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REMOVAL OF VANADIUM BY NANO-TITANIA FABRICATED RESIN FROM AQUEOUS SOLUTIONS

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ABSTRACT

Recent years have seen a surge in interest in the development of ecologically acceptable solutions for the treatment of toxic elements such as vanadium (USEPA Contaminant Candidate List) in wastewater. The objective of this experimental work is to develop and assess the Novel Nano Titania fabricated NTD-TA62MP anion exchange resin in removing vanadium, which was doped with nano titania particles, compared with the original resin TA62MP. Batch tests were conducted by stirring 40 ml of an aqueous vanadium solution and resin for three hours at different temperatures. Characterization of the modified resin before and after adsorption was closely studied by XRD for phase analysis (nano titania: anatase), SEM and EDX for titania presence, FTIR for functional groups, and BET for the specific surface area of the adsorbent. Vanadium content was determined by ICP-OES using USEPA Method 200.7. The mechanism of NTD-TA62MP's adsorption to vanadium in water is examined, and it was determined that the NTD's hydroxyl group and the resin's quaternary amine group were responsible. At pH 6.00 to 7.00 range, the resins NTD-TA62MP, and TA62MP adsorbed most of the ions of vanadium. As the medium's temperature rises, the rate of adsorption rises as well. Vanadium's maximum sorption capacity (Langmuir value qmax) was 36.9 mg/g for TA62MP and 37.4 mg/g for NTD-TA62MP. Under comparable circumstances, the TA62MP has a lower adsorption capacity than the NTD-TA62MP. These results demonstrate that fabricating nano titanium dioxide to anion-exchange resin enhances the effectiveness in the removal of vanadium from aqueous solutions and wastewaters.

Keywords: Vanadium Adsorption, Ion Exchange Resin, Nano Titanium Dioxide, Toxic Removal.

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INTRODUCTION

Vanadium, a hazardous element produced by chemical processes, is not readily removed from the effluents hence, cost-effective and environmentally friendly methods of removing vanadium from effluents are required. If not addressed, these elements might enter the edible food and drinkable water. Some hazardous ions of metal are passed into the environment from various sectors, which has a detrimental influence on the ecosystem and hence causes pollution.[1-3] Vanadium is the main target of several regulatory authorities since it is on the list of Contaminants.[4] The Indian Std's Bureau has determined the vanadium limit, which is set to 0.20 mg L^{-1} in-ground and drinkable water.[5] In bayers process leachates, vanadium is present as V (V), which is pentavalent form and is carcinogenic to humans.[6-8] Vanadium's higher valency movement is more than other valencies in solutions hence pentavalent vanadium [V (V)] is regarded as harmful.[9,10] When exposed to vanadium ions for an extended length of time, they can induce coughing, anemia, and stomach disorders in humans.[11] Adsorption, precipitation, Anion exchange,[12,53] and improved Ultra-filtrations are some of the purification techniques for polluted wastewater,[13-17] Some of the others are reverse osmosis, bioremediation, oxidation, coagulation, membrane filtration, and electrochemical treatment,[18,19] Flakes of chitosan are utilized to extract vanadium ions out of different solvents.[4] Activated carbon has been applied for Vanadium remediation.[20] However, adsorption techniques have been used to remove heavy metals, poisonous vapors, pesticides, and other contaminants,[19, 21] but Eco-friendly and cost-efficient processes are required for toxic removal.[22,23]As Environmental compliance rises, innovative cost-efficient industrial technologies with lesser energy usage and eco-friendly processes are the key global priority. Vanadium remediation from effluents has been accomplished using a variety of materials and procedures. Vanadium removal has been accomplished using adsorbents that include metal-hydrates on nano-materials and activated carbon.[24] The capacity of palm husk which was modified to absorb vanadium was investigated[25] For various vanadium valances, an extremely anionic gel was employed for extraction from solutions of

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water.[26] Iron-slag conjugated clay was utilized to remove vanadium from a wide range of pH solutions.[27] Novel (iodomethane and triethanolamine) saw-dust was used to extract vanadium from mine water.[28] Surface modification of materials is being studied, using quaternary ammonium groups grafted onto pine bark to remove the most vanadium from a pH 4 solution.[29] Ion Exchange techniques have been studied for the elimination of vanadium.[8,30] Vanadium adsorption on biogenic amorphous ferric hydroxide in water has been studied.[31] Some eco-friendly processes have also been experimented with for toxic vanadium removal like Hydroxyapatite modified biochars.[32] Vanadium removal performance of Chlorella vulgaris from water has been demonstrated.[33] A cation-exchange resin has also demonstrated remarkable sorption of V and Ni.[34] Research on chromium removal from water by titania fabricated ion exchange adsorbent has been conducted.[35] Also separation of chromium from water has been experimentally determined by using anion exchange resin doped iron-oxide. Titania and vanadium reactions have been explored in the literature where V catalysts are supported by titanium dioxide, the solutions with the desired vanadium concentration were prepared by dipping the titanium dioxide powder (P25) in solutions of ammonium metavanadate at various amounts.[36] Efficient adsorptive vanadium removal studies on strong base anion exchange resin have been determined experimentally.[37] The current work attempted to extract vanadium from an aqueous medium employing Nano-doped, ion exchange adsorbent. TA62MP commercially available resin was doped using Nano titania solution to remove vanadium from different pH solutions. NTD-TA62MP resin was used to remove vanadium at different pH and temperature. NTD-TA62MP was subjected to batch experiments to extract vanadium from different solvents. The implication of initial vanadium content, medium pH, and contact duration was investigated. The acquired vanadium removal data was validated using Freundlich and Langmuir isotherms.

