DETERMINATION OF VANADIUM (V) REMOVAL EFFICIENCY FROM AQEOUSE SOLUTION BY USING OF EGGSHELL

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ABSTRACT*: Vanadium, which is a highly toxic metal, has widespread industrial applications; hence, larger quantities of vanadium are discharged into the aquatic environments. In this study the ability of low-cost adsorbent of eggshell was examined and affecting factors such as: initial solution pH, adsorbent dosage, initial concentration vanadium (V) and particle size of adsorbent (Eggshell) was investigated. The experiments were designed based on response surface methodology in central composite design space by using Design of Expert software. Adsorption was studied in a batch system where adsorption was found to be pH dependent with maximum removal efficiency at 2.29. The removal efficiency of vanadium (V) decreased by increasing of initial solution pH, initial vanadium (V) concentration and particle size of adsorbent, but this efficiency increased with increasing of eggshell dosage. The experimental data was more satisfactorily fitted with Langmuir isotherm model with correlation coefficient of R^2=0.9912. The kinetics and the factor controlling adsorption process fully accepted by pseudo-second-order model were also discussed. The maximum adsorption capacity of vanadium (V) on to the powdered Eggshell was found to be 3.056 mg/g.*

Keywords: Eggshell; Langmuir isotherm; Kinetics; Adsorption; Response Surface Methodology; sorption isotherm

INTRODUCTION

Water of high quality and acceptable quality is essential for human life and agriculture, industrial, domestic and commercial uses, respectively. Also, all of these activities are responsible for polluting the water. It is well known that 70–80% of all illnesses in developing countries are related to water contamination, particularly susceptible for women and children. The extraordinary increase in use of heavy metals over the past few decades has indispensable resulted in an increased flux of metallic substance in aquatic environment [1]. Heavy metals are one of the most toxic types of water pollutants. The major toxic metal ions hazardous to humans as well as other forms of life are Cr, Fe, Se, V, Cu, Co, Ni, Cd, Hg, As, Pb, Zn etc. These heavy metals are of specific concern due to their toxicity, bio-accumulation tendency and persistency in nature [2, 3, 4]. Wastewater containing heavy metals originated mainly from metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides galvanizing plants, stabilizers, thermoplastics, pigment manufacture, etc. These industries discharge heavy metals and wastewater directly or indirectly into the environment especially in developing countries. Thus, treatment of industrial wastewater containing soluble heavy metals has become essential in order to increase the quality of water [5, 6, 7].

The task of providing proper treatment facility for all polluting sources is difficult and also expensive, hence there is pressing demand for innovative technologies which are low cost, require low maintenance and are energy efficient. Treatment processes for metals contaminated waste streams includes chemical precipitation, membrane filtration, ion exchange, evaporation recovery carbon adsorption, and co-precipitation/adsorption [2] .Most of these processes are suffer from high cost. Among these, adsorption process has been found as one of the most promising technology in water pollution control. The adsorption technique is economically favorable and technically easy to separate as the requirement of the control system is minimum. Adsorption is commonly being done using activated carbon which adsorbs dissolved organic substances in the water treatment. To avoid the high cost of activated carbon many low-cost adsorbents have been used and tested to remove heavy metal ions from dilute aqueous solutions [3]. According to Bailey *et al*. [4], a sorbent can be considered low-cost if it requires little processing, is abundant in nature or is a by-product or waste material from another industry. A large quantity of materials has been investigated as biosorbents for the removal of metals or organics extensively. The tested biosorbents can be basically classified into the following categories: bacteria, fungi, yeast, algae, industrial wastes, agricultural wastes and other polysaccharide materials, etc. The role of some groups of microorganisms has been well reviewed, such as bacteria, fungal, yeast, algae, etc. [11, 12].

