

Molybdenum(VI) removal from aqueous solutions using bentonite and powdered cockle shell; Optimization by response surface methodology

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Abstract

Removal of Mo(VI) from aqueous solutions by using bentonite and powdered cockle shell was conducted in this research. First, the effects of pH and initial Mo(VI) concentration on the Mo removal efficiency via shell and bentonite were studied. Results showed that Mo removal effectiveness increased as pH increased until 3.5. Removal efficiency of Mo via bentonite and shell also increased as initial Mo(VI) concentration increased to 30 or 40 mg/L, respectively, after which the removal efficiency decreased. Response surface methodology and central composite design were applied to optimize removal effectiveness. Initial concentration of Mo(VI) (mg/L), pH, and shaking time (min) were selected as independent factors. These results showed that bentonite is more effective in removing Mo from water than the shell. At the optimum condition of 5.8 pH, initial Mo concentration of 39.2 mg/L, and shaking time of 38.6 min, bentonite could remove 81.3% of Mo.

Keywords: Bentonite, Molybdenum(VI), Cockle Shell, RSM

1. Introduction

Non-stop release of industrial, urban, and agricultural wastes in rivers and lakes have resulted in the deposit of contaminants in environment. These contaminants include heavy metals that can endanger public health if incorporated in the food chain. Heavy metals are present in different types of industrial effluents and are responsible for environmental pollution (Barkhordar and Ghiasseddin, 2004). Incidence of heavy metal accumulation in fish, oysters, mussels, sediments, and other components of aquatic ecosystems has been reported (Kafshgari *et al.*, 2013). Mo is one of the most vital of heavy metals. Mo is a transition metal from Group 6 of the periodic table, but its chemical properties are more similar to those of tungsten and vanadium from Group 5 than those of chromium from Group 6. A range of oxidation states is known for Mo, from

-2 to +6, last one being the most common and stable oxidation state (de Castro Sousa, 2009).

Mo is considered a necessary trace element for both plants and animals. The conditionally recommended dietary intake of Mo is 75–250 $\mu\text{g}\cdot\text{day}^{-1}$ for adults and older children (Lian *et al.*, 2012; Moret and Rubio, 2003). Mo pollution has been reported in the past years. Given the large amounts of Mo-containing effluents from mine tailings without any pretreatment, such contamination has become a main water quality management issue in many regions of the world (Yu *et al.*, 2011).

Mo is also applied in a variety of industrial procedures, for example, as an alloying agent in steels and cast iron, pigments for printing inks, paints and ceramics, solid lubricants, missile and aircraft paints, reactor vessels, die casting (copper base alloys), and in special batteries. However, Mo is toxic at high concentrations, and the maximum permissible limit in drinking water is 70 $\mu\text{g}\cdot\text{L}^{-1}$ (Namasivayam and Sureshkumar, 2009).

Physical/chemical and biological methods can be used to remove metals from aqueous solutions. For example, some researchers have used electrochemical and electrocoagulation as a kind of physical/chemical method for metals removal (Vlachou *et al.*, 2013; Liao *et al.*, 2014; Kourdali *et al.*, 2014; Gatsios *et al.*, 2015). Some researchers use biological method such as activated sludge process for metals removal (Mojiri *et al.*, 2016). But the majority of them is costly, time-consuming, and generates high amount of sludge (Moideen *et al.*, 2015).

Among the many removal methods of metals, ion exchange and adsorption are the most effective and environmentally safe processes. Most ion exchangers are polymer matrices that immobilize various functional groups for metal ion uptake. Meanwhile, inorganic adsorbents are more commonly used due to both separation ability and physical properties such as resistance against heat and radioactivity (Nishihama and Yoshizuka, 2009). Several researchers

(Yamada *et al.*, 2001; Fujita *et al.*, 2006; Anto and Annadurai, 2012; Ragheb, 2013) have used adsorption and ion-exchange methods to remove pollutants such as heavy metals.

Krika and Benlahbib (2015) demonstrated that adsorption process is an effective technique because of its efficiency, capacity, and applicability on large scale dye-removal, as well as the potential for regeneration, recovery, and recycling of adsorbents. Several materials have been used to remove metals from water and wastewater such as ash, activated carbon, zeolite, and limestone (Aziz, 2012; Ragheb, 2013; Mojiri *et al.*, 2014). However, few studies have focused on improving the performance of cockle shell and bentonite for metal removal.