Resources and Procedures

Reagents and Chemicals of analytical grade were used in the analysis. Thermax Ltd, India, supplied the TA62MP ion exchanger in Cl form. The TA62MP structure is cross-linked with quaternary ammonium type I and has a macroporous structure. The resin was in diameter from 0.30 to 1.20 mm and contained 41.5% moisture, with an overall 0.72 m.eq./250 mg exchange capacity. After being rinsed with Millipore water, all the resins were pre-conditioned with sodium hydroxide and hydrochloric acid solutions and air-dried. The ion exchanger was doped by Nano titania and the experiments were done by Batch process in a shaker having a thermostat, with small quantities of Novel resin and original resin in 40 ml of vanadium-containing different pH solutions agitated for 3 h at 303 K. The vanadium content was determined using the USEPA Method 200.7 by ICP-OES. Eq. (1) is accustomed to checking the vanadium extraction factor.

$$\%R = \frac{C_a}{C_o} \times 100 \quad (1)$$

Where C_a and C_o denote the quantity of vanadium adsorbed on the material and during the initial solution, respectively (mg L^{-1}).

The coefficient distribution is constant. Eq. (2).

$$K_d = \frac{q_e}{C_e} \quad (2)$$

q_e and C_e reflect the concentration of ions (mg L^{-1}) adsorbed on the adsorbent and accessible in the medium.

EXPERIMENTAL

Nano Titania Doped Adsorbent Preparation

There are several methodologies for the preparation of hybrid ion exchange resins in the literature, some have been applied to remove Arsenic and Nitrate using Titania-based modified ion-exchange media. There have been studies on the removal of vanadium from solutions using Nano-Hydrous Zirconium Oxide-decorated ion exchange resin.[38,39] In the present study, the novel adsorbent was developed in situ by blending ion exchange resin with titania solutions and the mixture was heated at varied temperatures to form the nano-fabricated ion exchange resin. To make the slurry, a concentration of 0.020 - 3 Moles Nano titania was distributed in Millipore water, and 5g of resin was added to varied titania doses. This phase investigated the best method of preparation, by starting titania concentration and reaction time. The

materials were allowed to dry for 24 hours at 65°C after being treated with Millipore water to extract the unloaded titanium dioxide, and the adsorbent was stored in a vacuum desiccator for later use.

Adsorbent Characterization Techniques

Several approaches were used to investigate the different properties of TA62MP and NTD-TA62MP. The Nicolet iS5 Fourier Transform-Infrared Spectrometer was employed in analyzing the functional groups having 400 to 4000 cm^{-1} wave no. range. The Quantachrome's NOVA 4000e was used to check pore volume and SSA (specific surface area). The fabricated resin surface and the nano components were examined using an SEM (Hitachi-SU1500) with point-and-shoot method EDX for titania adherence. The size of the crystallite of titania was determined using X-ray Diffraction (XRD) analysis using the Scherrer Eq. (3).

Crystallite size, $d = \frac{k\lambda}{\beta cos\theta}$ (3)

Where λ = 0.1541 nm, k = 0.9 (Scherrer const.), Θ = Peak position (radian), β = Peaks FWHM.

Vanadium concentration was measured using an ICP-OES (PerkinElmer, Optima), using the USEPA procedure 200.7, and calibrated by Merck's Certipur ICP multi-element standard conc. 1, 2, and 5 mg L^{-1}, and samples were analyzed with intermediate quality control checks.

