Effective clay material enriched with thiol groups for Zn(II) removal from aqueous media: A statistical approach based on response surface methodology

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ABSTRACT

In the present work, the removal of Zn(II) ions from aquatic environments onto 3-mercaptopropyl trimethoxysilane modified kaolin (MK) was investigated in a batch system. Moreover, the optimization and effects of independent parameters such as pH, initial Zn(II) concentration (C_o, mg/L) and contact time (min) on the uptake of Zn(II) onto MK were examined by response surface methodology (RSM). Central composite design (CCD) in RSM, the most popular statistical technique, was successfully applied to optimize and model the selected parameters (pH, C_o, contact time) for Zn(II)% adsorption onto MK. The number of experiments based on CDD was *20*, a total of *20* sets which included fourteen factorial points and six center points were performed to obtain the maximum Zn(II) uptake from aqueous solutions. The optimum points obtained from CCD were 6.39, 50.09 mg/L and 76.10 min for pH, C_o, and contact time, in their given order. In these optimal conditions, the maximum removal percentage was found to be 86.19%. The results indicated that the removal yield of Zn(II) from aqueous media onto MK was successfully performed by CCD in RSM. It can be concluded that MK is also a promising material for the uptake of other heavy metals similar to Zn.

1. Introduction

Rapid industrialization and growing population have become critical environmental issues due to the increasing contamination of water resources by pollutants such as heavy metal ions [1]. Environmental pollution is one of the most significant issues for many forms of life [2], because the presence of heavy metals in aquatic media is a major concern owing to their toxic effects on all living organisms [3]. Zinc, a heavy metal, is found in various industrial effluents including those from galvanizing plants, leather industries, electroplating, paper mills, and mining [3, 4]. These toxic effluents in aqueous environments cause serious health risks like skin irritation, stomach cramps, anemia, cancer, nausea, brain damage, and accumulative poisoning [4]. Therefore, it becomes mandatory to remove Zn(II) ions as a toxic metal from aqueous environments.

Several traditional approaches were reported to eliminate heavy metal ions from aquatic environments like reverse osmosis, chemical precipitation, electrochemical treatment, membrane processes, and adsorption. These treatment procedures have some disadvantages because of economic constraints, sludge disposal, and inefficiency at low heavy metal ion concentrations [5]. Among these techniques, the adsorption approach is considered more economic and effective for uptake of contaminants from wastewater owing to high efficiency, low cost, and simplicity of operation [6]. The effectiveness of the adsorption process depends on cost, nature, and regeneration of the selected adsorbent. Hence, adsorbents with low-cost and abundant in nature such as clay minerals have attracted attention in the field of adsorption process. These materials, however, have some drawbacks such as low removal rate, high regeneration cost, low surface area and long adsorption equilibrium time [4, 5, 7]. Recently, surface-functionalized natural clay minerals gained increasing attention via to enhance the adsorption capacity the adsorption process [8]. For example, Olu-Owolabi and Unuabonah [9] reported that sulfur and phosphorus modified bentonite had enhanced removal capability for Zn(II) adsorption after surface modification in comparison with raw bentonite. Jemima et al. [10] evaluated the removal performance for Cr(VI) by modifying montmorillonite clay with various cationic surfactants. They reported that modified-

montmorillonite materials had excellent adsorption performance compared to unmodified clay.

Conventional methods require extra experiments, extra time, and large doses of materials because only one independent parameter affecting the adsorption is changed while the other parameters are kept at fixed points during these processes. These methods are therefore disadvantageous. Statistical programs such as response surface methodology (RSM) are promising to overcome these problems [11, 12].

The objective of this study was to model and optimize the removal of Zn(II) ions onto 3-mercaptopropyl trimethoxysilane-modified kaolin (MK) by using response surface methodology (RSM). A central composite design (CCD) was used to determine optimal conditions for the independent parameters, such as pH, initial Zn(II) concentration, and contact time, that affect the removal of Zn(II) onto MK from aqueous environments.

