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METODOLOGIA DE SUPERFÍCIE DE RESPOSTA PARA OTIMIZAÇÃO DA ADSORÇÃO DE METAIS PESADOS EM UMA SOLUÇÃO MULTI-METAIS POR PELLETS DE ZEÓLITAS DE BENTONITA-CAOLIM

RESPONSE SURFACE METHODOLOGY FOR OPTIMIZATION OF HEAVY METAL ADSORPTION IN A MULTIMETAL SOLUTION BY BENTONITE-KAOLIN-ZEOLITE PELLETS

METODOLOGÍA DE SUPERFICIE DE RESPUESTA PARA LA OPTIMIZACIÓN DE LA ADSORCIÓN DE PELLETS DE BENTONITA-CAOLÍN-ZEOLITA EN UNA SOLUCIÓN MULTIMETÁLICA

CARBONEL-RAMOS, Dalia Elisa[1*]; CHIRINOS, Hugo David[2]; GOMÉZ-MARROQUÍN, Mery Cecilia[3]; AGARWAL, Madhu[4].

[1,2] Faculty of Environmental Engineering, National University of Engineering, Peru

[3] Faculty of Geological, Mining and Metallurgic Engineering, National University of Engineering, Peru

[4] Department of Chemical Engineering, Malaviya National Institute of Technology Jaipur, India

** Correspondence author*
e-mail: dcarbonelr@uni.pe

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RESUMO

Introdução: A contaminação das águas superficiais e subterrâneas com metais pesados é um grande problema ambiental. Os minerais de argila são porosos e eficientes para adsorver íons metálicos. Entre as tecnologias de tratamento disponíveis, a adsorção é a mais econômica, fácil de operar, escalonável e replicável para remediar metais pesados da solução aquosa. **Objetivo:** O objetivo desse estudo foi avaliar o desempenho de adsorção de pellets de argila de aluminossilicatos naturais, bentonita (29%), caulim (4%) e zeólita (67%) para remoção de metais pesados de soluções aquosas. **Métodos:** O efeito de condições operacionais ótimas, como tempo de contato, dose de adsorvente, pH e concentração inicial de metais pesados, foi estudado. Estudos cinéticos e de equilíbrio também foram realizados. Os adsorventes foram caracterizados usando análise de FTIR. **Resultados e Discussão:** Os valores ótimos para tempo de contato, dose do adsorvente, pH e concentração inicial de chumbo, cobre e cádmio foram; 240 min; 25 g/L; 4,3; e 4mg/L, 7 mg/L e 2 mg/L, respectivamente. A isoterma de Langmuir foi o modelo de isoterma mais bem ajustado para os três metais. A cinética de adsorção mostrou que a adsorção de chumbo e cobre seguiu o modelo de pseudo-segunda ordem, enquanto o cádmio se adequou ao modelo de pseudo-primeira ordem. A seletividade dos pellets para os íons metálicos foi da ordem de Pb> Cu> Cd. **Conclusões:** A nova combinação de pellets de bentonita-caulinita-zeólita funcionou bem no tratamento de águas residuais terciárias e foi utilizada com sucesso como um adsorvente natural em solução multimetal. Os resultados confirmaram que os grânulos de argila usados têm melhor capacidade de adsorção do que muitos outros estudos relatados. A capacidade de adsorção máxima pode ser aumentada ajustando a temperatura de calcinação e aplicando tratamentos químicos aos grânulos de argila antes da extrusão. A análise da superfície de resposta avaliou os valores ideais previstos para os quatro fatores operacionais.

Palavras-chave: Pelotas de argila; Adsorção; Solução multimetal; Análise de superfície de resposta

ABSTRACT

Background: Heavy metals contamination of surface and groundwater is a major environmental problem. Clay minerals are porous and are efficient to adsorb metal ions. Amongst the available treatment technologies, adsorption is the most cost-effective, easy to operate, scalable, and replicable to remediate heavy metals from water solution. **Aim:** This study aimed to assess the adsorption performance of clay pellets of natural aluminosilicates, bentonite (29%), kaolin (4%) and zeolite (67%) to remove heavy metals from aqueous solutions. **Methods:** The effect of optimal operating conditions like contact time, adsorbent dose, pH, and heavy metals initial concentration has been studied. Kinetic and equilibrium studies were also performed. Adsorbents were characterized using FTIR analysis. **Results and Discussion:** Optimum values for contact time, adsorbent dose, pH, and initial concentration of lead, copper, and cadmium were; 240 min; 25 g/L; 4.3; and 4mg/L, 7 mg/L and 2 mg/L, respectively. The Langmuir isotherm was the best-fitted isotherm model for the three metals. Adsorption kinetics showed that the lead and copper adsorption followed the pseudo-second-order model while cadmium suited with the pseudo-first-order model. The selectivity of the pellets towards the metal ions was in the order of Pb > Cu > Cd. **Conclusions:** The new combination of bentonite-kaolinite-zeolite pellets worked well in tertiary wastewater treatment and successfully utilized as a natural adsorbent in multimetal solution. The results confirmed that the used clay pellets have better adsorption capacity than many other reported studies. Maximum adsorption capacity can be further increased by adjusting the calcination temperature and applying chemical treatments to the clay pellets before extrusion. The response surface analysis evaluated the predicted optimal values for the four operating factors.