RESULTS AND DISCUSSION

Adsorbents Analysis

X-ray Diffraction study (Fig.-1) revealed that the size of the average crystallite of titania was computed using Scherrer eq. (3) was 19.15 nm. From Fig.-2, the adsorbent was made up of faint yellow-colored beads, whereas the titania-doped adsorbent NTD-TA62MP was white. The TA62MP preserved its spherical shape even after being decorated with titania. TA62MP (Fig.-2a-b) depicts a smooth structure, whereas NTD-TA62MP (Fig.-3c-d) had an abrasive type structure due to titanium dioxide buildup. The EDX data of NTD-TA62MP is depicted in Fig.-4. TA62MP was discovered to contain C and Cl elements, which is related to the adsorbent composition having exchangeable ions. Furthermore, the Ti element was discovered in the NTD-TA62MP elemental composition, Titania as shown by this result, it was effectively loaded on the ion exchange adsorbent. The Fourier Transform-Infrared Spectroscopy of the adsorbent before titanium dioxide loading and after, depictions seen in Fig.-5. "Here hydroxyl group's O-H stretching vibration is at 3428 cm^{-1} in the Fourier Transform-Infrared spectra of ion exchange adsorbent" (Fig.-5a).[40,41]In anion exchange resin C-H stretching can be observed by three peaks at 3015, 2924, and 2824 cm^{-1} showing a polystyrene divinylbenzene structure.[42]At 1481 cm^{-1}, the adsorbents functional group quaternary ammonium exhibits CH_2 bending.[43] The peak pattern of NTD-TA62MP is identical to that of anion exchange resin, depicted in Fig.-5b. "However, titanium dioxide on adsorbent was readily apparent by broadband near 600.0 to 800.0 cm^{-1}, corresponding to the Ti-O-Ti stretching".[44] As titanium dioxide particles have a high surface-to-mass ratio, the NTD-TA62MPanalyzed had greater SSA of 24.59 m^2/g than TA62MP at 21.68 m^2/g, as demonstrated from data (Table-1). NTD-TA62MP has a slightly reduced pore volume than TA62MP, this observation might be attributed to pore obstruction caused by titania doping, resulting in lower adsorbent porosity. After vanadium adsorption on the resin, the FTIR band spectrum at 1119 cm^{-1} which is of V=O bonds, confirms Vanadium adsorption onto the resin matrix (Fig.-6).