Bentonite clay is a 2:1 mineral formed into a layer with one octahedral sheet and two silica sheets. Bentonite carries a net negative charge due to the broken bonds around the edges of the silica-alumina units. This phenomenon results in unsatisfied charges, which could be balanced by exchanging cations (Bhattacharyya and Gupta, 2008). Therefore, the ion-exchange and/or adsorbent properties of bentonite clay have been investigated because of its framework (Sajidu *et al.*, 2008). In the current study, cockle shell is another adsorbent which has also been used to adsorb metals. Cockle is a small and edible marine bivalve mollusk. Although many small edible bivalves are also called cockles, true cockles are species in the family *Cardiidae* ([https://en.wikipedia.org/wiki/Cockle_\(bivalve\)](https://en.wikipedia.org/wiki/Cockle_(bivalve))). The shell of a cockle is rich in calcite that can be useful in ion-exchange and adsorption processes. Some researchers used cockle shell to remove pollutants from water (Kohler *et al.*, 2008; Moideen *et al.*, 2015).

This research aimed to (1) remove Mo(VI) from water using bentonite and powdered cockle shells, (2) optimize removal efficiency using response surface methodology (RSM), and (3) compare the performances of bentonite and cockle shell.

2. Materials and Methods

2.1. Sampling Preparation

This section had three parts. First, the effect of pH on removal efficiency of Mo(VI) was investigated at conditions of 30 mg/L initial Mo concentration, shaking time of 30 min, and 2 g/L adsorbent dosage. Second, the effect of initial Mo concentration on removal efficiency was determined at pH of 4, 30 min shaking time, and 2 g/L adsorbent dosage. Finally, the Mo removal efficiency was optimized using RSM, with pH, initial Mo(VI) concentration, and shaking

time as independent factors. Based on preliminary experiments, the used adsorbent dosage was 2.5 g/L for optimization process.

The standard solutions of Mo(VI) were prepared by dissolving analytical grade sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) in deionized water in beakers with 200 mL working volume (Kafshgari *et al.*, 2013). The pH of influent solutions was adjusted using a pH meter (YSI incorporated, USA) with 0.1 M HCl and/or 0.1 M NaOH. Based on preliminary experiments, the samples were shaken at 200 rpm, which is in line with findings of Egute *et al.* (2011).

2.2. Bentonite and Cockle Shell Characteristics

The characteristics of bentonite and powdered cockle shells are shown in Table 1. In the current study, the sizes of powdered shell and bentonite ranged from 75 μm to 150 μm (Aziz *et al.*, 2011). Based on XRD results (Fig. 1), $\text{SiO}_2/\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ and CaCO_3 make up most of the bentonite, which is in line with findings of Naswir *et al.*, (2013). Based on the FTIR results (Fig. 3), peaks of 3400–3630, 2300, 1040, 690–790, and 460–600 could be O-H, O-H, C-O, C-H, and S-S or Si-Cl, respectively (Coates, 2000).

XRD results showed that CaCO_3 makes up most of the cockle shell (Fig. 2), which adheres to the findings of Kamba *et al.* (2013). Based on the FTIR results (Fig. 4), peaks of 700–800, 1424–1797, 2513–2872, and 3200–3500 could belong to C-Cl, carboxylic acid or carbonate ion, C-H, and Si-O-Si, respectively (Coates, 2000).

2.3. Analytical Methods

All experiments were carried out in accordance with the Standard Methods (APHA, 2005). The YSI Inc., USA was used to record the pH and temperature ($^{\circ}\text{C}$). Electrical conductivity (S/m) was monitored using SANXINMP515-03, and ICP (HITACHI, PS3500DD) was used to measure Mo concentrations.

2.4. Statistical Analysis

The Mo(VI) removal efficiencies were tested by identifying the target parameters before and after treatment. Removal efficiency was designed using the equation (Equation 1)

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

where C_i and C_f are the initial and final concentrations of the parameters, respectively.