Keywords: *Clay pellets; Adsorption; Multimetal solution; Response surface analysis.*

RESUMEN

Antecedentes: La contaminación por metales pesados en aguas superficiales y subterráneas es un grave problema ambiental. Entre las tecnologías disponibles de tratamiento para remover metales pesados de soluciones acuosas, la adsorción es la más rentable, fácil de operar, escalable y replicable. **Objetivo:** El objetivo de este estudio fue evaluar el rendimiento de adsorción de pellets de aluminosilicatos naturales de bentonita (29%), caolín (4%) y zeolita (67%) para eliminar metales pesados de soluciones acuosas. **Métodos:** Se estudió el efecto de las condiciones óptimas de funcionamiento, como el tiempo de contacto, la dosis de adsorbente, el pH y la concentración inicial de metales pesados. También se realizaron estudios cinéticos y de equilibrio. Los adsorbentes se caracterizaron mediante análisis FTIR. **Resultados y Discusión:** Los valores óptimos de tiempo de contacto, dosis de adsorbente, pH y concentración inicial de plomo, cobre y cadmio fueron; 240 min; 25 g/L; 4,3; y 4 mg/L, 7 mg/L y 2 mg/L, respectivamente. La isoterma de Langmuir fue el modelo de mejor ajuste para los tres metales. La cinética de adsorción mostró que el plomo y cobre se ajustaron mejor al modelo de pseudo-segundo orden, mientras que el cadmio se ajustó mejor al modelo de pseudo-primer orden. La selectividad de los pellets hacia los iones metálicos fue del orden de Pb> Cu> Cd. **Conclusiones:** Los pellets fabricados a partir de bentonita-caolín-zeolita demostraron ser efectivos como adsorbentes naturales en el tratamiento terciario de aguas residuales en una solución multimetálica. Los resultados confirman que los pellets usados tienen una mejor capacidad de adsorción que muchos otros estudios reportados. La capacidad máxima de adsorción podría aumentarse ajustando la temperatura de calcinación y aplicando tratamientos químicos a los adsorbentes antes de la extrusión.

Palabras clave: *Pellets de arcilla; Adsorción; Solución multimetálica; Análisis de superficie de respuesta*.

1. INTRODUCTION:

Heavy metal contamination of surface and groundwater is a major problem since the 1990s (UNEP, 2016). Agricultural runoffs contain high amounts of toxic inorganic and organic substances (Voulvoulis and Georges, 2016). Pesticides and fertilizers used in agriculture cause nonpoint-source pollution to surface water and groundwater. Natural geomaterials such as clay minerals and zeolites help control the release of fertilizers, pesticides, and herbicides (Manjaiah *et al*., 2019). Several studies explored the use of clay and zeolites to remediate toxic environmental pollutants (Calvo and Garcia-Lorenzo, 2018; Rao and Kashifuddin, 2016; Uddin, Ahmed, and Naushad, 2019).

Heavy metals are of special concern due to their toxic characteristics such as diffusion, persistence, toxic effects even at low concentration, bioaccumulation, and biomagnification. They can spread easily, which makes them ubiquitous, and they can be toxic at very low concentrations. The harmful effects of heavy metals can be long lasting and damage vital body organs. Various technologies have been implemented for the removal of heavy metals such as ion exchange (Dąbrowski, Hubicki, Podkościelny, and Robens, 2004), ultrafiltration and flocculation (Huang *et al*., 2016), membrane filtration (Alarifi *et al*., 2020), electrodialysis (Al-Shannag *et al*., 2015) and adsorption (Uddin and Nasar, 2020). Ion exchange is famous and commonly used for demineralization and disinfection of water. Although the ion-exchange system works well at low concentrations, yet the technique requires sophisticated equipment. Coagulation is a chemical procedure that is easy to operate and requires low maintenance but it generates large quantities of contaminated sludge. The membrane filtration process produces a pure effluent, but the energy demand is high as well as the operational and maintenance cost. Adsorption, however, shows the best performance in terms of removal efficiency of aqueous pollutants compared to other methods. Adsorption is a low-cost, reliable, simple to install method which is easy to operate, demands fewer energy requirements; is adjustable, and easily replicable. Adsorption mechanism is generally being of weak physical adsorption or strong chemical adsorption. The physical adsorption process includes Van der Waals or electrostatic interaction between the surface of the adsorbent and targeted pollutants. Chemical adsorption is generally fast and involves chemical bonding between adsorbent and pollutants.

The use of clays and zeolites in the adsorption process for wastewater treatment has many advantages over other existing technologies. They are natural, less expensive, and provide significant benefits in the removal of metal ions. However, it is crucial to generate information that allows its application at the industrial level, such as operation conditions, equilibrium, and adsorption kinetics. To prepare the novel ionic liquid clay, Kakaei *et al*. recently modify raw clinochlore with triazole and triazolium ligands (Kakaei, Khameneh, Hosseini, and Moharreri, 2020). The prepared ecofriendly modified adsorbent was applied for the removal of lead, cobalt, and zinc ions. The catalyst material proved to be functional for heavy metal adsorption. In another study, single and mixed pillared clays were successfully utilized to remove inorganic pollutants from the water (Mnasri-Ghnimi and Frini-Srasra, 2019). In comparison, it was found that natural pillared clays had better adsorption properties for cadmium, cobalt, and copper metal ions. Recently, three different forms of raw attapulgite clay were prepared for the removal of cadmium and lead, and it was found that the adsorbent prepared by hydrothermal reaction and calcination was shown excellent adsorption properties while all the three adsorbents showed high adsorption for lead ions (Huang *et al*., 2020). Ravikumar and Udayakumar mixed *Moringa oleifera* seeds with bentonite clay and prepared a novel green clay composite for heavy metals removal (Ravikumar and Udayakumar, 2020). The natural zeolite of Kamchatka region, Russia was chosen to minimize the contents of heavy metals in the wastewater of the region (Belova, 2019). It was found that Yagodninsky deposit zeolites are very effective to extract several toxic metal ions from polluted water. The adsorption was in the row of $Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+}$. Pottery sludge consists of silica, alumina, iron oxide was applied for copper removal (Uddin, Rao, and Chandra Mouli, 2018). Glaze, which consists of clay minerals, boron, silica, fluxes, and melting agents, was proved to be an excellent adsorbent for copper (II) removal (Rao and Kashifuddin, 2012). So, there are many studies related to removing metal ions using clay adsorbents; however, adsorption in multi-metallic solutions with cylindrical shape pellets is not studied. This paper presents the first time use of clay pellets for tertiary wastewater treatment. The use of the pelletizing process reduces the cost, which makes this study attractive. From an economic point of view, the development of this material makes the removal of heavy metals from wastewater quite profitable.

