

Vanadium(V) removal from aqueous solutions using a new composite adsorbent (BAZLSC): Optimization by response surface methodology

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(Received March 7, 2017, Revised July 26, 2017, Accepted September 12, 2017)

Abstract. Heavy metals, such as vanadium, are some of the most toxic types of water contaminants. In this study, vanadium was removed using a new composite adsorbent called BAZLSC. The impacts of pH and initial concentration of vanadium(V) on the elimination effectiveness of this metal by using BAZLSC were investigated in the first step of the study. Vanadium removal increased as pH increased to 3-3.5, and initial concentration increased to 60-70 mg/L. The removal efficiency then decreased. Central composite design and response surface methodology were employed to examine experimental data. Initial concentration of V ($\text{mg}\cdot\text{L}^{-1}$), pH, and dosage of adsorbent (g/L) were the independent factors. Based on RSM, the removal effectiveness of vanadium was 86.36% at the optimum of initial concentration (52.69 mg/L), pH (3.49), and adsorbent dosage (1.71 g/L). Also adsorption isotherm investigations displayed that the Freundlich isotherm could explain vanadium adsorption by BAZLSC better than the Langmuir isotherm. Beside them, desorption studies showed sorption was slightly diminished after six continuous cycles.

Keywords: adsorption isotherms; composite adsorbent; RSM; vanadium

1. Introduction

For several years, oxyanion pollutants that present numerous noxious metals and metalloids into the environment have gained worldwide consideration due to their toxicity to humans and wildlife. The actions of oxyanions in the environment and their toxicity depend on their redox

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potential and aqueous speciation (Padilla-Rodríguez *et al.* 2015).

Metal ions are one of the vital categories of toxic water contaminants entering the food-chain pyramid. Several toxic heavy metal ions are released into the environment through different industrial activities, constituting one of the main causes of environmental pollution (Volesky 2001, Bhatnagar *et al.* 2008, Dehghani 2015). Numerous industrial processes are vital sources of environmental pollution because of their high amount of some heavy metal ions. One of the most important heavy metals is vanadium.

Vanadium is clearly has a possibly important environmental effect, mainly in natural waters, and will possibly be included as a regulated contaminant by the United States Environmental Protection Agency in the near future; it is currently entered in the Contaminant Candidate List (Padilla-Rodríguez *et al.* 2015). Vanadium, a famous toxic metal that exists in the environment, is the main stable species of this component in oxidative conditions and is commonly applied in industries like photography, glass, rubber, ceramic, textile, metallurgy, and in plants producing industrial pigments and inorganic chemicals. In terms of environmental features, V is vital whereof it is discharged into the environment chiefly from industrial sources (Anirudhan and Radhakrishnan 2010).

Heavy metals are removed via various ways such as biological techniques, ion exchange, solvent extraction, adsorption, reverse osmosis and chemical precipitation. Among them, adsorption and ion-exchange processes have been considered one of the most capable technologies in water contamination control (Mojiri *et al.* 2016, Alqadami *et al.* 2016a).

Dogan and Aydın (2014) studied V elimination by adsorption onto activated carbon derived from starch industry waste sludge. Activated carbon gained from industrial sewage sludge was found to be effectual in eliminating vanadium from aqueous solutions.

Adsorption is a quantity transmission procedure by which a substance is moved from the liquid phase to the surface of a solid, then bound via physical interactions, chemical interactions, or both (Kurniawan *et al.* 2006, Mojiri *et al.* 2013). Some of the most effective adsorbents are activated carbon, limestone, cement, cockle shell, and ash, which have been used by researchers (Cravotta and Trahan 1999, Tsiamis 2007, Waly *et al.* 2007, Yan-Jiao 2011, Nowak *et al.* 2012, Sdiri and Higashi 2013, Mojiri *et al.* 2016, Basumatary *et al.* 2016, Khan *et al.* 2017).

In the current research, a new adsorbent named BAZLSC, which includes bentonite, zeolite, cement, activated carbon, limestone, and cockle shell, was used. This adsorbent can simultaneously carry out adsorption and ion exchange. Ion exchange is a reversible swapping of ions between solid and fluid phases without changing the solid structure. This treatment can effectively eliminate traces of metal impurities to meet more and more strict depletion standards in developed countries (Mojiri 2011). Some studies have used ion exchange and adsorption to remove V from aqueous solutions (Parks and Edwards 2006, Naeem *et al.* 2007, Bhatnagar *et al.* 2008). However, most of these studies neither optimized removal efficiency nor tried to use composite adsorbents.