2. Materials and methods

Clay minerals used as adsorbent in the current work were acquired from the JSC Glukhovetsky Kaolin Plant located in Ukraine. Prior to utilization as adsorbent, the obtained materials were washed with ultra-pure water and dried in a drying-oven at 120 ℃ for 18 h. The dried samples were then ground into fine powder using a mill and passed through a sieve. Finally, the prepared samples were modified based on the previously reported method in the literature [13].

Zn(II) stock solution (500 mg/L) was prepared by dissolving the calculated metal salt of $Zn(NO_3)_2 \cdot 6H_2O$ in 500 mL of ultra-pure water. The desired concentrations were prepared by using dilutions of the stock solution.

All tests were carried out by adding 0.25 g amount of MK in 50 mL to the heavy metal ion solution with desired pH, initial Zn(II) ions concentration (C_o, mg/L), and contact time (min). All tests for the three selected independent parameters of pH, C_o, and contact time were generated by CCD in RSM by taking fixed mixing rate of 700 rpm and room temperature. After that, the suspension of the adsorbent was separated by a centrifuge at 9000 rpm for 15 min. The obtained supernatant was analyzed by an atomic absorption spectrophotometer (AAS, Thermo Scientific iCE 3000 SERIES, USA). The removal percentage of Zn(II) with adsorption onto MK was determined by the following equation;

$$Zn(II)\%\ Adsorption = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (1)$$

where C_o and C_e (mg/L) are the initial and equilibrium Zn(II) concentration in the solution (mg/L), respectively.

CCD in RSM is the most effective program and was applied to optimize the selected independent parameters. The levels of

the selected parameters were coded as *+1* (upper), *0* (central), and *-1* (bottom), as presented in Table 1. A second-order polynomial model typifying system behavior is represented as follows:

$$\hat{y}_n = \beta_o + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{3} \beta_{ij} x_i x_j \qquad (2)$$

where $\hat{y}_n$ is the predicted response (Zn(II)% adsorption), X_i ($i = 1–3$) are the independent parameters being studied, β_0, β_i, β_{ii}, and β_{ij} are the intercept, the linear, the quadratic, and the interactive effects, respectively.

3. Results and discussion

3.1. Characterization of adsorbent

MK characterization was already reported in our previous study [13]. Based on the obtained results, transform infrared (FTIR) spectroscopy analysis results indicated that the peak representing –SH stretching vibration was present at 2550-2600 cm^{-1}, which was not observed in unmodified kaolin. Furthermore, the characteristic peak observed at 2931 cm^{-1} was due to methoxy groups ($-OCH_3$) in MK. From energy-dispersive x-ray spectroscopy (EDX) results, the sulfur peak was different from raw kaolin, indicating that the surface of the kaolin was successfully covered with –SH groups. X-ray diffraction (XRD) analyses showed that the diffraction signal intensity was diminished, relating to the formation of silanol groups on the kaolin surface and methoxy groups.

3.2. Experimental and statistical analysis

The CCD approach in RSM was successfully performed to evaluate the optimal process points for Zn(II) onto MK. The threeindependent parameters (pH, C_o, and contact time) were selected to maximize Zn(II) adsorption onto MK. These parameters were segregated into three levels with a coded value (*-1, 0, +1*). From CCD, *20* experimental runs were carried out as given in Table 1. These tests designated by CCD were performed against percentage removal of Zn(II) for each independent parameter. The second-order model equation obtained from CCD which indicates the relationship between Zn(II) removal efficiency and independent variables is given in the following:

$Zn\%\ adsorption = -47.54189 + 27.40655[pH] + 1.48875[C_o]+ 0.48135[Contact\ time]$
$+ 7.08333E\text{-}003[pH][C_o] - 0.018409[pH][Contact\ time]+ 3.00606E\text{-}003[C_o][Contact\ time]$ (4)
$- 2.45621[pH]^2 - 0.015857[C_o]^2 - 2.98873E\text{-}003[Contact\ time]^2$