Therefore, this study aimed to assess the adsorption performance of clay pellets of natural aluminosilicates, bentonite (29%), kaolin (4%) and zeolite (67%) to remove heavy metals from aqueous solutions.

2. MATERIALS AND METHODS:

The study was conducted in the Research Laboratory of the Environmental Engineering Faculty, National Engineering University, Peru. A third party laboratory present in the Science Faculty of the same university did some analysis.

2.1. Clay characterization

Kaolin and bentonite were obtained from a natural deposit in the city of Cajamarca, North Peru, while raw zeolite was obtained from Hydro Source, LLC. The analysis of the mineralogical composition of all the three aluminosilicates was done using spectrometry. Before adsorption, FTIR analysis was also conducted. Adsorbent pellets were ground in an agate mortar. Subsequently, about 100 mg of adsorbent powder was analyzed at room temperature (20.3 ºC) and 66% of relative humidity. The analysis was made using a Perkin Elmer Frontier MIR spectrometer, with a $4 cm^{-1}$ resolution and a KBr pressed disc technique.

2.2. Reagents

Lead nitrate ($Pb(NO_3)_2$), copper sulfate pentahydrate ($CuSO_4 \times 5 H_2O$), and cadmium nitrate ($Cd(NO_3)_2$) were acquired from Merck laboratory and used as metallic reagents. Multimetal solutions of lead (II), copper (II), and cadmium (II) were prepared by diluting the necessary amount of metal reagents in distilled water. Different molarities of H_2SO_4 and KOH were used to adjust the pH values.

Standard solutions for lead, copper, and cadmium were elaborated in four different concentrations, diluting standard stock solutions of

1000 mg/l concentration. This allowed obtaining the calibration curve. After adsorption and without further filtration, heavy metals concentrations were measured with an atomic absorption spectrometer (Model AA-700, Shimadzu), using an acetylene/air flame. The detection limit of the mentioned equipment for the three metals was between 0.001 mg/L and 0.009 mg/L. Wavelength measures for lead, copper and cadmium were 217 nm, 324.8 nm and 228.8 nm respectively. Slit width for all metals was 0.7 nm.

2.3. Pelletization

The method described in Miranda *et al*. was adapted for the preparation of pellets (Mejia Miranda, Laverde, Avella, and Peña Ballesteros, 2015). By using the dry and sieved material (particle size smaller than 33µm), aluminosilicates were mixed at a rate of 67% zeolite, 29% bentonite and 4% kaolin (based on the recommendation made by Salem and Akbari Sene (2012)). This mixture was moistened at a proportion of 42% (w/v). Pellets formed were dried at 100 °C and calcined at 600 °C in a furnace (Ciosek, Luk, Warner, & Warner, 2016).

2.4. Adsorption tests

2.4.1 Adsorption

Adsorption was done in a column system. 300 mL of multimetal solution was circulated using a peristaltic pump at the rate of 20 mL/min at different time intervals (45, 60, 120, 180, 240 and 300 minutes). The samples were taken for the measurement of adsorption efficiency. The effect of pH and contact time on the adsorption was also noted.

Removal efficiency percentage ($\%R_{em}$) was determined using Equation 1.

$$\%\mathrm{R_{em}} = \frac{\mathrm{C_o} - \mathrm{C_e}}{\mathrm{C_o}} \cdot 100 \qquad \text{(Eq. 1)}$$

Where C_o (mg/L) and C_e (mg/L) represent the initial and final concentrations of the heavy metals. The equilibrium adsorption capacity, Q_e (mg/g), was found with Equation 2.

$$\mathrm{Q_e} = \frac{\mathrm{Co} - \mathrm{C_e}}{\mathrm{m}} \cdot \mathrm{V} \qquad \text{(Eq. 2)}$$

Where C_e (mg/L) is the equilibrium concentration, m the total mass of adsorbent (g) and V the volume (L) of solution.

2.5. Response Surface Methodology (RSM) design

RSM with a central composite rotatable design (CCRD) was applied to determine the optimum operating conditions. Four variables (contact time, adsorbent dose, pH and initial heavy metals concentration) with five levels were chosen to employ CCRD. Table 1 shows the matrix of the factors and their coded levels. Many authors have also used CCD to analyze the adsorption data critically. Recently, 2^n factorial design with 20 experimental runs was used to optimize the effect of pH, time, and initial concentration on the biosorption of chromium (Bayuo, Abukari, and Pelig-Ba, 2020). In another study, the CCD results were obtained for pH, adsorbent dosage, and initial concentration and the maximum experimental removal of Cd^{2+} and Pb^{2+} was 98.90% and 99.99%, respectively (Mohd Zahri *et al*., 2020). Sheydai *et al*. illustrated the effects of initial pH, dosage, sonication time and temperature on Cu^{2+} ion removal efficiency using CCD (Sheydaei, Gasemsoltanlu, and Beiraghi, 2019). It was found that 97 % of Cu^{2+} ions were adsorbed using natural clinoptilolite and the optimum condition was dosage: 500 mg/L, pH: 6, sonication time: 12 min and sonication temperature: 45°C. Another RSM method i.e., Box-Behnken Design (BBD) is also used to analyze the adsorption data. Chromium (VI) adsorptionby Litchi peel was statistically analysed by BBD, statistical hypothesis test, ANOVA and comparison of t-tests (Uddin and Salah, 2018). Adsorption capacity of plant bark towards lead ions was determined and optimized by BBD using dose, concentration, and temperature as independent variables (Khatoon, Uddin, and Rao, 2018).