The current research mainly aimed to (1) remove V(V) from aqueous solutions, (2) used a new composite adsorbent named BAZLSC, and (3) optimize the removal efficiency by response surface methodology (RSM).

2. Materials and methods

2.1 Sample preparation

This section has three parts. In the first and second parts, samples were prepared for batch experiments to determine the impacts of pH and initial V(V) concentrations on V elimination. In these parts, adsorbent dosages were fixed on 1 g/L (Mojiri *et al.* 2017). In the final part, the V(V) removal has been optimized via response surface methodology (RSM).

2.1.1 Batch experiments to examine pH effect on V(V) removal

Initial vanadium concentration was fixed at 40 mg/L for determining pH effects on removal efficiency. In this part, adsorbent dosage and shaking time were 1 g/L and 30 min, respectively.

2.1.2 Batch experiments to examine initial V concentration effect on V(V) removal

The pH was fixed at 3.5 for determining initial vanadium concentration effects on removal efficiency. Also in this part, adsorbent dosage and shaking time were 1 g/L and 30 min, respectively.

2.1.3 Experiments to optimize V(V) removal

RSM was applied during the third part to find the optimum effects of pH, initial vanadium concentration, and adsorbent dosage on the removal efficiency of V(V). Based on previous studies (Manohar *et al.* 2005, Mthombeni *et al.* 2015), the values of pH, initial V(V) concentration (mg.L^{-1}), and adsorbent quantity (g/L) were set between 3-7, 40-80, and 0.6-1.8, respectively.

pH was adjusted using NaOH and HNO_3 during the experiments. Shaking time was 30 min in all experiments. Based on preliminary experiments, the samples were shaken at 200 rpm following with findings of Egute *et al.* (2011). Solutions of V were prepared by dissolving sodium orthovanadate (V) dodecahydrate ($\text{Na}_3\text{VO}_4 \cdot 12\text{H}_2\text{O}$; Sinopharm Chemical Reagent Co., China) in 250 mL of deionized water into beakers.

2.2 Composite adsorbent (BAZLSC) preparation

BAZLSC was prepared by grinding bentonite, zeolite, activated carbon, cockle shell, limestone, and Portland cement, passing them over a 300 mm mesh sieve and then blending them. The combination was then lightly poured in the mold after adding water. After 24 h, materials were removed from the mold and soaked in water for 3 days for the curing process. Materials were allowed to dry for 2 days, crushed, and passed through a sieve (Mojiri *et al.* 2016). Tables 1 and 2 show the values of raw materials for BAZLSC and the features of the BAZLSC with the autosorb (Quantachrome IQ, Germany) test, respectively. XRD and FTIR analyses results of BAZLSC are shown in Figs. 1 and 2, respectively. Bentonite, zeolite, cockle shell, and activated carbon are present in the composite adsorbent; hence, BAZLSC can do as both an adsorbent and ion exchanger. In the current study, powdered BAZLSC (PB) with a size range of 75-150 μm (Mojiri *et al.* 2016) was used as an adsorbent.

XRD results (Fig. 1) show that the most elements and compounds in BAZLSC are SiO_2 , Fe_2O_3 , Al_2O_3 , and CaCO_3 . CaCO_3 was detected in BAZLSC because of limestone and shell. Si, Al, and Fe were detected in BAZLSC because of zeolite, bentonite, and cement.

FTIR results (Fig. 2) show that peaks of 3435, 2300-2520, 1400-1800, 700-1000, and 600-700 cm^{-1} could belong to O-H, C-H, C-O, C-O-C, and C-C strong bonds (Coates 2000).

SEM testing of BAZLSC is shown in Fig. 3. Many pores are clear in this figure which can increase surface area of adsorbent. Increasing surface area could be useful to increase removal efficiency (Mojiri *et al.* 2016).