Statistical analysis was used to evaluate whether the adsorption process was significant. For this purpose, the importance of the suggested quadratic model for the removal of Zn(II) onto MK was determined by the analysis of variance (ANOVA). The ANOVA results (Table 2) showed that the suggested model for the removal percentage of Zn(II) ions onto MK was dependent on the selected parameters. Moreover, low *p*-value (< 0.0001) and the determination of

coefficient (R^2) value of 0.96 demonstrated that the obtained model has good fit for predicting the removal percentage of Zn(II) onto MK.

Table 2 illustrates that the linear factors (*A* and *C*), the interaction of factor (*BC*), and the quadratic of factors (A^2, B^2, and C^2) are statistically significant model terms. However, it can be said that any independent parameter has little effect on the model equation, even if the other parameters were insignificant terms to the response.

Table 1. *Uncoded and coded values of the independent parameters and CCD matrix corresponding to response values.*

Parameters	Uncoded and coded values		
	-1	*0*	*+1*
pH (A)	2	5	8
C_o (mg/L, B)	20	50	80
Contact time (min, C)	10	65	120

Run	A	B (mg/L)	C (min.)	Zn(II)% removal
1	5(0)	50(0)	65(0)	84.50
2	5(0)	50(0)	65(0)	84.41
3	8(+1)	50(0)	65(0)	72.12
4	8(+1)	80(+1)	10(-1)	41.93
5	5(0)	50(0)	65(0)	83.95
6	5(0)	50(0)	65(0)	83.88
7	5(0)	20(-1)	65(0)	75.53
8	2(-1)	20(-1)	10(-1)	22.93
9	2(-1)	50(0)	65(0)	66.36
10	2(-1)	20(-1)	120(+1)	36.74
11	5(0)	50(0)	10(-1)	81.86
12	5(0)	80(+1)	65(0)	78.62
13	2(-1)	80(+1)	120(+1)	57.55
14	5(0)	50(0)	65(0)	84.62
15	8(+1)	80(+1)	120(+1)	63.43
16	5(0)	50(0)	65(0)	84.25
17	8(+1)	20(-1)	10(-1)	38.41
18	8(+1)	20(-1)	120(+1)	45.86
19	2(-1)	80(+1)	10(-1)	18.11
20	5(0)	50(0)	120(+1)	82.75

Table 2. *ANOVA results.*

Source	Sum of squares	df	Mean square	F value	p-value (Prob > F)
Model (significant)	9222.80	9	1024.76	27.19	< 0.0001
A-pH	360.72	1	360.72	9.57	0.0114
B-C_o (mg/L)	161.36	1	161.36	4.28	0.0654
C-Contact time (min.)	690.39	1	690.39	18.32	0.0016
AB	3.25	1	3.25	0.086	0.7750
AC	73.81	1	73.81	1.96	0.1919
BC	196.81	1	196.81	5.22	0.0454
A^2	1343.85	1	1343.85	35.66	0.0001
B^2	560.06	1	560.06	14.86	0.0032
C^2	224.78	1	224.78	5.97	0.0347

R2 = 0.96

Adj. R2 = 0.93   C.V. % = 9.53   Press = 2590.92
Std. Dev. = 6.14   Adeq Precision = 14.82