The following quadratic model was constructed to explain the influence of adsorption factors (Equation 3):

$$y = \beta_0 + \sum_{j} \beta_j x_j + \sum_{i<j} \beta_{ij} x_i x_j + \sum_{j} \beta_{jj} x_j^2 + e \qquad \text{(Eq. 3)}$$

Where y is the response; βo is the intercept; βj, βij, βjj are the model coefficients; xj, xixj, xj^2 are the factors studied; and e the error. To determine the relevance of the model and the level of influence of the operating factors, the regression coefficients and the ANOVA method were determined.

2.6. Equilibrium and kinetic studies

Adsorption equilibrium tests were performed for 300 minutes with 300 mL of multimetal solution using the adsorbent dose of 15 g/L at pH of 4.5 ±0.5. The initial concentration of lead and copper was between 1.5 mg/L and 30 mg/L, while for cadmium between 0.5 mg/L and 15 mg/L. Langmuir (Equation 4) and Freundlich (Equation 5) models were studied.

$$Q_e = \frac{Q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \qquad \text{(Eq. 4)}$$

Where Q_e (mg/g) is the amount of solute adsorbed onto the adsorbent surface in equilibrium conditions, Q_{max} (mg/g) is the maximum removal capacity of the adsorbent, K_L (L/mg) and C_e (mg/L) are the parameters of affinity and equilibrium concentration of the solute.

$$Q_e = K_F \cdot C_e^{1/n} \qquad \text{(Eq. 5)}$$

K_F (L/mg)$^{(1/n)}$) indicates the adsorption capacity of the adsorbent while n the heterogeneity of the system. The separation factor, R_L, was calculated using Equation 6.

$$R_L = \frac{1}{1 + b \cdot C_o} \qquad \text{(Eq. 6)}$$

Where C_o (mg/L) is the initial concentration and b is the intercept of the non-linear equation.

To analyze the adsorption kinetics, 500 mL of multimetal solutions were prepared, with the initial concentration of 15 mg/L for both Cu and Pb, while 5 mg/L for Cd with an adsorbent dose of 10 g/L and pH of 4 ±0.5. The pseudo-first-order model (PFO) (Equation 7) and pseudo-second-order model (PSO) (Equation 8) were then analyzed.

$$Q_t = Q_e(1 - \exp(k_1 \cdot T)) \qquad \text{(Eq. 7)}$$

Where k1 (1/min) and Qe (mg/g) are the parameters of the model.

$$Q_t = \frac{Q_e^2 \cdot k_2 \cdot T}{1 + Q_e \cdot k_2 \cdot T} \qquad \text{(Eq. 8)}$$

Where k_2 (g.mg^-1.min^-1) is the equation parameter.

3. RESULTS AND DISCUSSION:

3.1 Adsorbent characterization

Table 2 shows the chemical composition of bentonite, kaolin, and zeolite. The main components of the adsorbent are silica, alumina, iron, calcium and magnesium oxides; this confirms the potential of these materials to be used as adsorbent (Uddin, 2017). Alkaline oxides and alkaline earth concentrations represent the feldspar content (Krupskaya *et al*., 2019). Ignition loss values indicate that these adsorbents have low carbonaceous matter and high mineral content (Shehata, Geundi, Ashour, and Abobeah, 2016).

Figure 1 depicts the FTIR spectrum of the pellets used in the adsorption column in the range between 400 cm^{-1} and 4000 cm^{-1}.

In the first region of the spectrum, no peaks in the curve were observed. The area between 3500 cm^{-1} 1600 and cm^{-1} represents the vibrations of surface and internal hydroxyl groups. From 2842.60 cm^{-1} to 1626 cm^{-1} region, the curve was flat which attributed the water adsorption in the aluminosilicate (Hofmeister and Bowey, 2006). The region related to the bonds between aluminum or silicon and oxygen found to has greater band intensity. For the latter peaks, especially at 1023.04 cm^{-1} correspond to T-O bonds (where T can be aluminum or silicon) while other six peaks correspond to the T-O-T vibrations in the range of 874.79 cm^{-1} to 447.00 cm^{-1} (Madejová, Gates, and Petit, 2017).

3.2 RSM models and ANOVA (coefficients values)

Table 3 shows the full results (both experimental and predicted) of adsorption percentage (response) of lead, copper and cadmium for each coded and actual values. Results show that both lead and copper were removed up to the maximum level of 88%. In comparison, cadmium percentage removal was lower (78%). Table 4 shows the regression coefficients results of the response surface model for lead, copper and cadmium. The standard error, t value and probability were determined for each coefficient and intercept of the model.

