer of the diffusion-controlled reaction between the sorbent and the metal ions can explain the increased sorption of metal ions with increasing contact time. (Sayed *et al.*,2010).

There are two steps in the adsorption process. The initial stage of adsorption was fast, but the sec-

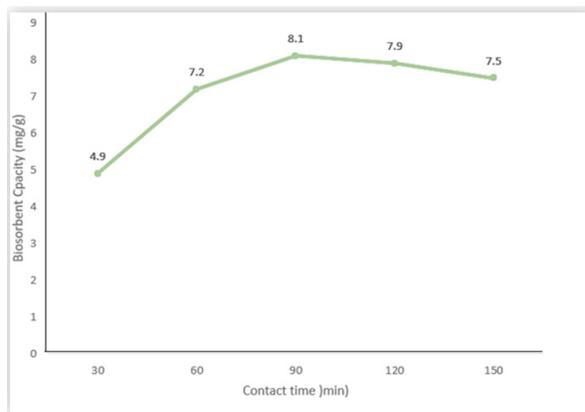


Fig. 9. Effect of contact time on the removal of V(V) by *Annona squamosa* biosorbent.

ond stage was slower. This can be explained as follows: in the beginning, a significant number of vacant sites may be present, resulting in rapid absorption; however, as the vacant sites are depleted, adsorption declines. As a result of repulsion between the solute molecules and the bulk phase (Qaiser *et al.*, 2009).

Effect of Temperature on the removal of V(V) ions

At different temperatures (25°C, 30°C, 35°C, 40°C, 45°C and 50°C), the adsorption of V(V) ions was investigated. The percentage of removal of V(V) ions increases with increasing temperature, reaching a high of 85% at 50°C given in Fig 10. The readings showed that the adsorption phenomenon is a chemisorption mechanism.

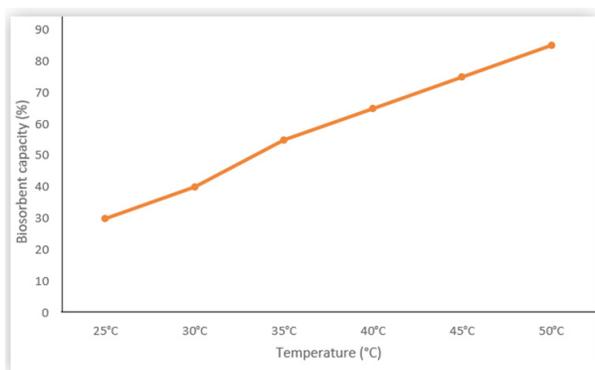


Fig. 10. Effect of temperature on the removal of V(V) by *Annona squamosa* biosorbent.

FT-IR Analysis-The FT-IR spectra of V(V) ions before and after adsorption are shown in the Fig 11. The peak shown between 3300 cm^{-1} and 3450 cm^{-1} is

of N-H stretching from -NH-OH group. The small sharp peak at 3250 cm^{-1} is due to O-H stretching also from -NH-OH group. The peak shown at 2821 cm^{-1} is due to N-H stretching in Primary amine. The shifting in the peak position in graph(a) and graph (b) clearly indicates that the adsorption takes place between V(V) ions and biosorbent so prepared from *Annona squamosa* leaves.

Conclusion

An improved analytical technique for determining vanadium at micro levels (sensitivity, 0.008 g/ml) has been created as a result of comprehensive DPP investigations. The DPP results were found to be pretty close to those obtained using the UV-VIS technique. Hopefully, the approach devised will be useful in research labs, metal companies, and pharmaceuticals for vanadium analysis. Further, the leaves of *Annona squamosa* due to their easy availability, low cost, and good adsorption capacity proved as promising biosorbents for the removal of V(V) ions from industrial wastewater. There is a need to be carried out further research to make the approach commercially viable to remove V(V) ions from industrial effluents.

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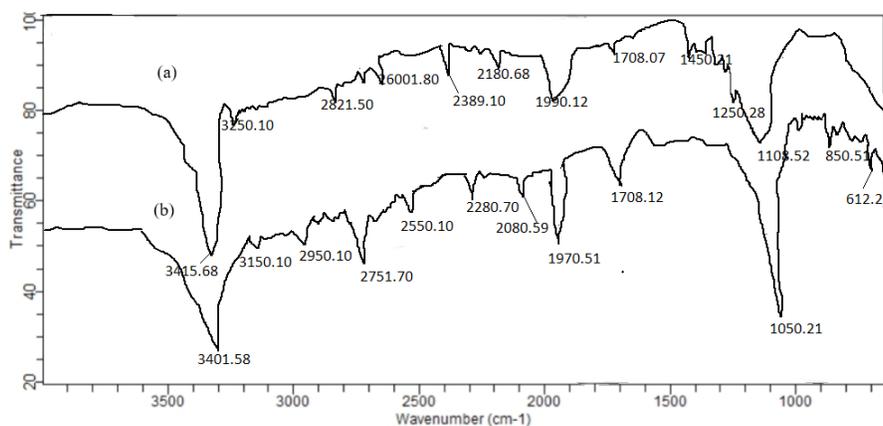


Fig. 11. FTIR spectrum of *Annona squamosa* biosorbent (a) before adsorption of V(V) ions (b) after adsorption of V(V) ions.

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