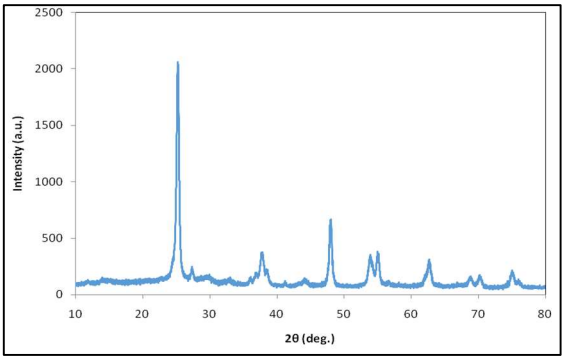

Fig.-1: XRD of Titania Nanopowder: Anatase

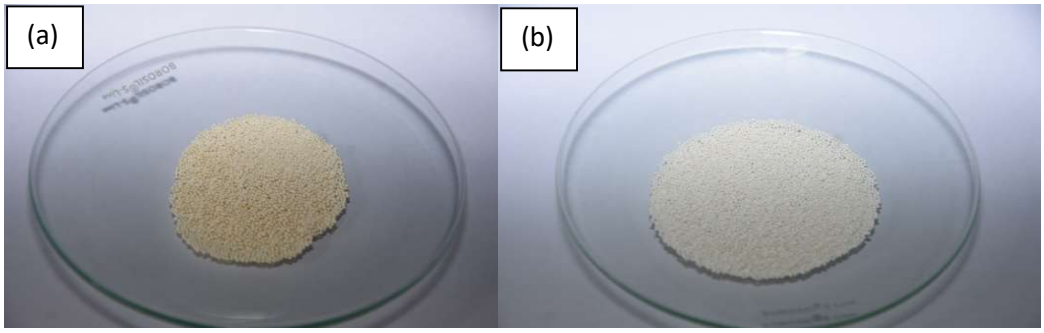

Fig.-2: Images of (a) TA62MP (b) NTD-TA62MP

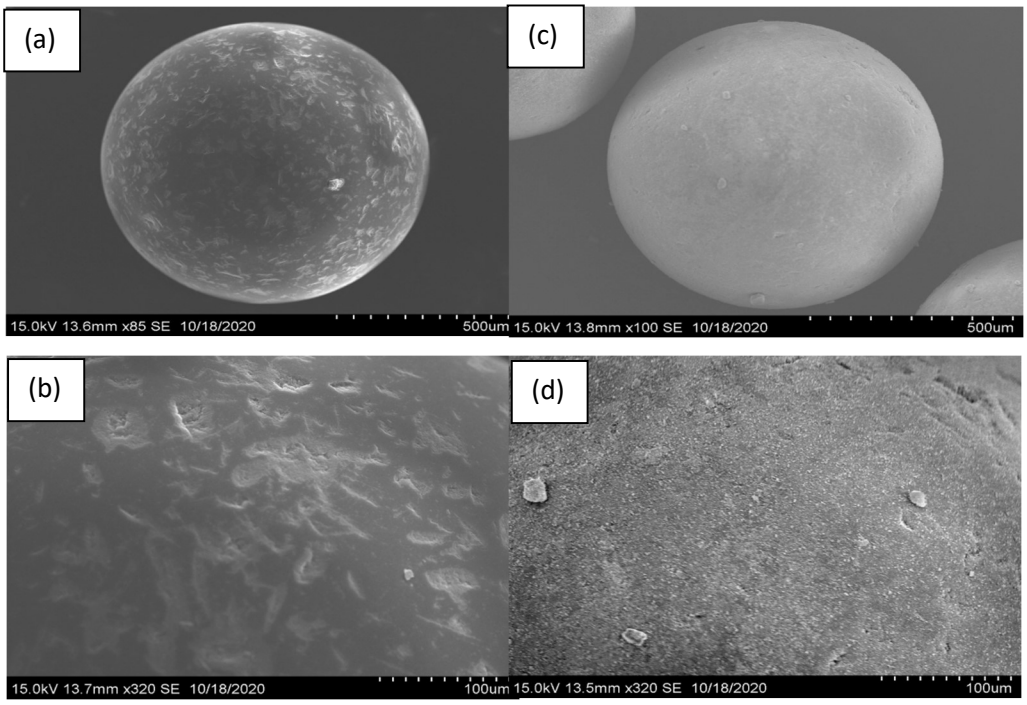

Fig.-3: Scanning Electron Microscope Images of (a-b) TA62MP and (c-d) NTD-TA62MP

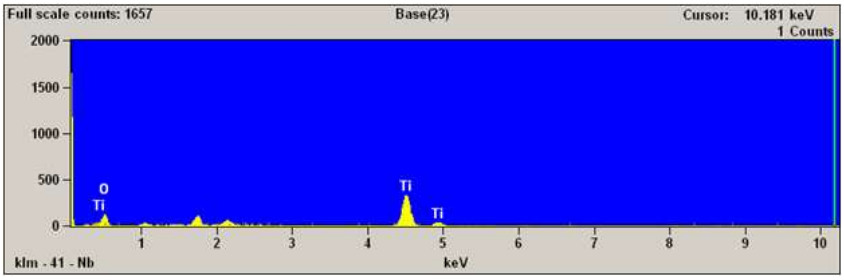

Fig.-4: Energy Dispersive X-ray Analysis of NTD-TA62MP

The pH Effect

The greatest uptake capacity of TA62MP and NTD-TA62MP may be found by varying the medium's pH. Vanadium sorption by TA62MP and NTD-TA62MP was studied at pH values 1 to 12, with temperature, contact duration, starting concentration (50 mg L^{-1}), and resin dose held constant. According to Fig.-8, NTD-TA62MPwas seen to have better adsorption capability than TA62MP, the percent removal of vanadium for TA62MP was 95.7%, while that of NTD-TA62MP was 98.1%, which was maximum in the pH range of 6.0 to 7.0. The elimination was greatest at this pH because of the amine group protonation's ability to maintain a stable acidic pH.

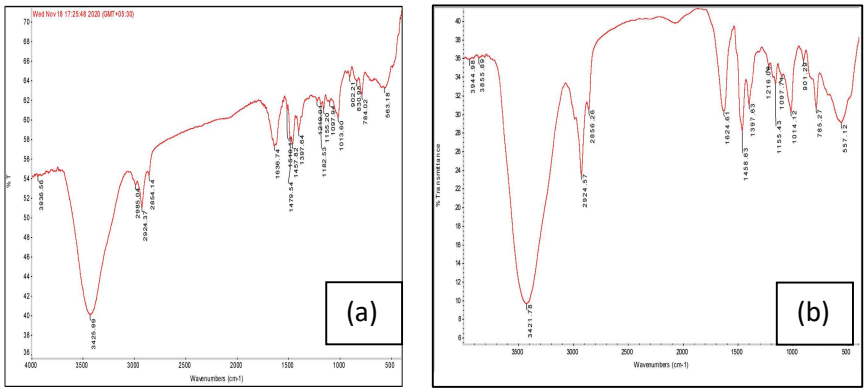

Fig.-5: Fourier Transform Infrared Spectra of (a) TA62MP (b) NTD-TA62MP

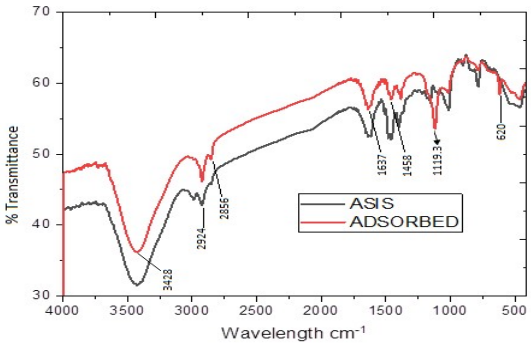

Fig.-6: FTIR scan of Resin before (--) and after (--) Vanadium Adsorption

Table-1: Surface Parameters

Resins	SSA by NOVA-BET	Pore vol.
TA62MP	21.84m^2/g	0.0150cm^3/g
NTD-TA62MP	24.59m^2/g	0.0116cm^3/g