Table 1. Characteristics of Bentonite and Oyster Shell

Parameters	Bentonite	Cockle Shell
Surface Area (m^2/g)	23.48ex +1	25.97ex +1
External Surface Area (m^2/g)	22.13ex +1	22.98ex +1
Micropore Area (m^2/g)	5.27ex +1	6.05ex +1
Micropore Volume (cc/g)	0.008ex +1	0.010ex +1

Thickness Method: DeBoer

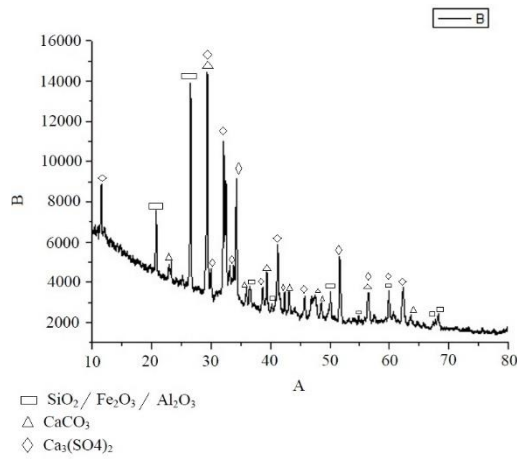


Figure 1. XRD Results of Bentonite

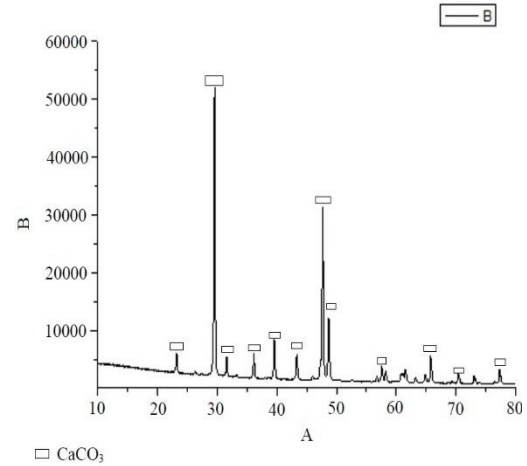


Figure 2. XRD Results of Cockle Shell

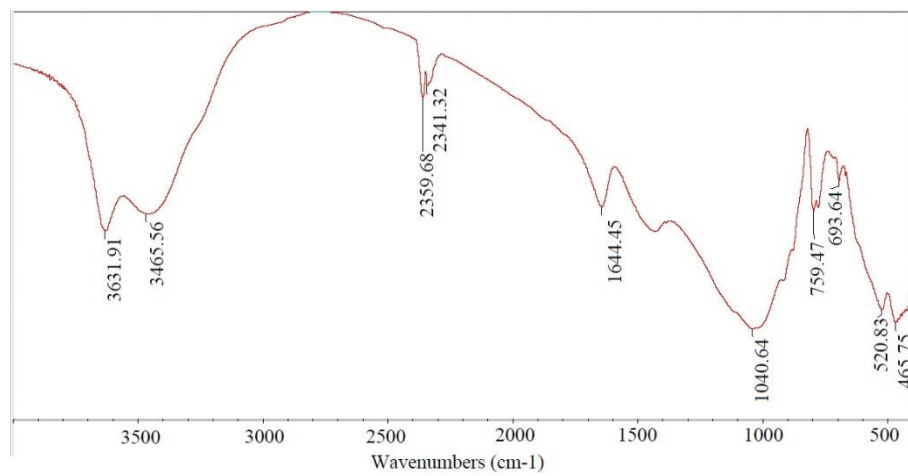


Figure 3. FTIR Results of Bentonite

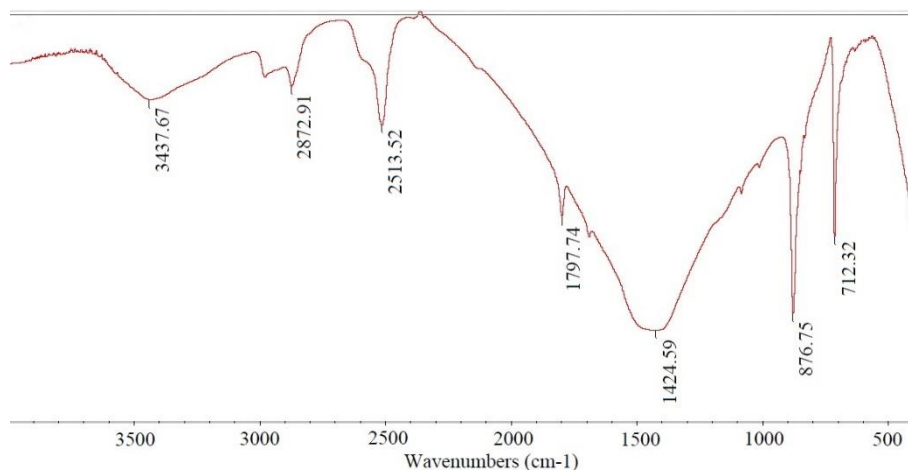


Figure 4. FTIR Results of Cockle Shell

Central composite design (CCD) and RSM were used to plan the experiments and data analysis. CCD was implemented with Design Expert Software Version 6.0.7. Equation 2, an empirical second-order polynomial model, accounts for the behavior of the system, which is expressed as