Eggshells are used in enormous quantities by food manufacturers, restaurants and household and the shells are disposed of as solid waste. Investigations have been conducted to explore the possibility of useful applications of eggshells, especially for wastewater. The porous nature of eggshells makes it an attractive material to be used as an adsorbent. The main aim of this study was to investigate the possibility of using powdered eggshells as adsorbent material. Eggshells were chosen as adsorbent due to its reasonable cost and ease of regeneration [5]. Eggshell can be used to adsorb heavy metal in wastewater due to its calcium carbonate content which is responsible for metal adsorption. This alternative method will not produce chemical sludge, hence no secondary pollution and it is more efficient and easy to operate compared to other methods [6].

Therefore this study was conducted to evaluate the effectiveness of powdered eggshell on the removal of vanadium (V) from aqueous solutions. The metal sorption was assessed based on the Langmuir and Freundlich adsorption isotherm models.

2. MATERIALS AND METHODS

2.1. Preparation of sorbent

Collected Hen eggshell were cleaned and boiled for maximum of 15 minutes. The membrane was removed from the inner parts of the shell carefully. The eggshells were crushed into smaller parts and then were heated for about 4 hours at a temperature of 150˚C. These eggshells were crushed with a mill to smaller sizes. After this time,

the powder was sieved by using available sieves of mesh number 80, 100, 140, 105, 200. After sieving, micro powder was kept in bottle in desiccator. Powders of adsorbent particle sizes 170, 105 and 74 µm were used in experiments throughout this work.

2.2. Sorption experiments

A 250 mL Erlenmeyer flask was filled by 100 mL of Ammonium metavanadate (NH_4VO_3) aqueous solution, then eggshell powder was added, also pH was set by Hydrogen chloride (HCL) and Sodium hydroxide (NaOH) solutions. The flask was sealed and placed on magnet mixer at constant speed at room temperature. Experiments were done in the form of batch study and in temperature 30± 2ºC.

After desirable time, adsorbent was separated by St. Pumps and then solution concentration was analyzed using flame atomic absorption spectrophotometer (FAAS) with regard to its concentration range.

The percent of vanadium (V) removal, R%,

$$R\% = \frac{(C_0 - C_e)\times 100}{C_0} \quad (1)$$

where C_0 and C_e are the initial and the residual vanadium concentrations (mg/L).

2.3. Sorption isotherm

Several mathematical models have been developed to quantitatively express the relationship between the extent of sorption and the residual solute concentration. The most widely used models are the Langmuir and Freundlich adsorption isotherm models.

The vanadium adsorption capacity of the eggshell powder was calculated as the (Eq. 2) below:

$$q = \frac{(C_0 - C)V}{m} \quad (2)$$

Where q, adsorption capacity per unit mass of eggshell powder (mg/g); C_0 initial concentration of metal ions in the aqueous solution (mg/L); C, equilibrium concentration of metal ions aqueous solution (mg/L); m, mass of eggshell powder; V, the volume of sample (L) [7].

Adsorption isotherm was obtained by agitating 1.5 g of eggshell powder in size 74 with 30 ppm to 150 ppm aqueous vanadium ion solutions, and pH was adjusted to 2.0. Contact time was 4 hours. Then for each sample of adsorbent, sample behavior was uptake and its concentration was measured as it was mentioned.

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2.4. Sorption kinetic

Batch kinetic experiments were performed by mixing 1.5 g adsorbent to each conical flask with 100 mL of metal ion solution of 50 mg/L concentration at room temperature (i.e. 30± 2ºC). A series of such conical flasks were then shaken at a constant speed of 500 rpm in a water bath shaker and samples were collected at different time intervals. Table 2.1 provides the experimental outline for the kinetic experiments.