Fig.-7: NTD-TA62MP Adsorbents Mechanism

In the pH range 6-7, the mechanism may be described by Eq. (4), where RA denotes TA62MP and NTD-TA62MP in the anionic form:

$$HV_{10}O_{28}^{5-} + 5RA \Leftrightarrow R_5HV_{10}O_{28} + 5A^- \quad (4)$$

The vanadium percent removal is maximum at 6-7 pH due to the presence of $HV_{10}O_{28}^{5-}$, showing the Anions presence on the surface of TA62MP and NTD-TA62MP, as stated in Eq. (4). At pH levels below 4.0, the removal percentage reduces fast due to the generation of V^{3+}, HVO^{2+}, and VO^{2+}.[4] Vanadium's stable oxidation states are V^{+3}, $V^{+4,}$ and V^{+5}. Under oxic circumstances, the most prevalent oxidation state V^{+5}, has better solubility. TA62MP and NTD-TA62MP had lesser vanadium removal at lower pH because vanadium VO^{2+} is predominant at low pH (Fig.-9) and adsorbents are unable to extract cations. At lower pH levels, less adsorption takes place as hydrogen ions compete for the adsorption sites.[40,45]

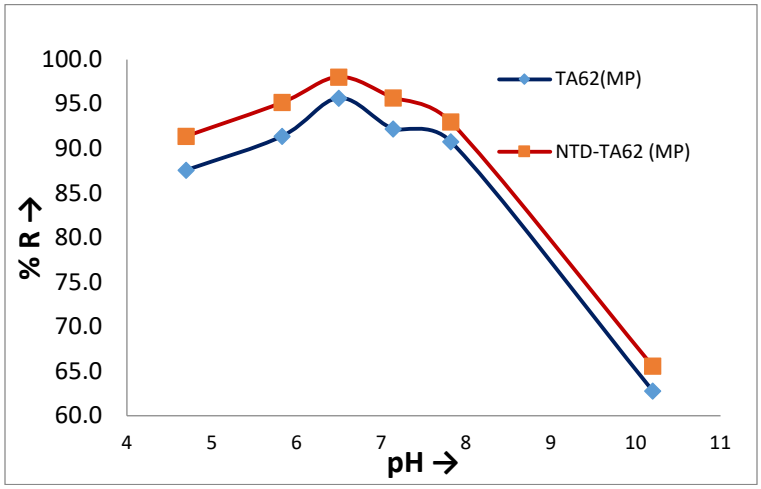

Fig.-8: Vanadium Removal at Different pH by TA62MP &NTD-TA62MP

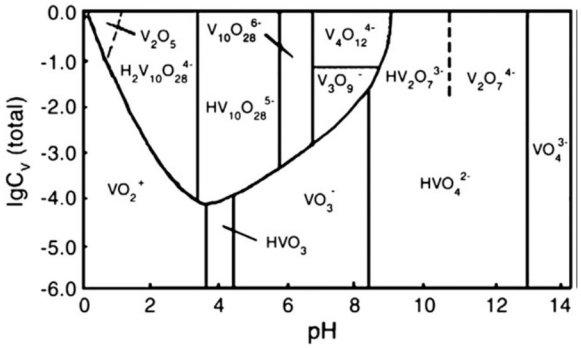

Fig.-9: Speciation of Vanadium[33]

Under particular pH conditions (Fig.-9), the vanadium removal mechanism (Fig.-7) by surface-activated adsorbents may be described by the equations in Table-2.

Table-2: Vanadium Adsorption Possible Reaction Equations

Reaction equations	pH Range
$HVO_4^{2-} + 2RCl \Leftrightarrow R_2HVO_4 + 2Cl^-$	11-12
$V_{10}O_{28}^{6-} + 6RCl \Leftrightarrow R_6V_{10}O_{28} + 6Cl^-$	7.2-8.2
$HV_{10}O_{28}^{5-} + 5RCl \Leftrightarrow R_5HV_{10}O_{28} + 5Cl^-$	5.5-7.2
$H_2V_{10}O_{28}^{4-} + 4RCl \Leftrightarrow R_4H_2V_{10}O_{28} + 4Cl^-$	2.5-5.5

Impact of Interaction Time

Vanadium adsorption kinetics on TA62MP and NTD-TA62MP are examined in a batch approach using 0.10 g resin beads in 40 ml of aqueous vanadium solutions. The quantity of vanadium present after the test was analyzed regularly using ICP-OES. As seen in Fig.-10, vanadium sorption increases with increasing equilibration period and decreasing vanadium concentration in solution. TA62MP and NTD-TA62MP are capable of removing about 91.3 & 93.9% of the vanadium in 90 minutes, respectively, demonstrating vanadium acquiring a monolayer on the adsorbent surface.[46] Vanadium removal is also initially swift as a large number of sorption places are available on the polymer. After attaining equilibrium, raising the interaction time had very little effect on the sorption of vanadium as saturation of bonding sites on the adsorbent.