$$\beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i < j}^k \sum_j \beta_{ij} X_i X_j + \dots + e \quad (2)$$

where Y represents the response, X_i and X_j represent the variables, β_0 represents a constant coefficient; β_i , β_{ii} , and β_{ij} represent the interaction coefficients of the linear, quadratic, and second-order terms, respectively; k is the number of studied factors; and e represents the error.

ANOVA was used to fully analyze the results obtained using the Design Expert Software. The design included k^2 factorial points supported by $2k$ axial points and a center point, where k represents the number of variables (Mojiri *et al.*, 2013). A number of researchers used RSM to optimize pollutant removal from leachates and wastewater (Mohajeri *et al.*, 2010; Umar *et al.*, 2011; Adlan *et al.*, 2011). In the current research, pH (3–6), initial concentration of Mo (VI) (20–60 mg/L), and shaking time (30–90 min) have been selected as independent factors.

2.5. Adsorption Isotherms

If the adsorbent and adsorbate interact long enough, the equilibrium will set between the amount of adsorbate

adsorbed and the amount of adsorbate in the solution. The equilibrium relationship is explained by adsorption isotherms. Adsorption refers to the adhesion of atoms, ions, biomolecules, or molecules of gas, liquid, or dissolved solids to a surface (Aziz *et al.*, 2012). The adsorption isotherm equation is (Equation 3)

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

where q_e is the quantity of solute adsorbed per unit weight of adsorbent (mg/g), C_0 is the initial adsorbate concentration, C_e is the equilibrium adsorbate concentration (mg/L), V is the volume of solution (L), and M is the mass of the adsorbent (g).

Table 2. Experimental variables and results for Mo removal by bentonite

Run	pH	Concentration of Mo(VI), (mg/L)	Shaking Time, (min)	Removal, (%)
1	4.50	40.00	40.00	79.49
2	4.50	50.00	40.00	78.88
3	4.50	40.00	40.00	78.92
4	3.00	20.00	20.00	58.25
5	4.50	40.00	40.00	79.13
6	4.50	40.00	40.00	80.03
7	3.00	20.00	60.00	58.27
8	4.50	30.00	40.00	72.51
9	6.00	60.00	60.00	48.45
10	4.50	40.00	30.00	70.31
11	4.50	40.00	50.00	73.56
12	3.75	40.00	40.00	81.37
13	4.50	40.00	40.00	78.89
14	5.25	40.00	40.00	78.79
15	3.00	60.00	60.00	56.98
16	3.00	60.00	20.00	60.27
17	6.00	20.00	20.00	52.03
18	6.00	20.00	60.00	46.39
19	6.00	60.00	20.00	47.67
20	4.50	40.00	40.00	79.41

Table 3. Experimental variables and results for Mo removal by shell

Run	pH	Concentration of Mo(VI), (mg/L)	Shaking Time, (min)	Removal, (%)
1	4.50	40.00	60.00	59.83
2	4.50	50.00	60.00	60.06
3	4.50	40.00	60.00	60.16
4	3.00	20.00	30.00	73.81
5	4.50	40.00	60.00	59.59
6	4.50	40.00	60.00	59.59
7	3.00	20.00	90.00	63.91
8	4.50	30.00	60.00	61.91
9	6.00	60.00	90.00	45.32
10	4.50	40.00	45.00	61.00
11	4.50	40.00	75.00	58.17
12	3.75	40.00	60.00	65.76
13	4.50	40.00	60.00	58.71
14	5.25	40.00	60.00	49.34
15	3.00	60.00	90.00	60.17
16	3.00	60.00	30.00	61.29
17	6.00	20.00	30.00	44.39
18	6.00	20.00	90.00	44.62
19	6.00	60.00	30.00	44.13
20	4.50	40.00	60.00	57.95

Langmuir and Freundlich isotherms were used in this study to display the characteristics of bentonite and shell adsorptions.