3. RESULTS AND DISCUSSIONS

3.1. Effect of pH on Vanadium (V) removal efficiency

To determine the effect of pH on V (V) removal by eggshell adsorbent, biosorption studies were carried out at pH 2.0, 4.0 and 6.0. Figure 3.1 also shows the effect of pH on V (V) uptake. It was found that vanadium binding to adsorbent was pH dependent and the maximum sorption of vanadium (V) to adsorbent (eggshell) was found having an initial pH of 2.0. This figure shows that the removal efficiency of V (V) increased as pH raised 2.0–3.0, and reached maximum efficiency at pH 2.5 to 3.0 range and then decreased as pH increased from 3.0 to 6.0. As mentioned above at pH 2.0, vanadium in the (+5) oxidation state occurs as the VO_2^+ cation, and adsorption might be due to its specific adsorption to the positively charged surface. The decrease in removal efficiency at higher pH values was due to competition between OH^- and vanadium anions for available surface sites of absorbent. This result is generally consistent with the previous observations of vanadium adsorption by Tiangang Wang *et al.* [8] who obtained maximum vanadium removal efficiency in pH 2.5 and showed that this removal efficiency decreases with increase solution pH. Naeem *et al.* [9] showed that when the initial pH was reduced from 7.4 to 4.0, the sorption efficiency increased from 43% to 95% for V. Kaczala *et al.* [10] reached maximum adsorption by metal (hydr)oxide in the pH range 3.0-3.5

Table 2.1: Kinetic experimental setup

Adsorbent size particle	pH	Concentration of Adsorbate (mg/L)	Adsorbent dosage (g/L)	Exp. Duration (min)
Optimum amount (adsorbent particle size= 74 µm)	optimum amount (pH=2.0)	Optimum initial Concentration (50 mg/L)	Eggshell powder optimum dosage (15 g/L)	60 120 240 360 480

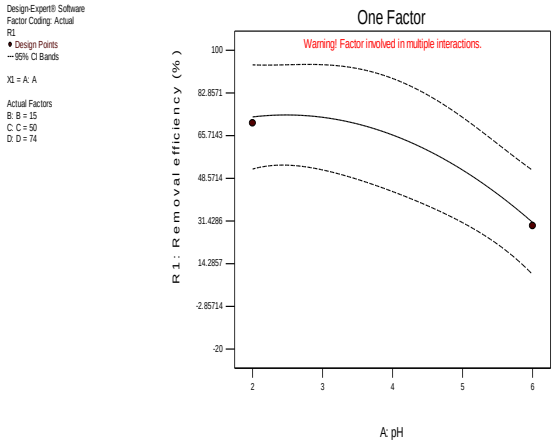

Figure 3.1: V (V) removal efficiency versus the various pH from 2.0 to 6.0

3.2. Effect of adsorbent dosage (Eggshell) on vanadium removal efficiency

The biosorption capacity for vanadium (V) ions varies with the biosorbent loading (Figure 3.2). This figure shows the effect of eggshell dosage in the range of 5.0 g/L to 15 g/L at initial pH 2.0, initial V (V) concentration 50 mg/L and sorbent particle size 74 µm. It was observed that percentage of vanadium (V) removal increased with increasing of adsorbent dose. Such a trend is mostly attributed to an increase in the sorptive surface area and the availability of more active adsorption sites. This figure also shows that adsorption efficiency not varies in higher adsorbent dosage. It might happen that the higher dose of eggshell causes particles to aggregate, overlapping and overcrowding, resulting in a decrease of the availability of the surface area as well as decrease of the sorption capacity.

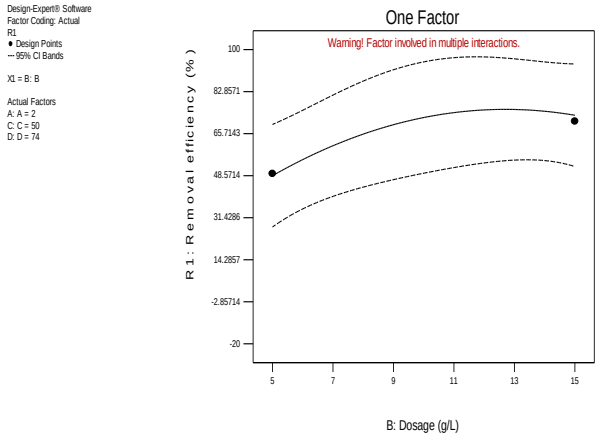

Figure 3. 2: V (V) removal efficiency versus the various adsorbent dosages from 5 to 15 mg/L