Table 1 The values of raw materials to prepare 1 ton of BAZLSC

Raw Materials	Value (kg)	Price per Ton (RMB*)	Unit Price (RMB)
Bentonite	258.8	1320.0	341.61
Zeolite	250.4	650.0	162.76
Portland Cement	240.4	350.0	84.00
Limestone	118.0	380.0	44.84
Activated Carbon	57.8	2000.0	115.60
Cockle Shell	40.0	500.0	20.00
Water	35.0	-	-
BAZLSC Fee	-	-	767.81

*China Currency

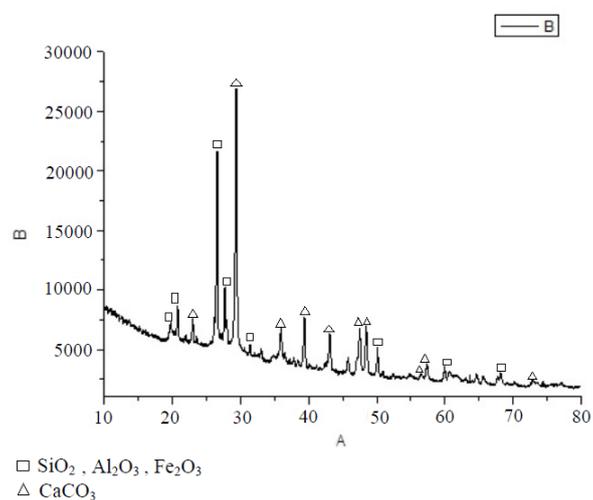


Fig. 1 XRD results of composite adsorbent

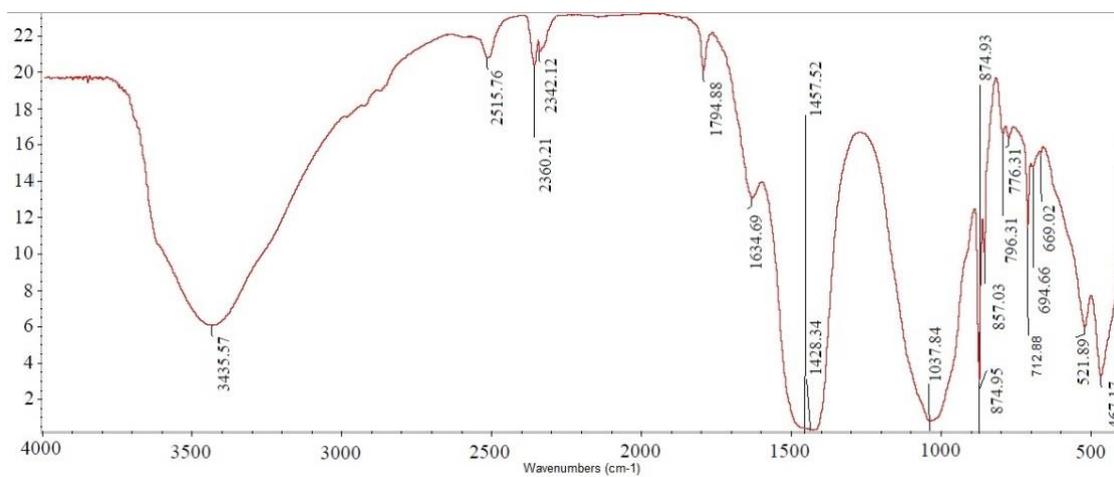


Fig. 2 FTIR results of composite adsorbent

Table 2 Powdered BAZLSC characteristics

Surface Area (m ² /g)	External Surface Area (m ² /g)	Micropore Area (m ² /g)	Micropore Volume (cc/g)
28.86exp +1	24.67exp +1	6.19exp +1	0.008exp +1

Thickness Method: DeBoer

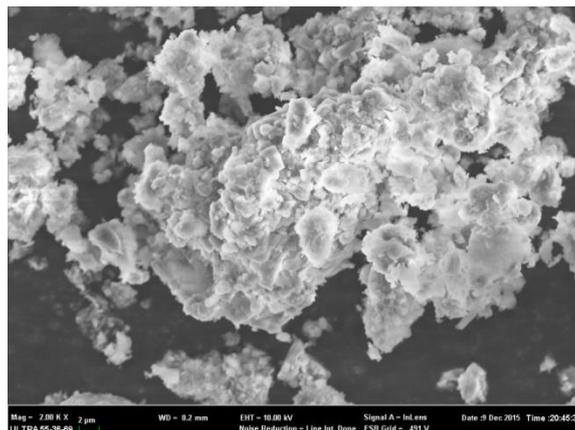


Fig. 3 SEM of BAZLSC

2.3 Analytical methods

All experiments were done in agreement with the Standard Techniques for the Examination of Water and Wastewater (APHA 2005). The INESA PHS-25 was employed to monitor the pH and temperature (°C). Electrical conductivity (ms/cm) was monitored using SANXINMP515-03. ICP (HITACHI, PS3500DD) was used to measure vanadium concentrations.