The most significant coefficient for lead was of first and quadratic order, which can be sorted according to their significance as D^2 > intercept > C > C^2 > D > B^2. For copper, the first order, two-way interaction and quadratic order coefficients were significant. According to the significance, the order of relevance is D^2 > AB > A^2 > B^2 > D. For cadmium, only the first-order and quadratic factors A and D were significant; the order is D^2 > D > A > A^2. According to the significant coefficients, response surface equations were constructed which are shown in the following equations:

$$\%\text{Rem Pb} = 2.95\text{E}{+}02 - 7.73\text{E}{+}01 \text{ x } C - 5.77\text{E}{+}00 \text{ x } D + 4.87\text{E}{-}02 \text{ x } B^2 + 6.90\text{E}{+}00 \text{ x } C^2 + 1.43\text{E}{-}01 \text{ x } D^2 \quad \text{(Eq. 9)}$$

$$\%\text{Rem Cu} = -2.88\text{E}{+}00 \text{ x } D + 1.15\text{E}{-}02 \text{ x } AB + 7.84\text{E}{-}04 \text{ x } A^2 + 9.09\text{E}{-}02 \text{ x } B^2 + 4.60\text{E}{-}02 \text{ x } D^2 \quad \text{(Eq. 10)}$$

$$\%\text{Rem Cd} = 4.84\text{E}{-}01 \text{ x } A - 8.97\text{E}{+}00 \text{ x } D - 6.56\text{E}{-}04 \text{ x } A^2 + 3.74\text{E}{-}01 \text{ x } D^2 \quad \text{(Eq. 11)}$$

The adjusted R^2-square was found greater than 0.9 (0.9406, 0.9237, and 0.9121 for lead, copper, and cadmium, respectively), p and F values were also highly significant (36.09, 27.81, and 23.98 for lead, copper, and cadmium, respectively). The experimental data fitted the quadratic model very well. The adjusted regression coefficient values were very close to the initial regression coefficient. The difference of less than 0.04 indicated a good fit between the experimental and expected values. These results show that the constructed model analyzed the data very well. The significance of each factor was varied with every model (Equations 9, 10 and 11). The initial concentration of heavy metals found to be effective for all the three metals; time was significant in terms of copper and cadmium; the adsorbent dose was relevant for lead and copper while pH had the impact on lead removal, which can be explained by the selectivity of the solute for the active sites. It can be observed that because lead occupies the active sites faster, for this reason, the time had no such influence. Cadmium adsorption was lower, probably due to the competition with the lead and copper solutes in multimetal solution (Elkhatib, Mahdy, Sherif, and Elshemy, 2016).

3.3 Effect of operating conditions

To illustrate the combined effect of studied factors on the adsorption efficiency (response) and find the optimum values, response optimizer function in MINITAB 17 was used. The plot is shown in Figure 2. The optimization plot shows that the adsorption percentage of the studied metals augmented with the increase in time and dose, while it decreased with an increase in pH and concentration. The optimum conditions to get the maximum results can be noticed in the plot as the red color vertical line.

Moreover, linking the predicted values further validates the adequacy of the experimental data. It can be seen in Figure 3 that the actual values are much closer to the expected (predicted) ones, which confirms the statistical validation of the study.

3.3.1 pH

pH is one of the most important operating parameters in adsorption pH was evaluated between 4 and 6 (Glatstein and Francisca, 2015; Mahdi, Yu, and El Hanandeh, 2019). The effect of pH is visible in the percentage of copper removal. From a pH below 5.5, the efficiency was increased and reached close to 90%. For lead, the influence was not appreciated in the graph, although this factor was significant in the adsorption model. The analysis of the model contour curves allowed the identification and it was found that with a pH of less than 4.5, the lead removal efficiency was increased up to more than 90%. For cadmium, pH range between 4 and 6 did not affect the adsorption efficiency.

In the case of lead and copper, when the pH was more significant than 4.5, the adsorption efficiency was reduced, which can be understood that this is the maximum point of the pH curve. Hosseini *et al*. obtained similar results while analyzing the nickel adsorption in the raw zeolite between pH 2 and 5 (Hosseini, Khosravi, Tavakoli, Esmhosseini, and Khezri, 2015). The authors noted that the removal percentage was first increased and then decreased between 5 and 8. For cadmium, pH values greater than 6 did not affect the adsorption, but it was decreased with pH values under 4 (Akpomie and Dawodu, 2016). Despite the variations identified for lead and copper, response surface graphs indicate that pH between 4 and 6 had no major influence on the adsorption system. Other authors obtained similar results while studying the lead adsorption onto bentonite (Khan, Hegde, and Shabiimam, 2017; Zhu and Qin, 2017). This could mean that the adsorption mechanism that predominates in the system is ion exchange (Kyziol-Komosinska *et al*., 2015).

From this analysis, it was found that the optimum pH range was between 4 and 6. At an acidic pH, the density of positively charged active sites increases (Shi, Fang, Zhao, Sun, and Liang, 2015); this causes an electrostatic repulsion between the metal ions and the positive adsorption surface (Hu *et al*., 2015). As the pH increases, competition between metal and hydrogen ions reduced, leaving the adsorption sites free, which increased the metal removal (Hosseini *et al*., 2015). At pH values greater than 6, a reduction in efficiency may be due to the formation of complexes between metal and hydroxyl ions that precipitate in the adsorbent and cause greater metal retention.

3.3.2 Adsorbent dosage

The dose evaluated was between 5 g/L and 25 g/L. It can be observed from Figure 2 that as the dose increases, the adsorption efficiency also rises. Similar results were obtained when analyzing copper, nickel, and zinc adsorption in bentonite (Esmaeili, Mobini, and Eslami, 2019), the optimal adsorbent doses for all the three metals were 22 g/L, 30 g/L, and 60 g/L, respectively.