3.3. Effect of initial Vanadium (V) concentration on V (V) removal efficiency

The effect of initial V (V) ions concentration on V (V) uptake was studied in a range from 50 to 150 mg/L. The percentage removal of vanadium (V) decreased with increase in initial vanadium concentration (figure 3.3) and showed a little decrease at higher concentrations. This is probably due to increase the ratio of ions/adsorbent and also the fact that for a fixed adsorbent dose, the total available adsorption sites are limited, which become saturated at a certain concentration. This result is in agreement with Ahmad *et al*. [11], who showed that sorption efficiency decreased as initial metal concentration increased for each of the three metals (Pb^{2+}, Cu^{2+} and Cd^{2+}). Adsorption by eggshells decreased gradually from approximately 100% to 78.9%, 84.7% and 20.8% for Pb^{2+}, Cu^{2+} and Cd^{2+}, respectively, as the initial metal ion concentrations increased from the lowest initial concentration (10 mg/L) to the highest initial concentration (150 mg/L for Pb^{2+} and 60 mg/L for Cu^{2+} and Cd^{2+} respectively).

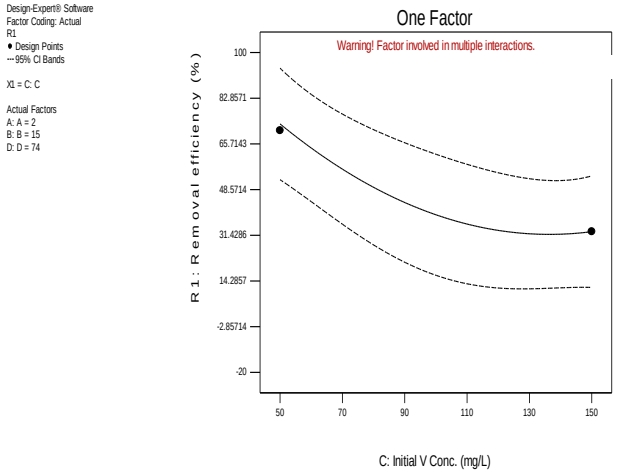

Figure 3. 3: V (V) removal efficiency versus the various initial vanadium (V) conc. From 50 to 150 mg/L

3.4. Effect of adsorbent (Eggshell) particles size on V (V) removal efficiency

The effect of adsorbent particle size was investigated by using the average particle size (74, 105 and 170 µm). The result is shown in figure 3.4. This shows that increase in particle size from 74 to 170 µm decrease the adsorption efficiency. It may be due to the smaller particle size of adsorbent gives large surface area, increases the adsorption capacity. It appears that the uptake is considerably influenced by the size distribution of sorbent particles. Maximum uptake is a function of the specific area, or external surface of the sorbent.

These results are correct when compared to the similar studies. Mokhtar Arami *et al*. [12] showed particle size is an effective parameter in removal efficiency. They concluded that decreasing the particle size of eggshell increasing adsorption efficiency of dye. This rising in the dye removal is the direct effect of the increasing the surface area of the adsorbent by decreasing the particle size.