Resin Dose Effects

TA62MP and NTD-TA62MP equilibrium capacities experiments were performed at 6.5 pH using a conc. of 50 mg L^{-1} and altering the number of adsorbents ranging from 0.020-0.140 g as shown in Fig.-11. The

resin dose required for optimal vanadium absorption is 0.1 g, over 0.1 g removal efficiency is less.[42,47]Given that particular areas of adsorption are left unfilled throughout the sorption stage, it is reasonable to deduce that increasing the adsorbent dose increases removal efficiency while lowering adsorption density. According to experiments, the elimination of vanadium increases with resin content because there are more accessible sites.

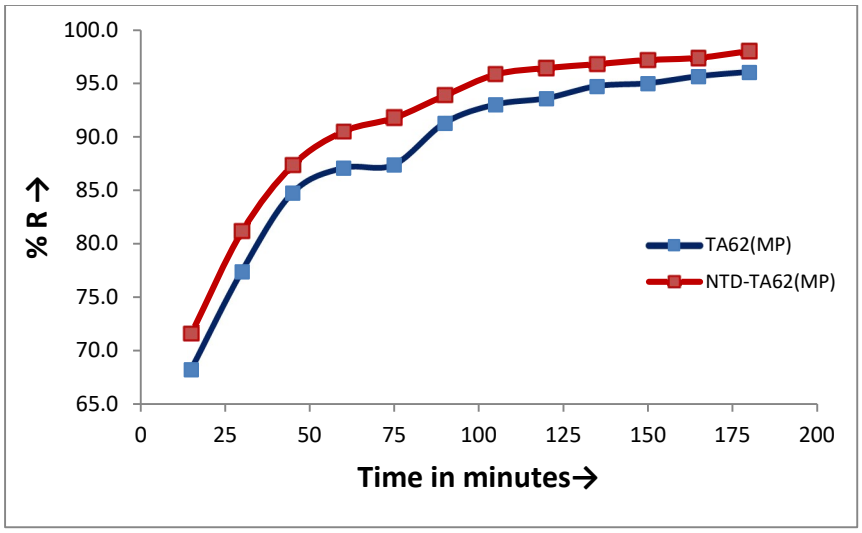

Fig.-10: Time of Interactivity's Impact on the Absorption of Vanadium by TA62MP &NTD-TA62MP

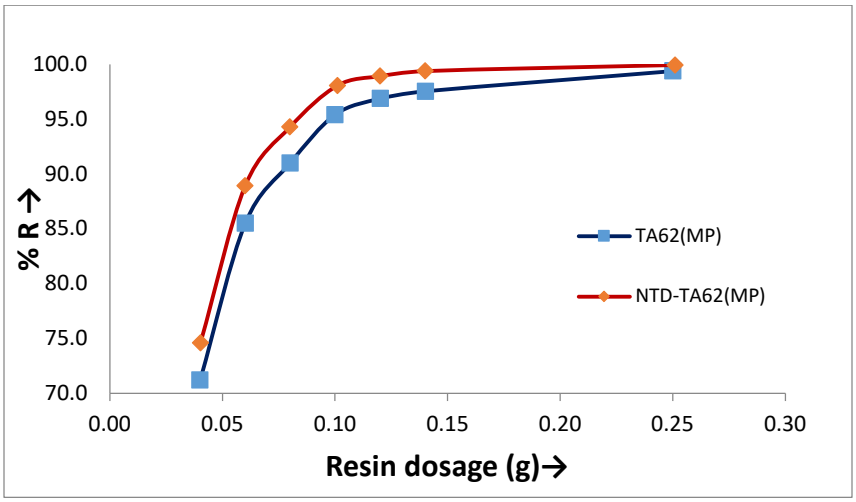

Fig.-11: Different Resin Weight's Impact on Sorption of Vanadium by TA62MP &NTD-TA62MP

Different Vanadium Concentrations and their Impact

Effect of initial vanadium conc. on TA62MP and NTD-TA62MP in vanadium removal is being investigated. As seen in Fig.-12 vanadium solution concentrations ranged from 30 to 100 mg L^{-1}. The extraction of vanadium diminishes as the beginning adsorbate concentration in the solution rises at an unchanged temperature of 303K. This is because adsorbent begins with the highest number of adsorption sites available, and as the vanadium ion concentration increases, the resin sites are filled with vanadium ions, and the quantity of vanadium that is absorbed is reduced as a result.