2.4 Statistical analysis

Removal efficiencies of vanadium (%) were tested by assessing the goal factors before and after treatment. Elimination effectiveness was assessed using Eq. (1)

$$\text{Elimination (\%)} = \frac{(C_i - C_f) \times 100}{C_i} \quad (1)$$

where the preliminary and final concentrations of the factors are C_i and C_f , respectively (Galhoum *et al.* 2016).

Experimental design for optimum removal of vanadium from aqueous solutions was conducted via the RSM. The RSM is statistical and mathematical systems that are valuable to chemical reaction optimization and engineering procedures and are normally employed for experimental designs (Bashir *et al.* 2010). In contemporary research, RSM was applied to measure the relationship among reaction (V elimination, %) and independent variables plus to enhance the relevant situations of variables to guess the top value of responses. Central Composite Design (CCD), the utmost commonly applied RSM approach, was employed to control the impact of

operational variables on elimination effectiveness (Mojiri *et al.* 2016). CCD and RSM were launched with the aid of the Design Expert 6.0.7 software program. The three main independent variables remarked in this research were pH (A), initial concentration of V mg/L (B), and adsorbent amount g/L (C). The pH, initial concentration of V (mg/L), and adsorbent dosage (g/L) were 3-7, 40-80, and 0.60-1.80, respectively. Every independent variable varied over three levels between -1 and $+1$ at measured ranges. The collected sum of experiments for the three factors was 20 ($=2k+2k+6$), where k is the sum of features ($k=3$). Hence, a quadratic model is an applicable model, as shown in Eq. (2). The impacts of the interaction of all variables on responses were then investigated (Table 3).

$$Y = \beta_0 + \sum_{j=1}^k \beta_j X_j + \sum_{j=1}^k \beta_{jj} X_j^2 + \sum_{i < j=2}^k \sum_{i=1}^k \beta_{ij} X_i X_j + e_i \quad (2)$$

where the response is represented by Y ; X_i and X_j are the factors; β_0 is an established coefficient; β_j , β_{jj} , and β_{ij} signify the interaction coefficients of linear, quadratic, and second-order terms, respectively; k represents the sum of evaluated parameters; and e represents error (Mojiri *et al.* 2016).

2.5 Sample preparation

The adsorption isotherm is a vital curve that explains the retention (or release) or movement of a substance from the aqueous porous media or aquatic environment in a solid point at steady pH and temperature. The adsorption equilibrium (proportion between the adsorbed amounts to that remaining in the solution) is attained when an adsorbate- comprising stage has been in connection with the adsorbent for an appropriate period. In this case, the adsorbate concentration in the bulk solution is in a dynamic equilibrium with the interface concentration. The mathematical correlation, which is significant in operational design, modeling analysis, and utilization of the adsorption systems, is narrated via graphically stating the solid phase against its residual concentration (Foo and Hameed 2009).

The quantity of adsorbate at equilibrium [q_e (mg/g)] can be considered to determine the removal percentage of adsorbate based on Eq. (3). (Kamaruddin *et al.* 2013)

$$q_{e=} = \frac{(C_0 - C_e)V}{M} \quad (3)$$

where C_0 and C_e (mg/L) are the initial and equilibrium liquid-phase concentrations of the adsorbate, respectively; V is the volume of the solution (L); and W is the mass of the adsorbent used (g).

The Langmuir and Freundlich isotherms are two of the best-known adsorption isotherms. These isotherms were originally derived for the adsorption of gases by solids (Aydin *et al.* 1996).

In the current study for adsorption isotherm testing, 20 mg/L of V was added to water in beakers with working volume of 250 mL. These beakers have contained different ratios of adsorbent between 0 g/L to 1.5 g/L. Beakers were shaken for 30 min at 200 rpm.