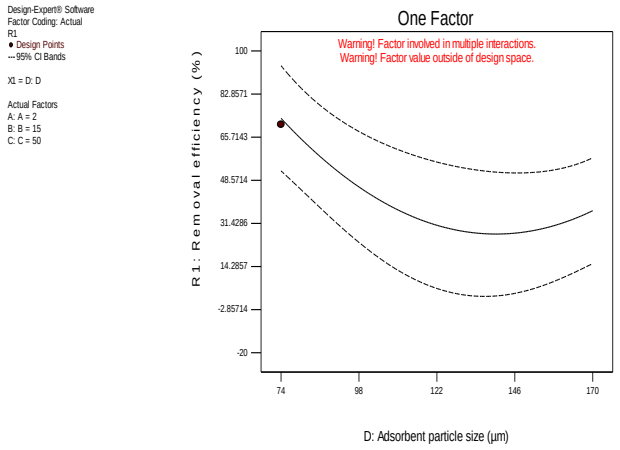

Figure 3. 4: V (V) removal efficiency versus the various adsorbent particle size from 74 to 170 (µm)

3.5. Equilibrium modeling

3.5.1. Langmuir isotherm

According to Langmuir, the sorption occurs at the surface of the sorbent in a homogeneous way and the atoms/ions form a monolayer, having no mutual interactions, on the sorbent surface. Although it gives no information about the mechanism, it is still used to obtain the uptake capacities of the sorbents. It is shown as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \qquad (3)$$

Where $q_m\ (mg/g)$ and b are the maximum adsorptive capacity and the Langmuir constant, respectively [13].

For Langmuir isotherm, the essential characteristics can be expressed in terms of a dimensionless equilibrium parameter called equilibrium parameter, (R_L). The separation factor (R_L) defined by Weber and Chakkravorti is an important parameter of the Langmuir isotherm that can be used to verify if the adsorption in the system to be unfavorable, linear, or favorable which is defined by the following equation:

$$R_L = \frac{1}{C_0 b} \qquad (4)$$

where C_0 is the initial Vanadium (V) concentration (mg/L).

If R_L>1, then it follows an unfavorable adsorption, a value of 1.0 for R_L indicates linear, a value of R_L less than 1.0 indicates favorable, and a value of R_L equal to zero suggests irreversible adsorption [14]. The coefficient of determination (R^2) for Langmuir model was found to be 0.9912. The maximum biosorption capacity (q_{max}) was found to be 2.9886 mg/g for the biosorption of the V (V) on to eggshell powder. Figure 3.5 shows the plot of the linearized Langmuir isotherm model fitting for the adsorption of V (V) onto eggshell powder.

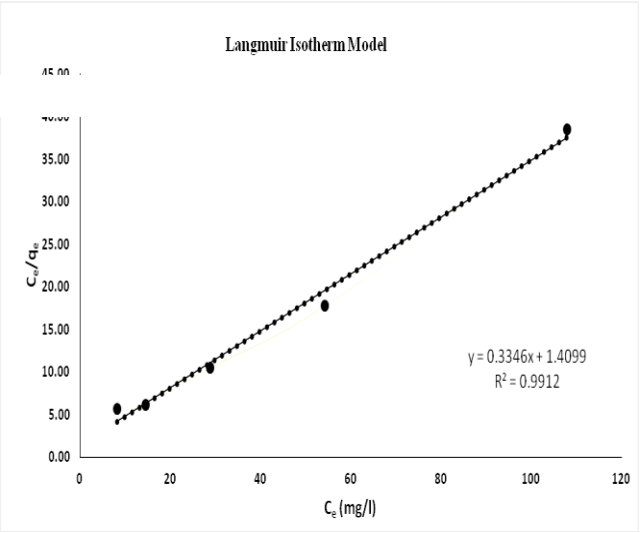

Figure 3. 5: Langmuir isotherm of vanadium ions adsorbed on eggshell powder

The values of q_{max}, b and R^2, derived from application of Langmuir's equation to the V (V) adsorption data of the egg shell are shown in Table 3.1.

From Eq. 4, $0.028 \leq R_L = \frac{1}{C_0 \times 0.2373} \leq 0.14$. this shows favorable adsorption.

