

# Magnetic Zeolite-Polymer Composite as an Adsorbent for the Remediation of Wastewaters Containing Vanadium

Nomcebo H. Mthombeni, Sandrine Mbakop, and Maurice S. Onyango

**Abstract**—Magnetic natural zeolite-polypyrrole composite was prepared for removal of vanadium from aqueous solution. The effects of initial pH, sorbent dosage, adsorption isotherms on removal efficiency were investigated. Up to 75% removal efficiency was obtained when the pH was 5 and the initial vanadium concentration was 100 mg/L. The isotherm data fitted well to the Langmuir isotherm model. The maximum adsorption capacity determined from the Langmuir isotherm was 57.803 mg/g at 25 °C.

**Index Terms**—Vanadium, magnetic, zeolite, adsorption.

## I. INTRODUCTION

The presence of heavy metals ions in water bodies is becoming a serious threat to public health and the environment. Of these heavy metals, vanadium has recently received more attention because of its adverse effect on human health and the environment. At high concentration vanadium is an environmentally harmful substance and causes diverse toxic effects on humans such as anaemia, cough, emaciation, and irritation of mucous membrane, gastrointestinal disturbances, and bronchopneumonia [1], [2].

Treatment processes for vanadium contaminated waste streams include chemical precipitation, filtration, ion exchange [3], reverse osmosis, solvent extraction [4] electro-deposition adsorption and biological methods [5] among others. Due to limitations in terms of equipment cost and space requirement, incomplete metals removal, massive waste generation and high reagent consumption of some of these methods, adsorption is the most commonly used technique in industries where large volumes of waste effluents are generated. Adsorption is a simple, low-cost, rapid, versatile and non-hazardous purification method that facilitates the recovery of treated metals for reuse [6].

Since the choice of the sorbent material for any adsorption process is important and depends on its cost, availability and suitability to remove the given pollutant; scattered studies have been conducted for the past years to develop adsorbents mainly from several agricultural and industrial waste materials with the dual aim of low cost as well as

effectiveness for adsorption process optimization [5].

Materials such as ZnCl<sub>2</sub> active carbon [7], alumina, metal sludge [8], goethite [9], hydrotalcite [10] crystalline hydroxyl apatite, amine-functionalized - grafted tamarind fruits hull [2], chitosan [6], [11], persimmon tannin gel [12] and metal hydroxide [1] have been used as adsorbents for removal of vanadium (V) from aqueous solution. Because of its sorption capacity for numerous pollutants, its abundance and relatively low cost; clinoptilolite has been recognized as an efficient adsorbent for a large number of water treatment applications including removal of heavy metals from industrial wastewaters. However the diffusion restrictions (specially within macromolecules) causing low sorption capacity and kinetics, the difficulties of separation from wastewater or the generation of secondary wastes, the high cost and limited active surface sites of these conventional adsorbents represent a major drawback to this separation technology. Therefore it is important to develop novel material that will overcome these limitations.

Nanotechnology has been regarded as a powerful platform for the 21st century technologies. The application of nanoadsorbents in wastewaters treatment has gained interest in recent years. Due to their high their exceptionally large surface area, active sites and short diffusion length resulting in high sorption capacity and fast kinetics nanomaterials provide the opportunity to solve several environmental issues including water quality [13]. Among existing nanoadsorbents, magnetic nanocomposites have been extensively investigated and have been reported to offer optimum adsorption processes. This is because; unlike traditional nanoadsorbents they are easily separated and recovered from aqueous solutions [14].

Magnetic nanocomposites are often composed of magnetic nanoparticles dispersed in a polymer matrix including natural and synthetic polymers. Recently polypyrrole has increasingly received more attention due to its relatively good environmental stability, low-cost, ease of preparation and nontoxicity which are favorable for various types of applications. Different studies have revealed the effectiveness of adsorptive removal of heavy metal ions using magnetite-polypyrrole nanocomposite as sorbent media [15].

This study seeks to synthesize magnetic zeolite-polypyrrole and assess its application in adsorptive of vanadium from synthetic wastewater. There is very limited research on the application of nano-scale sorbents to remove vanadium from aqueous solutions. Moreover, there is rarely any information on the application of this technique in South Africa. Consequently in this work a technique combining adsorption and nanotechnology is proposed in order to provide an alternative technology for improved removal of

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vanadium from wastewaters.