3. Results and discussions

Heavy metal-polluted environments have been a vital issue in the past decades (Yin *et al.*

2015). A transition metal is V which is well distributed in soil, water, crude oil and air; its compounds may have oxidation states ranging from -3 to +5 (Pessoa *et al.* 2015). In the current research, V was removed from aqueous solutions by using a new composite adsorbent, BAZLASC. The 3D surface plots to delete the contaminant (V) are shown in Fig. 5. ANOVA consequences for response parameters and response value under optimum situations are presented in Tables 4 and 5, respectively.

3.1 Effects of pH on V(V) removal

The elimination efficiencies of V (Fig. 4(a)) varied from 46.1% (pH=7) to 72.1% (pH=3.5). Based on Fig. 4(a), vanadium removal decreased with increased pH of above 3.5, and maximum removal occurred at pH 3-3.5. This finding agrees with those of Naeem *et al.* (2007) and Kaczala *et al.* (2009).

Awual *et al.* (2015) and Alqadami *et al.* (2016b) investigated pH effects on adsorption of metals by adsorbent. Chaudhari (2007) stated that the pH of the aqueous solution is a vital controlling factor in adsorption. The percentage removal of V(V) was observed to decrease with increasing pH. At a lower pH, the adsorbent surface is altered via H⁺ ions. Given the electrostatic attraction between the anionic vanadate species and the adsorbent surface, maximum elimination is achieved at lower pH (Prathap and Namasivayam 2010). Bolboli *et al.* (2015) stated that the decreased removal efficiency at higher pH values may be due to OH⁻ and vanadium anions competing for available surface sites of adsorbent. In addition, heavy metal removal decreases at in pH>3 because H⁺ ions interact with the metal cation for adsorption locations in the system (Abdel-Ghani *et al.* 2007).

Table 3 Experimental variables and results

Run	pH	Concentration of V(V) (mg/L)	Adsorbent Dosage (g/L)	Removal (%)
1	5.00	60.00	1.20	80.93
2	5.00	70.00	1.20	82.44
3	5.00	60.00	1.20	80.66
4	3.00	40.00	0.60	62.31
5	5.00	60.00	1.20	80.51
6	5.00	60.00	1.20	81.53
7	3.00	40.00	1.80	85.02
8	5.00	50.00	1.20	80.73
9	7.00	80.00	1.80	62.39
10	5.00	60.00	0.90	70.21
11	5.00	60.00	1.50	91.22
12	4.00	60.00	1.20	92.49
13	5.00	60.00	1.20	81.77
14	6.00	60.00	1.20	68.21
15	3.00	80.00	1.80	78.49
16	3.00	80.00	0.60	66.77
17	7.00	40.00	0.60	62.07

Table 3 Continued

Run	pH	Concentration of V(V) (mg/L)	Adsorbent Dosage (g/L)	Removal (%)
18	7.00	40.00	1.80	62.23
19	7.00	80.00	0.60	60.27
20	5.00	60.00	1.20	79.14

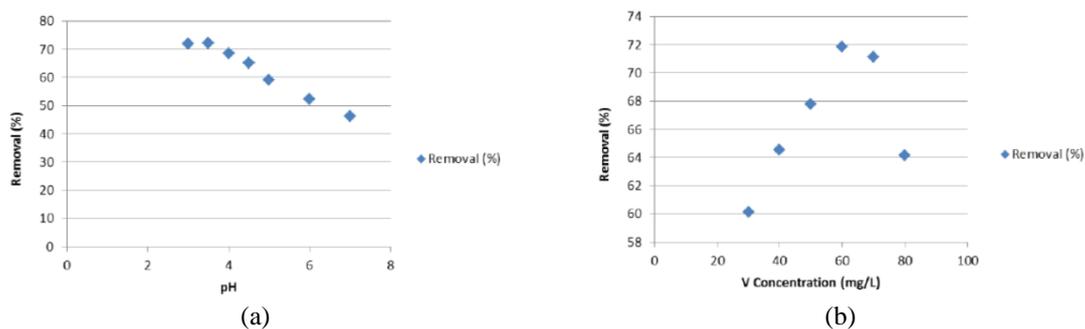


Fig. 4 (a) Effects of pH on removal efficiency and (b) Effects of initial concentration of vanadium(V) on removal efficiency