3.5.2. Freundlich isotherm

The Freundlich expression is an exponential equation and therefore assumes that as the adsorbate concentration increases so too does the concentration of adsorbate on the adsorbent surface:

$$q_e = K C_e^{1/n} \qquad (5)$$

In this equation k and $b_F = \frac{1}{n}$ are the Freundlich constants, $C_e\ (mg/L)$, is the aqueous-phase equilibrium concentration $q_e\ (mg/g)$ is the solid-phase equilibrium concentration. This expression is characterized by the heterogeneity factor, b_F, and so the Freundlich isotherm may be used to describe heterogeneous systems. Theoretically, using this expression, an infinite amount of adsorption can occur. To determine the constants k and b_F, the linear form of the equation may be used to produce a graph of $\ln q_e$ against $\ln C_e$ [15]:

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e \qquad (6)$$

Figure 3.6 and Table 3.2 show the plot of the linearized Freundlich adsorption data and parameters for removal of V (V), respectively. The value of $1/n$, which is obtained from the Freundlich model, was found to be 0.2388 for the biosorption of the V (V) onto eggshell. The $1/n$ values were between 0 and 1, indicating that the biosorption of the V (V) onto eggshell was favorable under the conditions studied.

Table 3. 1: Regression analysis for sorption of V (V) by eggshell and the parameters estimated using Freundlich model

Table 3. 2: Regression analysis for sorption of V (V) by eggshell and the parameters estimated using

	Langmuir isotherm		
Adsorption parameter	b(L/mg)	$q_{max}(mg/g)$	R^2
	0.2373	2.9886	0.9912
	Freundlich isotherm		
	K_f	n	R^2
Adsorption parameter	1.077	4.1876	0.679

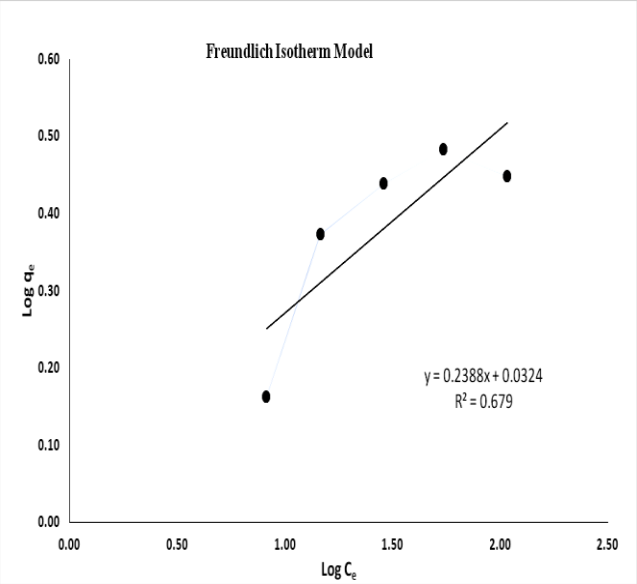

Figure 3. 6: Freundlich isotherm of vanadium ions adsorbed on eggshell powder

3.6. Kinetic studies

3.6.1. Pseudo-first-order model

The linearized pseudo-first-order kinetic model takes the following form:

$$\ln(q_e - q) = \ln q_e - k_1 t \qquad (7)$$

Where $q(mg/g)$ and $q_e\,(mg/g)$ are the amounts of vanadium (V) adsorbed at time t and equilibrium, respectively, and $K_1\,(min^{-1})$ is the first-order reaction rate constant. Values of adsorption rate constant (K_1) for V (V) adsorption on eggshell powder were determined from plotting $\log(q_e - q_t)$ vs. t.

Figure 3.7 shows a plot of linearized form of pseudo first-order equation at the studied concentration. The values of the Lagergren constants, q_e and k_1, and the correlation coefficient are presented in Table 3.3. This finding suggests that the adsorption process does not follow the pseudo first-order adsorption rate expression of Lagergren. If the intercept value does not equal $\log q_e$, the reaction is not likely to obey a pseudo first-order kinetic model, even this plot has not a high correlation coefficient with experimental data too.