Modeling of Adsorption Isotherms for Study

A sorption study is essential in forecasting how adsorbate ions will be distributed between a solid and a solution. Freundlich and Langmuir isotherms may be used to illustrate the metal adsorption by various adsorbents.[48,49] Further down, Broad explanations of the models are provided. The following are the details of the Langmuir isotherm model:

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L q_m}\right) + \frac{C_e}{q_m} \quad (5)$$

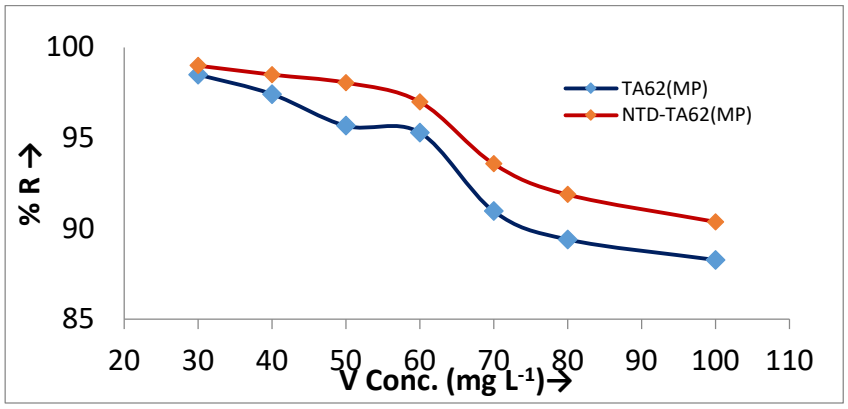

Fig.-12: Initial Concentration's Effects on Elimination of Vanadium by TA62MP&NTD-TA62MP

The parameters K_L and q_m denote energy of adsorption and capacity of ion exchange respectively, whereas C_e and q_e reflect metal ion concentrations in the preliminary and equilibrium environments. Here the linear curvature depicted the sorption process of TA62MP and NTD-TA62MP, which follows the Langmuir isotherm (Fig.-13). The surface of resins exhibits monolayer homogeneous sorption having similar energy of activation, according to this isotherm. Table-3 displays the results of the research.
A linear eq. that illustrates a surface heterogeneous system is the Freundlich adsorption isotherm model (6).

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (6)$$

Here q_e is the equilibrium sorption capacity and C_e is the equilibrium ion conc. Figure-14 shows the curve of $\log q_e$ vs. $\log C_e$, which produces the constants n and KF. TA62MP and NTD-TA62MP adsorption capacity increases as KF increases. This revealed that the equilibrium data followed both the Freundlich and Langmuir models, as indicated in Table-3. As a result ($0 < RL=0.99< 1$), vanadium adsorption on TA62MP and NTD-TA62MP was favorable.[50] Because the Freundlich-Langmuir isotherm is combined with the Redlich-Peterson isotherm, the process of sorption is a mixture of the two and does not follow ideal monolayer sorption. The linear version of the R-P equation is as follows.

$$\ln\frac{C_e}{q_e} = \beta \ln C_e - \ln A \quad (7)$$

Here A (L/g) is the Redlich-Peterson isotherm's constant factor, and the exponent β is a value between 0 and 1.

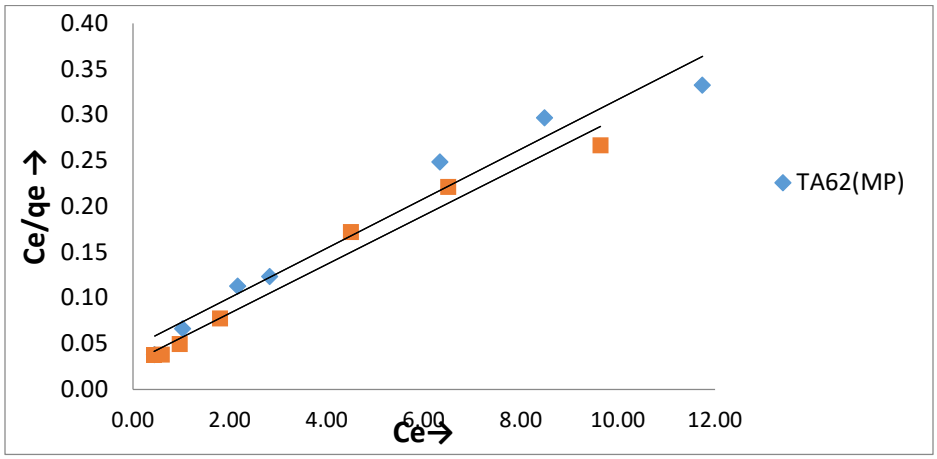

Fig.-13: Langmuir Isotherm for Vanadium Adsorption byTA62MP&NTD-TA62MP

Table-3: Adsorption Isotherms

Resin	Freundlich Isotherm			Langmuir Isotherm				Redlich-Peterson Isotherm		
	K_F (L/mg)	n	R^2	K_L (L/g)	A_s(mg/ g)	R^2	R_L	β	A(L/g)	R^2
TA62MP	15.3	3.20	0.980	0.59	36.9	0.964	0.266	0.704	0.015	0.9964
NTD-TA62MP	17.7	3.28	0.937	0.90	37.4	0.976	0.242	0.703	0.018	0.9817