In the present investigation for adsorption isotherm testing, 30 mg/L of Mo was added in 200 mL beakers containing different ratios of adsorbents between 0–2.5 g/L. Beakers were shaken for 30 min at 200 rpm. And the pH has been fixed on 4

3. Results and Discussion

This study treated Mo(VI)-polluted water using adsorbents. Tables 2 and 3 show the experimental variables and results of Mo removal by bentonite and shell based on RSM design. This study follows up two main points, namely, the effects of pH and initial concentration of Mo on Mo removal by bentonite and shell and the optimization of Mo removal using RSM

3.1. Effects of pH on Molybdenum Removal

With the use of bentonite, the removal efficiency of Mo(VI) varied from 62.2% (pH=6) to 71.14% (pH=3.5) (Fig. 5). Mo removal decreased with increasing pH, where maximum removal was stable at pH 3.5 and decreased after exceeding pH 4.5. This result coincides with the findings of Rabelo *et al.* (2007).

Using cockle shell, the removal efficiency of Mo(VI) varied from 45.8% (pH=6) to 65.1% (pH=3.5) (Fig. 5). Mo removal decreased with increasing pH, where the maximum removal was stable at pH 3.5. This observation agrees with the findings of Pagnanelli *et al.* (2011) and Meena *et al.* (2010).

The pH of the solution is a vital factor in adsorption processes (Mehdizadeh *et al.*, 2014). Usually, more metals are adsorbed at lower pH. In literatures, mostly researchers have used acidic pH to neutral pH in removing metals with adsorption methods because metals are more extractable and harmful in acidic pHs (Olaniran *et al.*, 2013). The heavy metals are completely released under extreme acidic conditions (Annadurai *et al.*, 2003). However, in extremely low pH (>3), metal removal declines because H^+ ions compete with metal cations for the adsorption sites in the system (Abdel-Ghani *et al.*, 2007).

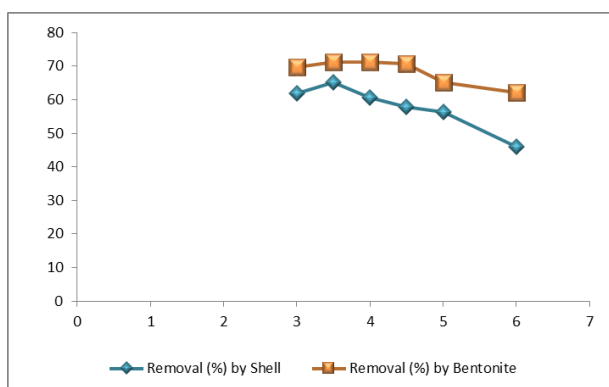


Figure 5. Effects of pH on Removal Efficiency

3.2. Effects of Initial Concentration

In removal using bentonite, the removal efficiency of Mo(VI) varied from 60.7% (initial concentration=60 mg/L) to 69.88% (initial concentration=40 mg/L) (Fig. 6). Mo removal increased along with the initial concentration until 40 mg/L was reached, where maximum removal was stable at 40 mg/L to 50 mg/L and decreased afterward.

In removal using cockle shell, the removal efficiency of Mo(VI) varied from 48.1% (initial concentration=60 mg/L) to 63.0% (initial concentration=30 mg/L) (Fig. 6). Mo removal efficiency increased as initial concentration increased up to 30 mg/L, after which the removal efficiency declined.

This can be clarified that each adsorbent has a fixed number of active adsorption sites, which are accessible to adsorb more metal ions at lower concentrations, but as the concentration increases, the active sites becomes saturated leading to a reduction in the percentage removal. On the other hand, an increase in the uptake capacity for metal ions with increase in initial metal ion concentration was obtained. This sorption characteristic indicated that surface saturation is a function of the initial metal ion concentration in solution (Akpomie and Dawodu, 2015).

At high concentrations, there are more heavy metal ions than available adsorption sites. Hence, the percent removal of heavy metals depends on the initial metal ion concentration; percent removal decreases as initial metal ion concentration increases (Meena *et al.*, 2005).