## II. MATERIALS AND METHOD

### A. Synthesis of an Adsorbent

Magnetic zeolite was prepared by chemical co-precipitation of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  ions at a ratio of 2:1 in the presence of zeolite [12]. The  $\text{Fe}^{3+}/\text{Fe}^{2+}$  solution was added drop wise to the vigorously stirred mixture of zeolite and sodium hydroxide maintained at 95 °C under  $\text{N}_2$  atmosphere. This generated the formation of a black precipitate of magnetic zeolite. The reaction was carried out for an additional hour under the nitrogen environment. The obtained magnetic zeolite powder was washed repeatedly with deionized water until a neutral pH was attained. Then resulting magnetic zeolite was dried under vacuum for 12 hours.

Magnetic zeolite polypyrrole nanocomposite was synthesized using *in situ* chemical oxidative polymerization method [8]. A known amount of magnetic zeolite powder was dispersed by adding 80 mL of deionized water and the mixture was placed under ultrasonication for 20 minutes. Pyrrole monomer was syringed into the mixture then hand shaken thoroughly for 5 minutes. The polymerisation process was facilitated by adding 6 g of anhydrous ferric chloride to the mixture while shaking therefore, forming a pitch black precipitate of magnetic zeolite-polypyrrole nanocomposite. The mixture was shaken for 3 h at room temperature to allow the polymerization to go into completion. Afterwards, the precipitated magnetic zeolite polypyrrole nanocomposite was vacuum filtered and thoroughly rinsed with distilled water and acetone to sterilize the material and stop the polymerization process. The synthesized powder was dried at 80°C for 6 hours.

### B. Batch Adsorption Studies

Adsorption performance of the synthesized magnetic zeolite-polypyrrole composite was studied by batch technique. Initially, the optimum pH for the adsorption of vanadium onto the nanocomposite was determined by studying the effect of solution pH on the process. The initial pH was adjusted from 2 to 10 by using either 0.1 M of hydrochloric acid or 0.1 M of sodium hydroxide; then 0.1 g of magnetic zeolite-polypyrrole nanocomposite was added to 100 mL sample bottles containing 50 mL solution of vanadium with a concentration of 100 ppm. The bottles were placed in a thermostatic shaker 24 hours. The samples were analyzed by Inductively Couple Plasma- Emission Spectroscopy (ICP-OES) to determine the residual vanadium concentration. Once the solution pH for optimum adsorption was determined; the synthetic vanadium aqueous solution pH was adjusted to this optimum value and the above procedure was repeated to evaluate the effect of the remaining parameters. The effect of adsorbent mass on the amount of vanadium removed was explored by varying the mass of the sorbent material from 0.01 to 0.2 g whereas the effect of initial ion concentration was assessed by varying the concentration of vanadium aqueous solution from 100 ppm to 800 ppm. Finally the adsorption isotherm was explored using vanadium solutions of concentrations ranging from 100 ppm to 800 ppm at temperature of 25 °C. The percentage removal

of vanadium was calculated using the formula:

$$\% \text{ removal} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

where  $C_o$  (mg/L) is the initial vanadium concentration and  $C_e$  (mg/L) is the concentration of vanadium at equilibrium.

## III. RESULTS

### A. Effect of pH

The initial pH of the solution is one of the most significant parameters in adsorption experiments. The initial solution pH ranged from 2-8 for an initial concentration of 100 ppm at a temperature of 298K. Fig. 1 shows the sorption ability of the composite at different pH values. From the plot, the results shows that vanadium removal is pH-dependent and that maximum removal occurs between at pH 4-5.

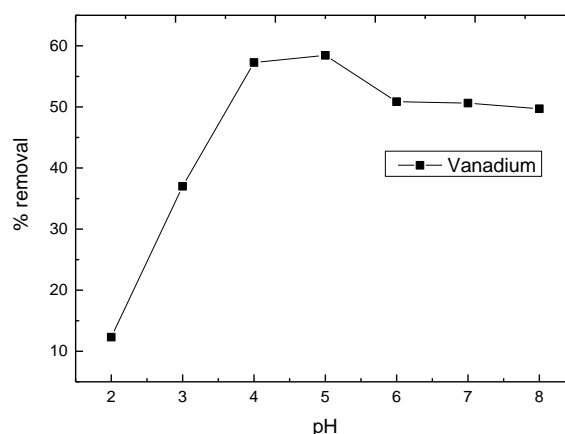


Fig. 1. Effect of initial solution pH on vanadium adsorption onto magnetic zeolite polypyrrole (Temp. 298K, initial conc.100 ppm, sorbent mass 0.1 g, duration 24h).