The comparison of values predicted by the model vs observed for the removal percentage of Zn(II) is presented in Figure 1a. The observed data are quite close to the predicted data, indicating that the suggested model satisfactorily describes the correlation between independent parameters and adsorption of Zn(II) on MK. The normal probability plot of the residuals for Zn(II) adsorption is illustrated in Figure 1b. From Figure 1b, the errors are normally distributed, indicating that the obtained quadratic model could perfectly estimate the experimental values.
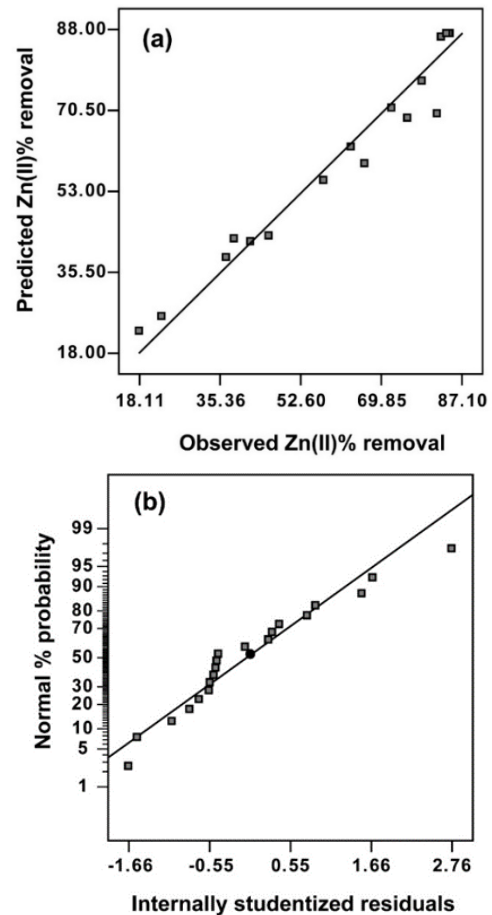

Figure 1. *(a) Predicted versus observed values and (b) residual plots for Zn(II)% removal.*

Figure 2a and b show the simultaneous effect of pH and C_o on the removal efficiency of Zn(II) and the main effect of pH on the removal percentage of Zn(II), respectively. According to Figure 2a and b, increasing the pH of the solution from 2 to ~6 resulted in an increase in Zn(II)% removal. This is attributed to Pearson's Hard and Soft Acid-Base (HSAB) theory, indicating that –SH groups and Zn(II) ions have a strong bond for each other [13]. Moreover, the surface of MK is negatively charged at higher pH values. Therefore, the removal of Zn(II) gradually increases while pH increases due

to electrostatic attraction between negatively-charged MK and Zn(II) ions [14]. When the pH was increased to the upper level of 6, the removal rates for Zn(II) rapidly reduced. This can be explained by the $Zn(OH)_2$ formation of Zn(II) ions [1, 7].
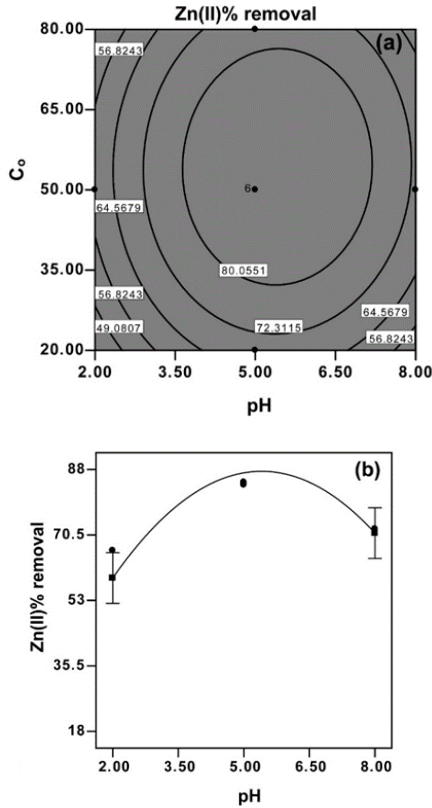

Figure 2. *(a) Contour plot of pH and Co, (b) the main effect plot of pH for Zn(II)% removal onto MK.*