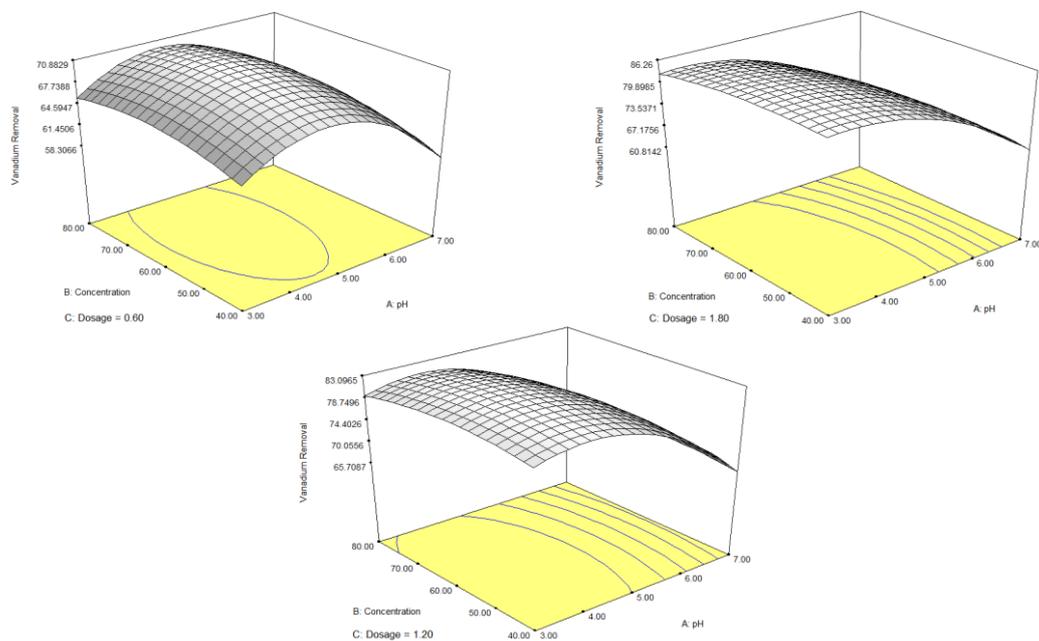


Fig. 5 The 3D surface plots of vanadium(V) removal

3.2 Effects of initial concentration (mg/L) on V(V) removal

The removal efficiencies of V (Fig. 4(b)) varied from 60.1% (initial vanadium concentration=30 mg/L) to 71.8% (initial vanadium concentration=60 mg/L). Based on Fig. 4(b),

vanadium removal increased when initial vanadium concentration was increased to 60-70 mg/L. This finding agrees with that of Ahmad *et al.* (2012).

Baboli *et al.* (2015) reported that vanadium removal decreased when initial vanadium concentration was increased from 50 mg/L to 150 mg/L. Total available adsorption sites are limited in a fixed adsorbent dosage, thus removal decreased because of the increased ratio of ions/adsorbent. Thus, adsorption sites might be saturated at a certain concentration.

3.3 Statistical analysis

Design and analysis of experiments (DOE) have been extensively used in arrangement, evaluating, and experiments in various fields, such as food analysis, wastewater treatment, material production, and medication intake, which aid researchers gain their objective with less cost, effort, and time. DOE was been widely applied in industries wastewater because it aids effective data assembly and decreases error by excluding non-significant features from the experiment, as well as increasing result correctness to the target range. The well-known RSM comprises of statistical and mathematical skills suitable for analyzing and modeling issues. This method purposes to optimize response by determining the best operating conditions of input variables (independent variables) that influence the response (Lim *et al.* 2014). In the current study, RSM and CCD have been applied to evaluate experimental data.

The removal efficiencies of V(V) removal (Table 3) varied from 60.2% (pH=7, initial concentration=80 mg/L, and adsorbent quantity=0.6 g/L) to 92.4% (pH=4, initial concentration=60 mg/L, and adsorbent quantity=1.2 g/L). Optimum vanadium elimination (86.36%) was achieved at a pH=3.4, with initial concentration=52.6 mg/L and adsorbent dosage=1.7 g/L. Based on RSM, increasing the adsorbent dosage from 0.6 g/L to 1.2 g/L increased removal efficiency, which agrees with the findings of Mthombeni *et al.* (2015).

In final equations, where A is pH; B is initial concentration of V (mg/L), and C is dosage of adsorbent (g/L).