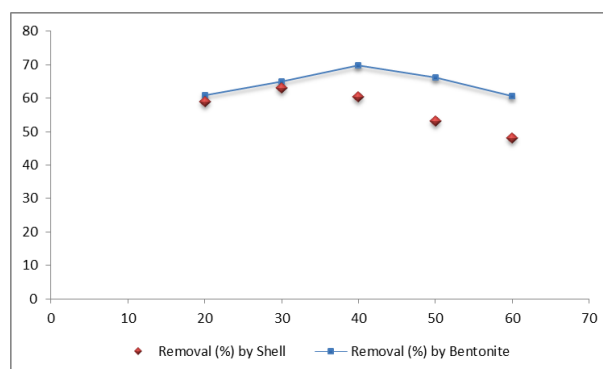


Figure 6. Effects of Initial Concentration of Molybdenum(VI) on Removal Efficiency

3.3. Optimization Process

Tables 4 and 5 show the ANOVA results for response parameters and the value of response at optimum conditions, respectively. Also the 3D surface plots of molybdenum(VI) removal by bentonite and shell are shown in Figure 7. The removal percentage of Mo by shell was highest at pH 3.3, initial Mo(VI) concentration of 20.0 mg/L, and shaking time of 30.0 min. However, the removal percentage of Mo was greatest at pH 5.8, initial Mo(VI) concentration of 39.2, and shaking time of 38.6, showing that bentonite is more efficient than the powdered shell in removing Mo(VI). Mojiri (2011) stated that ion-exchange is the most important way to remove metals. Bentonite is clay which can facilitate ion-exchange because of its

aluminosilicate structure. Adsorption process of metal ions into pores of clays occurred quickly at the first moments. The ion exchange could be a further process for elimination of metals onto bentonite (Galindo *et al.*, 2013). Also bentonite, as clay, has a reasonable cation exchange capacity (CEC) which shows clays can play a strong role in removing metals. Beside these reasons, bentonite surface area is more than the cockle shell surface area based on table 1. So these reasons show why bentonite performance in removing metals is more than cockle shell performance.

Table 4. ANOVA results for response parameters

Adsorbent	Final equation in terms of actual factor	Prob.	R ²	Adj. R ²	SD	CV	PRESS	Prob. LOF
Bentonite	$33.020 - 35.648A + 1.873B + 4.806C + 3.693A^2 - 0.023B^2 - 0.060C^2 - 0.012AB - 0.006AC + 0.0009BC$	0.0001	0.9842	0.9700	2.22	3.27	737.04	0.6312
Shell	$60.455 + 23.753A - 1.502B - 0.179C - 3.953A^2 + 0.012B^2 - 0.0008C^2 + 0.069AB + 0.034AC + 0.02BC$	0.0001	0.9733	0.9493	1.78	3.10	472.05	0.0822

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.

In final equations, where A is pH; B is initial concentration of Mo (mg/L), and C is shaking time (min).

Table 5. The value of response at optimum conditions

Adsorbent	Independent Factors			Responses
	A	B	C	Mo(VI) rem., (%)
Bentonite	5.89	39.27	38.62	81.38
Cockle Shell	3.31	20.00	30.00	73.69

(A): pH; (B) Initial Concentration of Mo (mg/L); (C): Shaking Time (min)

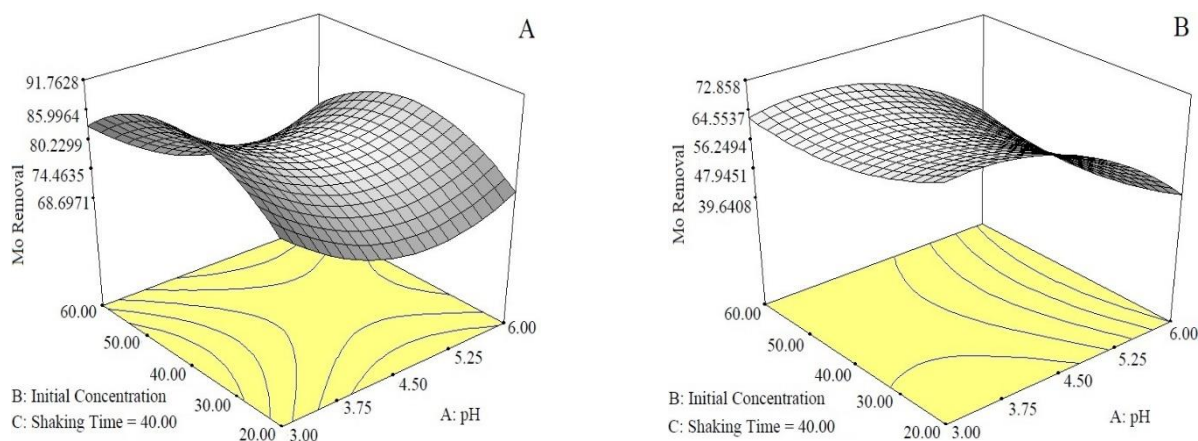


Figure 7. The 3D Surface Plots of Molybdenum(VI) Removal by (A) Bentonite, and (B) Shell