Similarly, the contour plot of C_o and contact time and the main effect of C_o on Zn(II)% removal onto MK is shown in Figure 3a and b, respectively. Analysis of the C_o effect revealed that as C_o increased in the ranges from 20 to 50 mg/L, the removal rate of Zn(II) increased; however, it decreased when C_o was more than 50 mg/L. The results imply that available binding sites for Zn(II)% removal were saturated with heavy metal ions and equilibrium was reached [14]. The correlation between the removal efficiency for Zn(II) ions and contact time vs pH and the main effect of contact time on Zn(II)% adsorption are given in Figure 4a and b, respectively. As can be understood from Figure 4a and b, Zn(II)% removal increased with an increase in contact time from 10 to 90-100 min and did not change significantly with contact time after 90-100 min. This observation confirmed that an equilibrium state results at about 90-100 min for Zn(II)% removal [15].
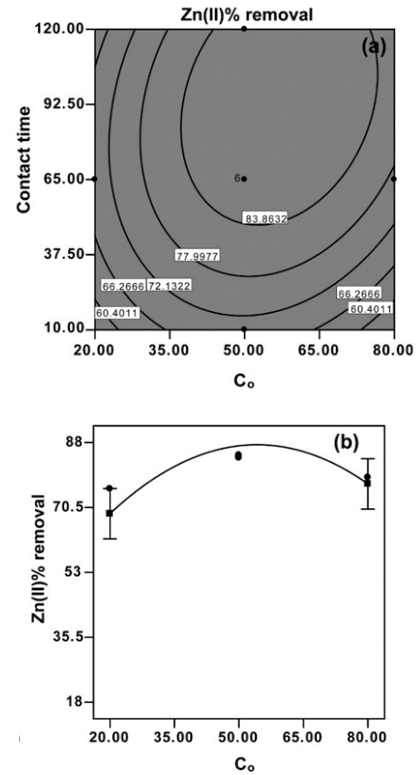

Figure 3. *(a) Contour plot of C_o and contact time, (b) the main effect plot of C_o for Zn(II)% removal onto MK.*
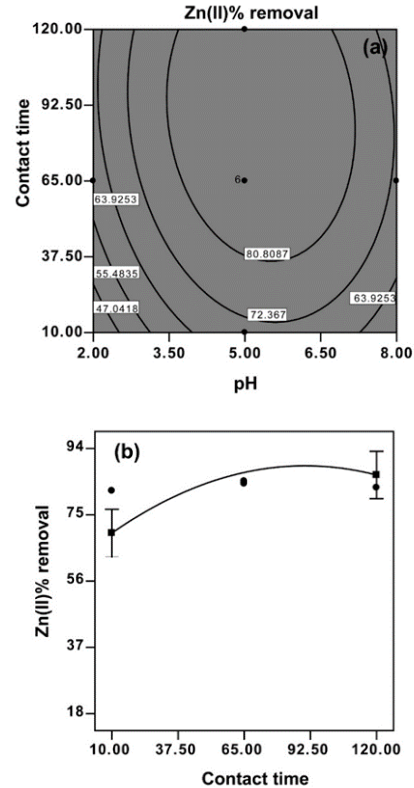

Figure 4. *(a) Contour plot of pH and contact time, (b) the main effect plot of contact time for Zn(II)% removal onto MK.*

3.3. Numerical analysis results

It is important to maximize the Zn(II) ion removal rate onto MK. This method utilized a quadratic model to maximize Zn(II)% removal within the selected experimental range. The numerical analysis approach in CCD was used to determine the optimal points for Zn(II)% removal onto MK. The optimal process points for Zn(II)% removal were found to be pH = 6.39, C_o = 50.09 mg/L, and contact time = 76.10 min. At these points, the maximum Zn(II)% removal was found as 86.19%. Some tests were made to evaluate Zn(II)% removal at the obtained optimum adsorption points. The findings indicated that the removal percentage of Zn(II) onto MK is markedly increased compared to raw kaolin (49.15%).

The maximum values for Zn(II) adsorption with different adsorbents are given in Table 3. These results indicated that the adsorption performance of MK are substantially good for Zn(II) adsorption and it is an ideal material for removal of Zn(II) from aqueous media.