For lead, an adsorption efficiency of 90% can be achieved with a dose of 17 g/L. The most efficient dose for 90% removal for copper and cadmium was 22 g/L. The lead had higher adsorption efficiency than copper and cadmium; when the lead was in solution, it had a greater affinity for active sites (Park *et al*., 2016). Copper and cadmium appeared to be more selective and require a greater amount of adsorbent to have more available active sites. As the adsorbent dose was increased, more adsorption sites were available; as the dose was reduced, so did the active sites.

3.3.3 Heavy metal concentration

Figure 2 shows that adsorption efficiency is higher at lower initial concentrations of the heavy metals. For lead, an efficiency higher than 80% was reached with an initial concentration of 6 mg/L. For copper and cadmium, 2 mg/L of initial concentration in the solution provided an efficiency greater than 70%. It is expected that a higher concentration of heavy metals will affect the adsorption due to the saturation of active sites at the interface (Drweesh *et al*., 2016). Khan *et al*. examined that the removal of lead onto the bentonite using the initial pH range of 1 mg/L to 180 mg/L and determined an optimal initial concentration of 35 mg/L) (Khan *et al*., 2017). Malima *et al*. reported an optimal initial concentration of 5 mg/L for cadmium adsorption using kaolin (evaluated between 5 mg/L and 25 mg/L (Malima *et al*., 2018). Naseef *et al*. analyzed copper adsorption using activated bentonite (Nassef, Mahmoud, Salah, and El-Taweel, 2017). The authors explained that the lower adsorption efficiency was at higher heavy metal concentrations due to the lesser availability of adsorption sites. This could have happened in the present study. Although higher initial heavy metals concentrations reduce adsorption efficiency, in turn, adsorption capacity is used to increase. By increasing the number of adsorbates in the solution, the concentration gradient is magnified; this gives the impulse to overcome the mass transfer resistance between the adsorbent and the adsorbate (Malima, Lugwisha, & Mwakaboko, 2018).

3.4 Comparison with other adsorbents

From the study of the response surface graphs and contour curves, optimal adsorption ranges were identified. Selected optimal values were obtained from the resolution of the equations constructed for each metal. In cadmium, to achieve a 70% removal, a very long time is required, compared to lead and copper.

Table 5 compares the optimal values selected in this study with other reported studies. The suggested optimal values for lead, copper, and cadmium found to be almost similar to those proposed in other reported studies. Despite this, the values obtained differed from each other, which shows that conditions were specific for each system according to the adsorbent characteristics, adsorbate type, and operating factors.

3.5 Equilibrium isotherms

Table 6 shows the parameters and coefficients of determination of each tested model. R^2 values indicated that the Langmuir model fits better with the experimental data for all the three metals studied. Other authors have obtained similar results in the adsorption of heavy metals with different clays (Abu-Hawwas, Ibrahim, and Musleh, 2018; Mu'azu, Bukhari, and Munef, 2020; Rao and Kashifuddin, 2016). The better fit to the Langmuir model suggests that the process occurred in monolayer formation, which is the typical physisorption characteristic. The maximum adsorption capacity predicted by the Langmuir model was 7.27 mg/g, 1.45 mg/g and 0.68 mg/g for lead, copper, and cadmium. KL parameter measures the adsorption intensity between adsorbate and adsorbent (Ismadji, Soetaredjo, and Ayucitra, 2015). In this case, values were higher for cadmium and lower for lead. The separation factor RL allows to know the viability of the adsorption; values between 0 and 1 indicate that adsorption is feasible (Chaudhry, Khan, and Ali, 2016; Ismadji *et al*., 2015). According to RL values, the present study shows feasible adsorption.

In the Freundlich model, parameter KF is related to the removal capacity in multilayers and n with the adsorption intensity, which varies with interface heterogeneity (Ismadji *et al*., 2015; Yang, Xu, Yu, and Zhang, 2016). The value of n allows understanding the process and the complexity of the system. The magnitude of n value between 1 and 10 is considered favorable. In this study, the results show that the process is viable and that the adsorption tends to be stronger in cadmium, then copper and finally lead. The isotherm models were used to describe the data, the R^2 values, between 0.968 and 0.986 indicating sufficient adsorption. Padmavathy and Murali (Padmavathy and Murali, 2017) presented a similar result in chromium retention with clay nanocomposites. This can be attributed to the fact that active sites can be characterized as monolayer or multilayer and the interface as heterogeneous (Padmavathy and Murali, 2017).

3.6 Kinetics

Relationship between adsorption efficiency and time is shown in Figure 4. In the case of lead and copper adsorption, it can be seen that after the four hours of adsorption, the system reached close to the equilibrium condition. Adsorption was slow at the start and then gradually increased until it began to show less variation due to the progressive occupation of adsorption sites (Meroufel and Zenasni, 2018).

In Table 7, the coefficient of determination indicates that the PSO model fitted more efficiently with lead and copper data while the PFO model suited well with cadmium data. Mu'azu *et al*. also observed a similar result and reported that the PSO model fitted well for copper and nickel adsorption onto bentonite (Mu’azu *et al*., 2020). Adsorbents based on bentonite and zeolite in lead solutions also fitted better with this formula (Melichová and Ľuptáková, 2016). Usually, in heavy metal adsorption, the kinetic data shows a better fit for the PSO model (Uddin and Fazul Rahaman, 2017). However, other researchers have noted the opposite outcomes in which the results of kinetics studies indicated that chemisorption could be the step that controls lead and copper adsorption (He, Gan, and Feng, 2017).