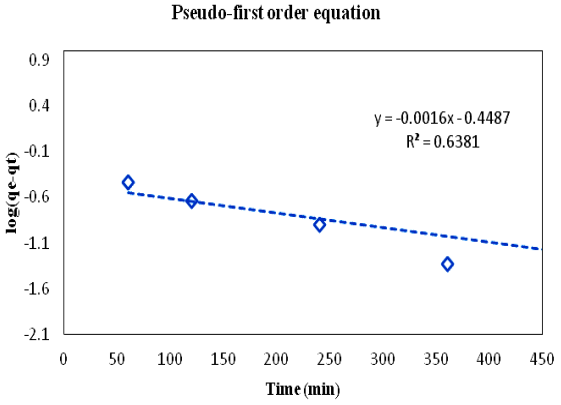

Figure 3. 7: Pseudo first-order kinetic model fitting for adsorption of V (V) by eggshell powder

Table 3. 3: Pseudo first-order kinetic parameters for the removal of V (V) by eggshell powder

Pseudo first-order model			
C_0(mg/L)	q_e (mg/g)	K_1 (min^{-1})	R^2
50	0.3559	0.00368	0.6381

3.6.2. Pseudo-second-order model

The pseudo-second-order kinetic model considered in this study is given as

$$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \qquad (8)$$

Where $K_2\,(gmg^{-1}min^{-1})$ is the second-order reaction rate constant. The adsorption rate constant (K_2) for V (V) adsorption on eggshell powder were determined from plotting t/q vs. t. The initial adsorption rate, $h\,(g\,mg^{-1}min^{-1})$ at $t \to 0$ is defined as:

$$h = K_2 q_e^q \qquad (9)$$

A linear relationship is observed for the vanadium-eggshell system. The value of the sorption capacity of the adsorbent q_e, the pseudo second-order rate constant K_2 and the coefficient of determination R^2 were evaluated from the plot and presented in table 3.4. The value of correlation coefficients R^2 for the pseudo second-order kinetic model is greater than 0.999 for the contact time of 240 min and the calculated value of q_e estimated from the seudo second-order kinetic model in this study is much closer to the experimental value of q_e than that of pseudo first-order model. Therefore, the sorption of vanadium by eggshell in this study was better fitted to the pseudo second-order model.

4. CONCLUSION

The role of eggshell powder as an adsorbent for removal of vanadium (V) from aqueous solution using batch

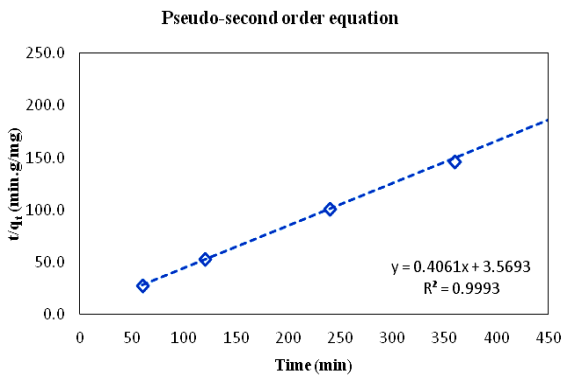

Figure 3. 8: Pseudo second-order kinetic model fitting for adsorption of V (V) by eggshell powder

Table 3. 4: Pseudo second-order kinetic parameters for the removal of vanadium (V) by eggshell powder

Pseudo second-order model			
C_0(mg/L)	q_e	K_2	R^2
50	2.46	0.046	0.9993

technique has been established. The maximum adsorption occurred at pH 2.5 – 3.0. Experimental equilibrium data provided best fit with the Langmuir isotherm model, indicating monolayer sorption on a homogenous surface (maximum monolayer sorption capacity was 2.9886 mg/g at 30± 2ºC). The adsorption kinetics followed pseudo-second-order kinetic model.

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