3.4. Langmuir Isotherm

Langmuir quantitatively demonstrates the formation of a monolayer adsorbate on the outer surface of the adsorbent. Thus, Langmuir displays the equilibrium distribution of ions between the solid and liquid phases (Dada *et al.*, 2012). The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. Langmuir equation can be summarized as (Altig, 2013).

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

where x/m is the mass of the adsorbate adsorbed per unit mass of adsorbent (mg adsorbate per g activated carbon), a and b are the empirical constants, and C_e is the

In addition, the optimum shaking time set to remove Mo using shell and bentonite was 30 and 39 min. Meena *et al.* (2005) stated that the contact time required to attain equilibrium is dependent on the initial concentration of heavy metals. For the same concentration, the percentage removal of heavy metal increases with increase of contact time until equilibrium is attained.

equilibrium concentration of adsorbate in the solution after adsorption (mg/L).

The adsorption capacities (Q) of Mo using bentonite and shell were 0.981 mg/g, and 0.975 mg/g, respectively (Table 6; Fig. 8–9). Mojiri *et al.* (2016) reported $Q=0.70$ mg/g for adsorption of Fe by composite adsorbent. The energy of adsorption values (b) for removal by bentonite and shell were -8.671 and -6.519 L/mg, respectively. The negative values indicated that the increase in C_e caused a decrease in x/m (Aziz *et al.*, 2012). The R^2 values (goodness fit criterion) for both isotherms were calculated using linear regression, and R^2 of removal by bentonite and shell were 0.9847 and 0.980, respectively. These results show that the Langmuir isotherm can be used to explain the adsorption by bentonite and shell.

The same R^2 values were reported by Doddiba *et al.* (2010) regarding Mo adsorption by Pb–Fe-based adsorbents. A dimensionless equilibrium parameter separation factor (RL) could be used to express the characteristics of the

Langmuir isotherm (Isa *et al.*, 2007). The RL values for Mo(VI) adsorption by bentonite and shell were -0.003 and -0.005, respectively.

Table 6. Langmuir equation for Mo(VI) removal by bentonite and shell

Adsorbent	Q_0 (mg/g)	b	R^2	$R_L = \frac{1}{1+bC_0}$	Isotherm type*
Bentonite	0.981	-8.671	0.9847	-0.003	unfavorable
Shell	0.975	-6.519	0.980	-0.005	unfavorable

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

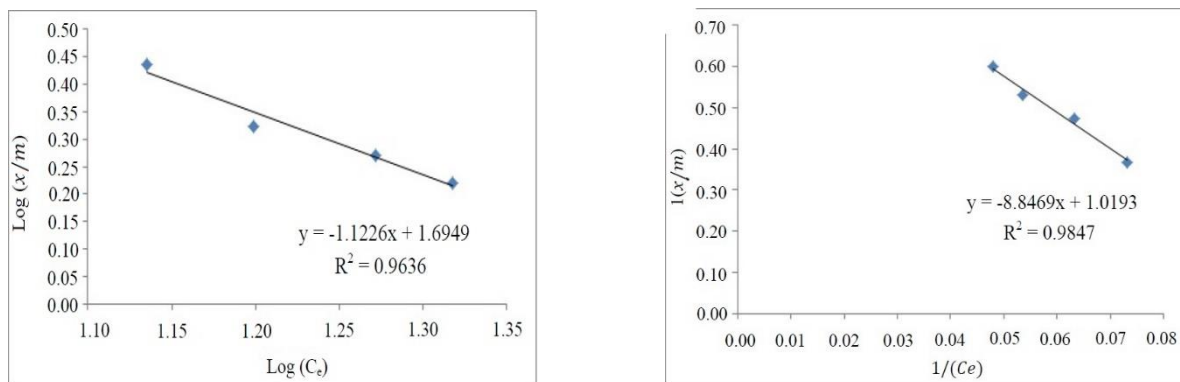


Figure 8. Freundlich and Langmuir Isotherms Regression for Removal by Bentonite

3.5. Freundlich isotherm

The Freundlich isotherm is commonly used to describe the adsorption characteristics for heterogeneous surfaces (Dada *et al.*, 2012). The Freundlich equation can be written as

$$\frac{x}{m} = K_f C_e^{1/n} \quad (5)$$

where K_f is a constant indicative of the relative adsorption capacity of the adsorbent ($\text{mg}^{1-(1/n)} \text{L}^{1/n} \text{g}^{-1}$) and n is a constant that refers to the intensity of the adsorption (Hamdaoui and Naffrechoux, 2007).