4. CONCLUSIONS:

Clay pellets have shown their reasonable adsorptive properties towards various metal ions. Despite having relatively low values of maximum adsorption capacity, this study proposes that the adsorption could be increased by adjusting the calcination temperature of pelletization and also by applying chemical treatments to clay pellets before extrusion. According to the results, the experimental adsorption data was fitted better with Langmuir isotherm, but Freundlich isotherm also had high correlation values (R^2 between 0.968 and 0.986). It can be concluded that the active adsorption sites can be characterized as monolayer or multilayer and the adsorption surface as heterogeneous. The kinetics study showed that after 300 minutes, adsorption efficiency began to stabilize for all three metals. Copper and lead data fitted well with the PSO model while cadmium with the PFO model. The response surface analysis allowed defining optimal values for the evaluated operating factors. For a multimetal solution, optimum values of the studied factors were 240 minutes of contact time, 25 g/L of adsorbent dose, pH 4.3, and initial heavy metal concentrations of 4 mg/L, 7 mg/L, and 2 mg/L of lead, copper, and cadmium, respectively.

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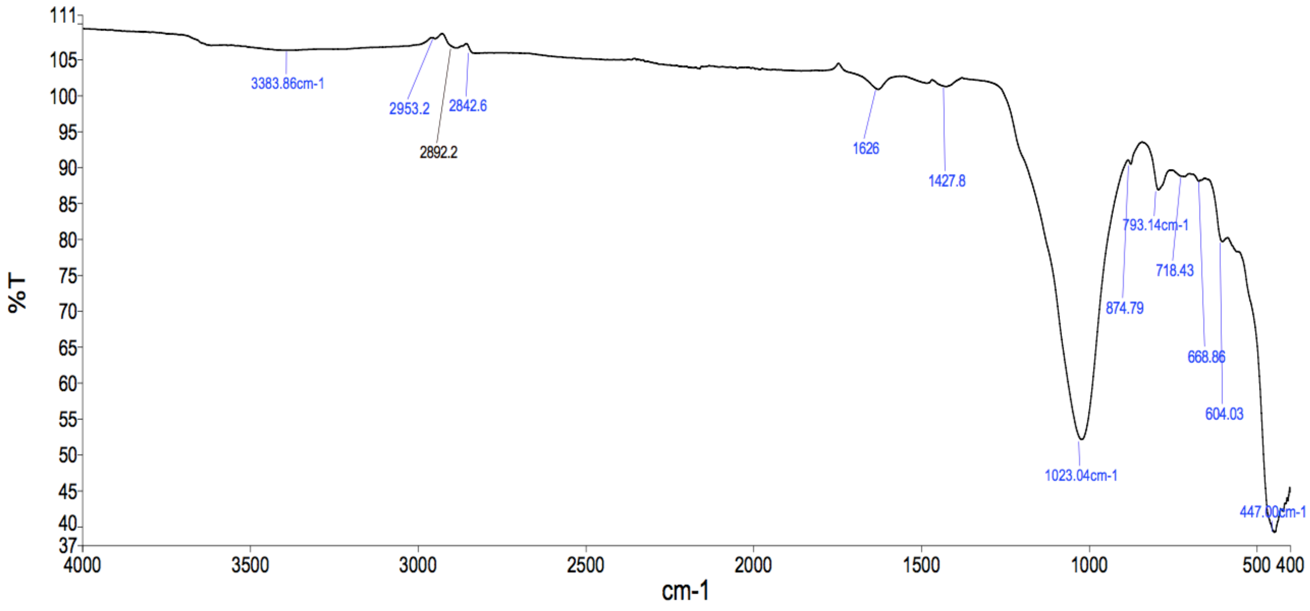