3.4. Adsorption mechanism

MK was used as an adsorbent to remove Zn(II) ions from aqueous environments. The revelation of the possible mechanism has major significance to evaluate the nature of the process and show how MK as adsorbent interacts with Zn(II) as adsorbate. Figure 5 shows the proposed model for Zn(II)% removal onto MK. During Zn(II) adsorption, Zn(II) ions first pass to the MK surface and reach the surface of MK by transfer from the boundary layer between the aqueous solution and MK. Subsequently, Zn(II) ions are affected by functional groups on MK. Then, Zn(II) ions are adsorbed onto MK. According to HSAB theory, there is strong interaction between thiol groups on the surface of MK and Zn(II) ions with each other [16]. Therefore, Zn-S bonding could be formed with –SH groups on the surface owing to the electrostatic interactions [17-19].

Moreover, the surface charge of the adsorbent is directly related to the solution pH. At low pH-values, the surface is positively charged and presence H^+ ions in the solution, leading to the decrease of Zn(II)% removal due to electrostatic repulsion between Zn(II) ions and positively charged adsorbent. On the other hand, an increase in pH of Zn(II) solution results in the reduction of positive surface charge, indicating that the electrostatic attraction between the negatively charged adsorbent surface and the positively charged Zn(II) ions. It is true that the predominant species of Zn(II) is $Zn(OH)_2$ at pH > 8, corresponding that decrease in adsorption yield compared to neutral conditions [2, 20].

Table 3. *A comparison of Zn(II) adsorption for previous studies in literature.*

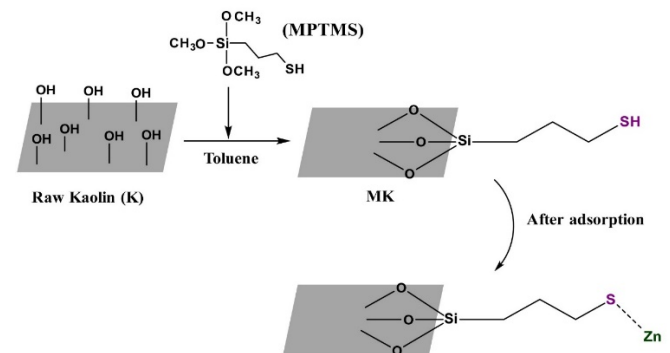| Material	C_o (mg/L)	Ads. Dosage (g/50 mL)	q_{max} (mg/g)	Zn(II) % removal	Ref.
Seed pods	50.13	0.15	13.04	78.02	[14]
Palm kernel shell based activated carbon	55	0.55	4.29	85.82	[3]
Oil palm empty fruit bunches	200	0.4	15.18	25.49	[21]
Maghemite (γ-Fe_2O_3)	50	0.24	4.79	45.41	[5]
Modified bentonite	50-200	0.5	35.21	43.88	[22]
Gracilaria Corticata	100	1	4.75	95	[12]
MK	50.09	0.25	8.64	86.19	**This work**

Figure 5. *Possible adsorption mechanism for Zn(II) onto MK.*

4. Conclusions

The influence of independent parameters such as pH, C_o, and contact time on the removal of Zn(II) from aqueous environments by MK was studied using CCD based on RSM. A quadratic model for Zn(II)% removal was developed using CCD, indicating that the obtained model fitted well to experimental values. ANOVA results showed that *p*-value is quite low (< 0.0001). It can be said that the quadratic model is sufficient to predict experimental data. From numerical analysis results, the maximum removal rate of 86.19% for Zn(II) by MK was found at pH of 6.39, C_o of 50.09 mg/L, and contact time of 76.10 min. Consequently, the results suggest that MK has potential use as adsorbent for the removal of heavy metal ions such as Zn from aqueous environments. Moreover, it can be said that RSM is a promising approach to optimize and model the independent parameters affecting adsorption technology.

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