The obtained Freundlich capacity factors (K) for Mo(VI) removal by bentonite and shell were 49.57 and 22.72

Table 7. Freundlich equation for Mo(VI) removal by bentonite and shell

Adsorbent	K_f (mg/g (L/mg) $^{1/n}$)	$1/n$	n	R^2
Bentonite	49.578	-1.122	-0.890	0.9636
Cockle Shell	22.727	-0.833	-1.199	0.9286

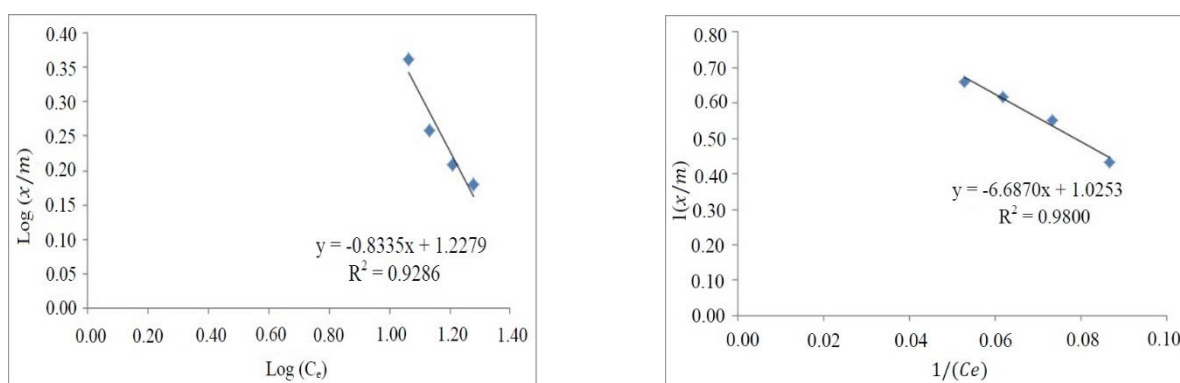


Figure 9. Freundlich and Langmuir Isotherms Regression for Removal by Shell

(mg/g) (L/mg) $1/n$, respectively (Table 7, Figs. 8–9). Namasivayam and Sureshkumar (2009) reported K_f values of 17.1 mg/g. Higher K values showed greater capacities of adsorption (Aziz *et al.*, 2004). The obtained $1/n$ values for Mo (VI) removal by bentonite and shell were -1.12 ($n=0.89$) and 0.323 ($n=-1.19$), respectively. The $1/n$ (slope of the line) was negative because increasing the $\log(C_e)$ caused the decrease of $\log(x/m)$. R^2 values for Mo removal by bentonite and shell were 0.9636 and 0.9286, respectively. These observations show that the adsorption of Mo by bentonite and shell could be well explained by the Freundlich isotherm. The same R^2 values have been reported by Lian *et al.* (2012).

4. Conclusions

Environmental pollution has rapidly increased because of urbanization and industrialization. Several pollutants such as heavy metals accumulate in water and soil. Mo is a heavy metal and a toxic pollutant. The effects of pH and initial Mo(VI) concentration on removal of Mo using bentonite and cockle shell were investigated, and CCD and RSM were used to optimize removal efficiency. The main conclusions of this study are presented below.

- (1) Mo(VI) removal increased as pH increased until 3.5.
- (2) Removal efficiency increased as initial concentration increased. When initial concentrations exceeded 30-40 mg/L during shell and bentonite treatments, the removal efficiency decreased.
- (3) Compared with the shell, bentonite was more efficient in removing Mo from water. Bentonite could remove 81.3% of Mo and shell could remove 73.6% of Mo from water.
- (4) Adsorption of Mo(VI) by bentonite and shell could be explained based on the resulting R^2 values of the Langmuir and Freundlich isotherms.

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