The adsorption effectiveness different initial solution pH of V(V) is greatly related to the speciation of V(V) in aqueous solution as well as the surface characteristics of the composite. The decrease removal efficiencies below pH 3.0 might be due to the existence of  $\text{VO}_2^+$  ion, which experiences electrostatic repulsion from the protonated amino groups of the adsorbent [2], [6]. The composite and sorbate properties could be used to understand these observations. By increasing the solution pH, the magnetite surface was deprotonated and its exchange capacity increased [16]. The decrease of amount of vanadium removed between the pH range of 6-9 could be explain by the polymerization ability of vanadium at various pH. Crans [17] reported that vanadium forms polymeric species on a variation of pH. The presence of polymeric species could limit the removal efficiency of vanadium species even at optimum pH especially when high concentration of vanadium is involved. Moreover, the chemistry of vanadium (V) in aqueous solution is complex [18].

### B. Effect of Adsorbent Mass

The effect of sorbent mass on the remediation efficiency of the synthetic vanadium aqueous solution was explored at temperature 298K, with sorbent dose between 0.025-0.2 g and an initial pH of 5. Fig. 2 illustrates the effect of adsorbent

mass on vanadium removal efficiency. The optimum adsorbent dosage was found to be at 0.15 g. The amount of vanadium adsorbed increases with increasing sorbent dosage. This could be the result of more available active sites for vanadium sorption which directly proportional to the adsorbent mass.

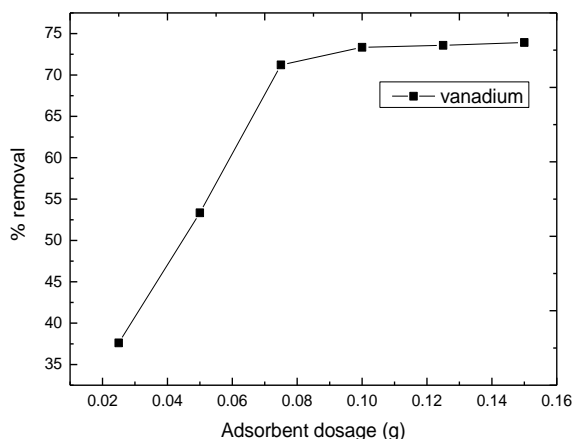


Fig. 2. Effect of adsorbent dosage on vanadium Adsorption (Temp. 298K, initial Conc. 100 ppm, pH 5 and duration 24h).

### C. Adsorption Isotherms

The equilibrium data obtained from sorption experiments were analyzed using various isotherms in order to find a suitable model capable of describing the interaction between adsorbate and adsorbent for effective design of an adsorption process. The Langmuir and Freundlich adsorption isotherms equation were used. Furthermore the linear regression method was employed to fit these experimental data and to describe the model that fits best [19].

### D. Freundlich Isotherm

The Freundlich isotherm assumes heterogeneous surface with a non-uniform distribution of heat on adsorption. The Freundlich isotherm is characterised by the following equation:

$$q_e = K_F \times C_e^{1/n} \quad (2)$$

where  $q_e$  is the equilibrium solid phase concentration (mg/g),  $C_e$  is the equilibrium liquid phase concentration (mg/L),  $K_F$  and  $n$  are indicative isotherm parameters of adsorption capacity and intensity respectively. The linear representation of the above equation is given by the following mathematical expression [20]:

$$\ln q_e = \ln K_F + \frac{1}{n} \times C_e \quad (3)$$

Fig. 3 shows a plot of  $\ln q_e$  versus  $\ln C_e$  and the value of the Freundlich parameters  $K_F$  and  $1/n$  are presented in Table I. Therefore, the adsorption of the vanadium molecules onto magnetic zeolite-polypyrrole composite cannot be well described by Freundlich isotherm model.