Table 4 ANOVA results for response parameters

Responses	Final equation in terms of actual factor	Prob.	R ²	Adj. R ²	SD	CV	PRESS	Prob. LOF
V(V) Rem.	$-18.065 + 17.444A + 0.635B + 66.990C - 1.690A^2 - 4.554B^2 - 14.726C^2 + 0.001AB - 3.348AC - 0.094BC$	0.0001	0.8369	0.6901	5.67	7.52	2643.0	0.0059

Notes: Prob: Probability of error; R²: Coefficient of determination; Adj. R²: Adjusted R²; Adec. P: Adequate precision; SD: Standard deviation; CV: Coefficient of variance; PRESS: Predicted residual error sum of square; Prob. LOF: Probability of lack of fit.

Table 5 The value of response at optimum conditions

Independent Factors			Responses
A	B	C	V(V) rem. (%)
3.49	52.69	1.71	86.36

(A): pH; (B) V(V) Concentration (mg/L); (C): Adsorbent dosage (g/L)

3.4 Adsorption and desorption

The Langmuir and Freundlich isotherms are the two most significant adsorption isotherms, which were formerly derived for the adsorption of gases by solids (Aydin *et al.* 1996). Daneshvar *et al.* (2017) studied the Langmuir and Freundlich isotherm for monitoring metals removal mechanism by adsorption method. In current study after doing adsorption, BAZLSC was treated with 0.01 M HCl (Alqadami *et al.* 2017) to extract V. After each elution process, the BAZLSC was rinsed with water for next sorption action. And this process was repeated seven times to monitor desorption capacity of BAZLSC (Fig. 7).

3.4.1 Langmuir

The Langmuir equation establishes the relationship between the coverage or the adsorption of molecules on a solid surface and the gas pressure or concentration of a medium over the solid surface at a stable temperature (Aziz *et al.* 2012). The Langmuir isotherm model presumes a monolayer adsorption on a homogeneous surface. Langmuir adsorption isotherm is defined as follows (Eq. 4)

$$\frac{x}{m} = \frac{abC_e}{(1+bC_e)} \quad (4)$$

where x/m is the mass of adsorbate adsorbed/unit mass of adsorbent (mg adsorbate per g adsorbent), a and b are empirical parameters, and C_e is the equilibrium concentration of the adsorbate in the solution following adsorption (mg/L) (Mojiri *et al.* 2016).

Fig. 6(a) displays the Langmuir isotherm regression for V(V) removal using BAZLSC. Table 6 displays all the correlation coefficients, constants, and R^2 values reached from Langmuir isotherm. The maximum adsorption capacity (Q_0) and the energy of adsorption values (b) were 2.19 and -0.29, respectively. Negative values of b were reported by Mojiri *et al.* (2014) for metal removal using a composite adsorbent. The negative value indicated that the increase in C_e caused a decrease in x/m (Aziz *et al.* 2012).

Dimensionless equilibrium factors R_L might be applied to declare the characteristics of Langmuir isotherm (Isa *et al.* 2007); the value of R_L was -0.20. Based on R^2 (0.822), the adsorption of vanadium by BAZLASC can follow the Langmuir adsorption isotherm. Abdulrasaq and Basiru (2010) reported $R^2=0.88$ for metal adsorption by ash.

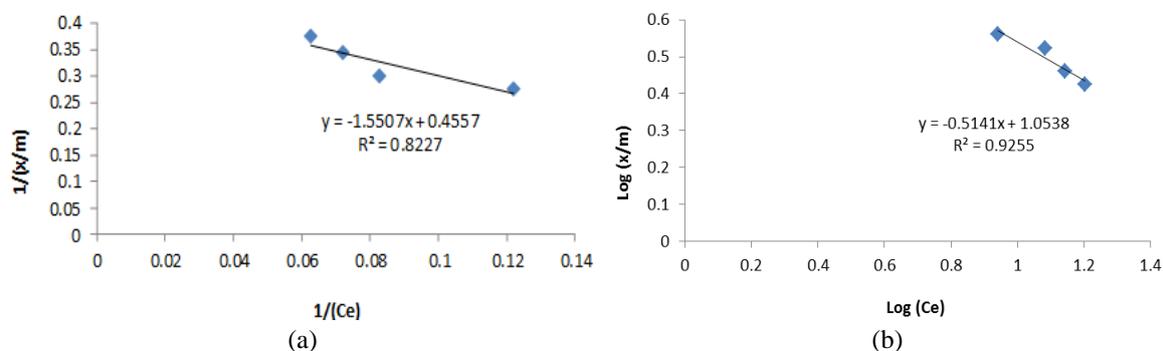


Fig. 6 (a) Langmuir isotherm regression and (b) Freundlich isotherm regression

Table 6 Langmuir equation for V(V) removal

Parameters	Q_0 (mg/g)	b	R^2	$R_L = \frac{1}{1 + bC_0}$	Isotherm type*
V	2.194	-0.296	0.822	-0.203	unfavorable