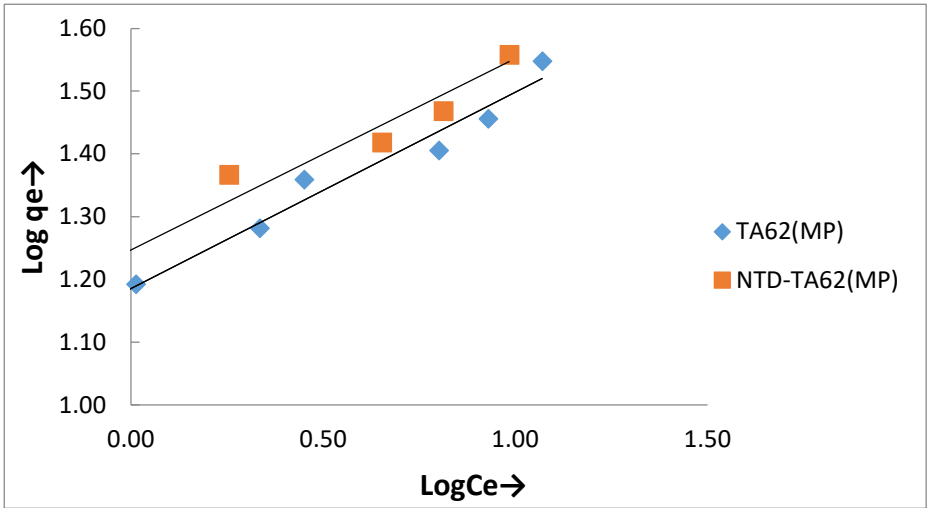

Fig.-14: Freundlich Isotherm, Vanadium Sorption byTA62MP&NTD-TA62MP

Thermodynamic Parameters

The formulas below were used to generate thermodynamic quantifiable values such as Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) from the temperature influence on vanadium sorption using TA62MP and NTD-TA62MP.[51-52]

$$\mathrm{InKd} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{8}$$

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

$$\mathrm{Kd} = \frac{Cs}{Ce} \tag{10}$$

Vanadium's equilibrium concentration in aqueous media is measured by Ce (mg L^{-1}), whereas the equilibrium concentration of vanadium adsorbed on the resin surface is measured by Cs (mg L^{-1}). The intercept-slope of the $\ln K_d$ vs. 1/T plots is taken to calculate enthalpy and entropy values. Table-4 displays the thermodynamic characteristics ofTA62MP and NTD-TA62MP. Negative ΔG values indicate that adsorption occurs spontaneously. ΔH positivity demonstrated the process to be endothermic, with more heat seeming more acceptable. ΔS positivity indicated higher uncertainty throughout the adsorption process across the liquid-solid interface.

Table-4: Parameters of Thermodynamics in the Adsorption of Vanadium Through TA62MP and NTD A-62(MP)

Resin	*T* K	lnK_d	ΔG^0 kJ mol^{-1}	ΔH^0 kJ mol^{-1}	ΔS^0 kJ $mol^{-1}K^{-1}$
TA62MP	303	3.20	-8.00	28.31	0.120
	313	3.48	-9.20		
	323	3.90	-10.40		
NTD TA-62(MP)	303	3.58	-8.9569	34.87	0.145
	313	3.95	-10.4034		
	323	4.44	-11.8500		

CONCLUSION

The surface-activated Nano titania doped Anion exchange resin NTD-TA62MP has been discovered to be a competent nanoparticle-modified polymeric compound capable of removing vanadium from contaminated water. In the pH range of 6.0 to 7.0, the resins TA62MP and NTD-TA62MP adsorbed most of the vanadium ions. As the dosage of the NTD-TA62MP modified resin was increased to 0.25g, 99.99% of vanadium was removed from the 50 mg L^{-1} Vanadium solution. The kinetics of vanadium sorption are analyzed by the amount of resin and the vanadium concentration. The sorption of vanadium increased with the increased period of agitation, reaching equilibrium after 180 minutes. From the equilibrium data, the Freundlich constant was found to be 3.28 (n) for NTD-TA62MP and 3.20 for TA62MP, which indicates better interactions between vanadium ions and the resins. The found value of the R_L between 0 and 1 (separation factor) suggests favorable vanadium sorption. Under optimum circumstances, the NTD-TA62MP has a much higher sorption capacity than TA62MP, hence the novel titania doped resin can be used to successfully extract vanadium from solutions of water.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

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Abbreviations

TA62MP: Tulsion A62(Macroporous)
NTD-TA62MP : Nano titania doped Tulsion A62(Macro porous)
Q_o: Langmuir's const. (mg g^{-1})
C_o: Resins starting conc. (mg L^{-1})
C_e: Resins conc. at eq-time (mg L^{-1})
EDX: Energy-dispersive x-rays
SSA: m^2 g^{-1} surface area
R_L: Equilibrium parameter

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