### E. Langmuir Isotherm

The Langmuir isotherm assumes that adsorption takes place at specific homogenous sites within the adsorbent. The isotherm equation is given as:

$$q_e = \frac{X_m K C_e}{(1 + K C_e)} \quad (4)$$

where  $K$  and  $X_m$  are the Langmuir constants related to the adsorption capacity and energy adsorption respectively. The linear representation is as follows:

$$C_e/q_e = \left(1/X_m\right) \times C_e + \frac{1}{K \times X_m} \quad (5)$$

Fig. 4 illustrates a typical graphical representation of the linearized Langmuir adsorption isotherm. The values of the Langmuir parameters,  $X_m$ ,  $K$  and  $R^2$  extracted from the plot are presented in Table I. From Table I the Langmuir isotherm parameters  $X_m$  which measures the monolayer capacity of the sorbent material was found to 57.803 mg/g. When comparing the correlation coefficient values obtained, Langmuir adsorption isotherm was a better fit for the batch equilibrium data with higher correlation coefficient values of 0.99 for all cases.

TABLE I: LANGMUIR AND FREUNDLICH ISOTHERMS PARAMETERS FOR Cr(VI) ADSORPTION ONTO MZ/PPY

Parameters	Langmuir constants	Parameters	Freundlich constants
$X_m$ (mg/g)	57.803	$K_F$ (mg/g)	20.725
$K$ (L/mg)	0.08831	$n$	5.5617
$R^2$	0.99	$R^2$	0.40

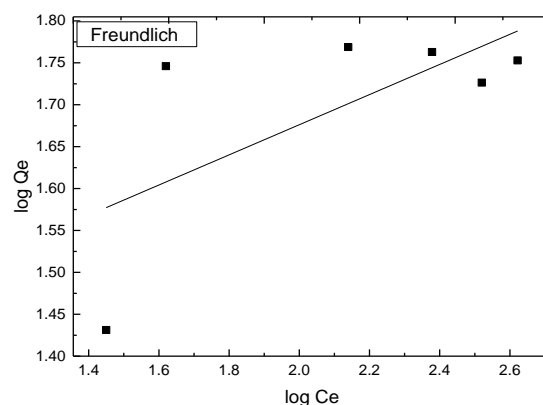


Fig. 3. Freundlich isotherm for vanadium sorption onto magnetic zeolite-ppy.

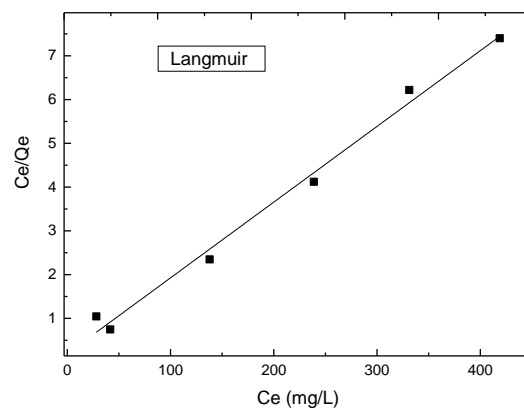


Fig. 4. Langmuir isotherm for vanadium sorption onto magnetic zeolite-ppy.

## IV. CONCLUSION

This work has established the adsorption of vanadium onto

synthesized magnetic zeolite-polypyrrole. It was found that the magnitude of adsorption was primarily dependent of the solution initial pH, the sorbent dosage. A pH of 5 was determined to be favorable for optimum removal of vanadium. This is consistent with literature expectation as the removal of vanadium from aqueous solutions is predicted by literature to be optimum at pH range of 4-6. An optimum media dosage was found to be 0.15 g of magnetic zeolite-polypyrrole which achieved 75% adsorption of vanadium from 100 ppm initial concentration at pH 5. The adsorption equilibrium was described better by Langmuir isotherm. The description of the equilibrium data by the the Langmuir isotherm was a demonstration of the homogeneous structure of the sorbent material and a confirmation that the adsorption of vanadium by magnetic zeolite-polypyrrole involves the attachment of only one layer of molecules to the surface (i.e. Monolayer adsorption). Because of the low cost of clinoptilolite and the relatively good sorption capacity achieved with magnetic zeolite-polypyrrole, this synthesized composite can be considered as a good prospective material for treatment of vanadium contaminated wastewaters.

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