*Note: $0 < R_L < 1$ =favorable; $R < 1$ =unfavorable

Table 7 Freundlich equation for V(V) removal

Parameters	K_f (mg/g (L/mg) ^{1/n})	1/n	n	R^2
V	11.326	-0.514	-1.945	0.9255

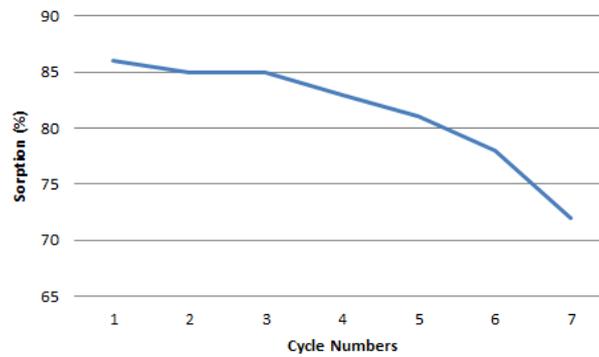


Fig. 7 Elution operation with 0.01 M HCl after V adsorbed onto the composite adsorbent

3.5 Freundlich

Freundlich adsorption isotherm is a curve that establishes the relationship between solute concentration on the surface of an adsorbent and in the fluid. In 1909, Freundlich proposed an empirical expression of the isothermal variation of the gas amount adsorbed with pressure using the unit mass of the solid adsorbent. This equation is identified as Freundlich adsorption equation or Freundlich adsorption isotherm. The Freundlich equation can be expressed as follows (Eq. 5) (Hamdaoui and Naffrechoux 2007)

$$q_m = K_f C_e^{1/n} \tag{5}$$

where K_f is a fixed representing the relative adsorption capability of the adsorbent ($\text{mg}^{1-(1/n)} \cdot \text{L}^{1/n} \cdot \text{g}^{-1}$), and n is a fixed representing adsorption intensity (Mojiri *et al.* 2016).

The obtained Freundlich capacity factors (K) and $1/n$ were 11.32 and -0.51, respectively. Higher $1/n$ values mean that the adsorption bond is weak. Increasing $\log(C_e)$ resulted in a decreased $\log(x/m)$. Thus, $1/n$ (slope of the line) is negative (Aziz *et al.* 2012). Negative values of $1/n$ have been reported by Aluyor and Badmus (2008). In the current study, $R^2=0.925$, which is approximately in line with the findings of Doğana and Serdar Aydın (2015). Based on R^2 in Langmuir and Freundlich isotherms, V adsorption could clearly follow the Freundlich isotherm better than the Langmuir isotherm. Fig. 6(b) shows the Freundlich isotherm regression for V(V) removal using BAZLSC.

Desorption studies (Fig. 7) shows sorption was slightly diminished after six continuous cycles.

4. Conclusions

Water of high or acceptable quality is essential for human life, agriculture, and industrial, domestic, and commercial uses. All of these activities, however, are responsible for polluting the water. Approximately 70-80% of all illnesses in developing countries, particularly those among women and children, are known to be related to water contamination. Heavy metals, such as V, are one of the most toxic types of water pollutants. Thus, V removal was investigated in this study. CCD and RSM were used to optimize parameters. The main conclusions of this study are listed below.

- V(V) removal increased as pH increased to around 4; afterward, the removal efficiency decreased.
- Removal efficiency increased as V(V) concentration in the water increased until 60 mg/L; afterward, the removal efficiency decreased.
- Based on RSM, optimum vanadium removal would be accorded at pH=3.4, initial vanadium(V) concentration of 52.6 mg/L and adsorbent dosage of 1.7 g/L.
- Adsorption isotherms have showed that the adsorption of vanadium by BAZLSC could follow the Freundlich isotherm better than the Langmuir isotherm.

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