Figure 1. *FTIR spectra of adsorbent pellets*

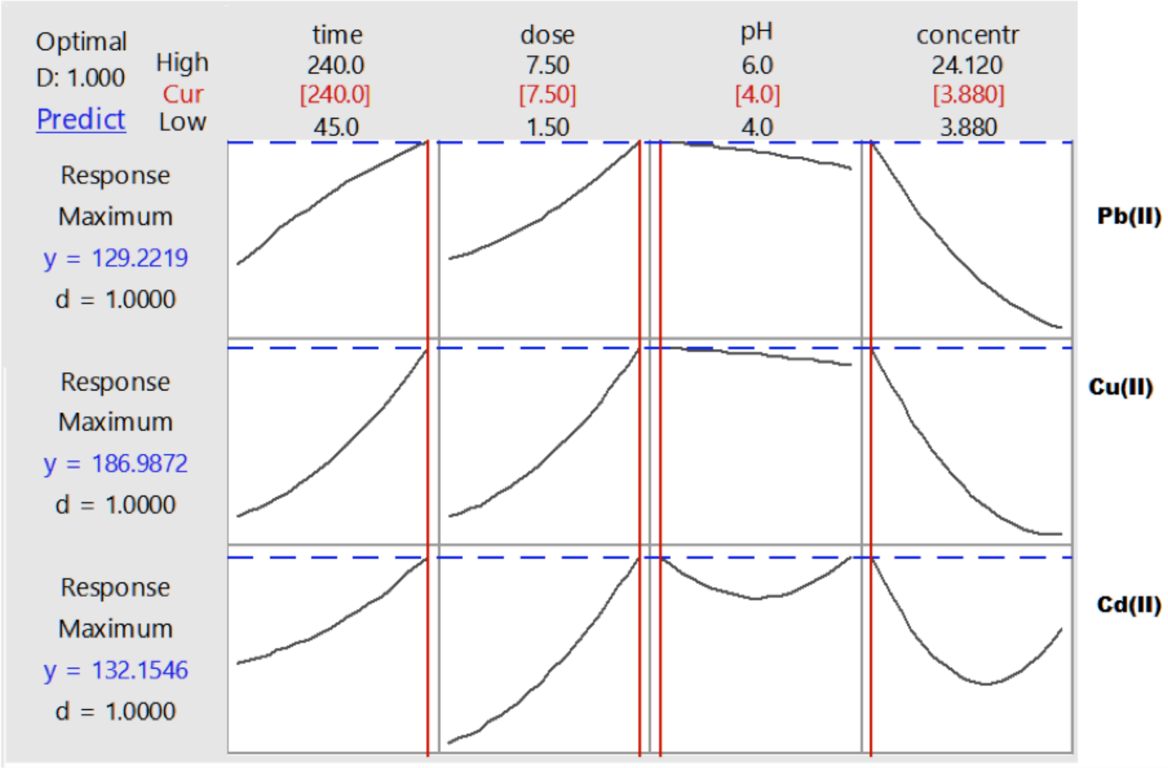
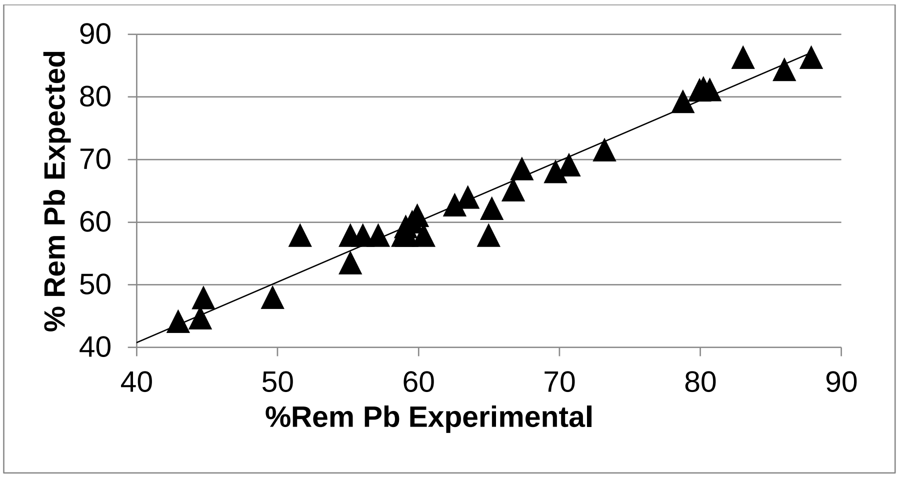
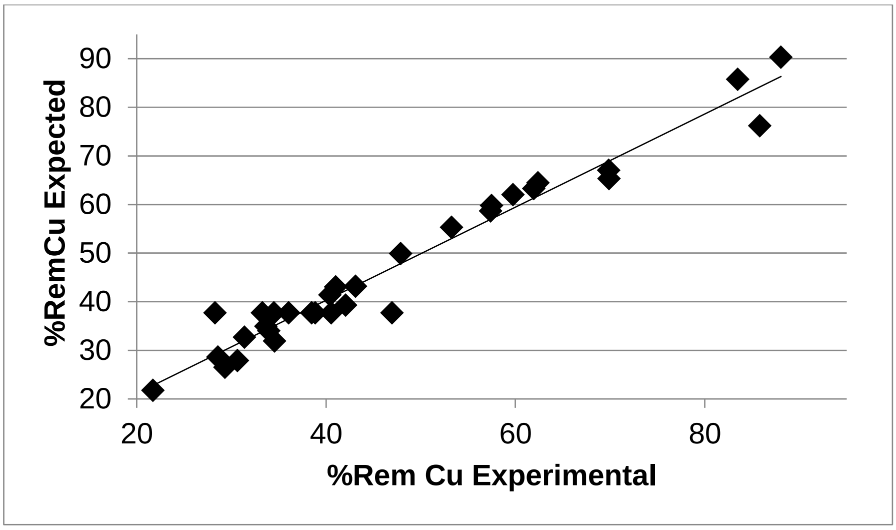


Figure 2. *Response optimization plot*



(a)



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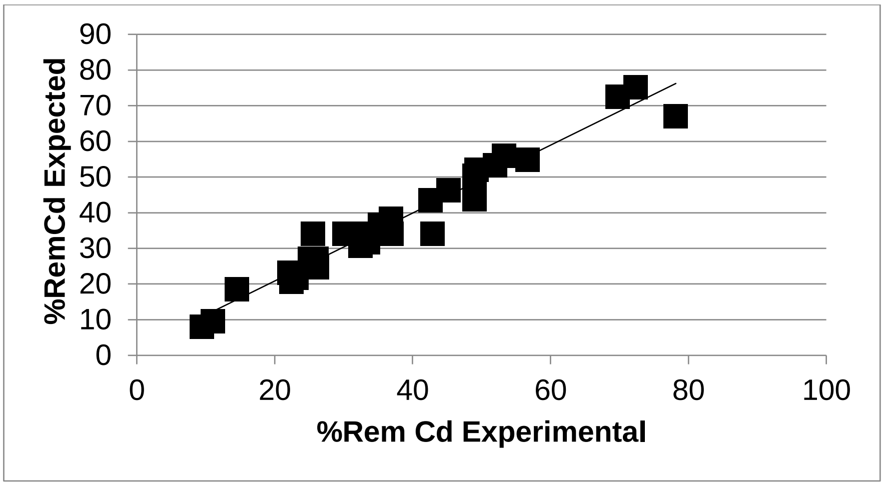

(c)

Figure 3. *Experimental vs expected values for removal efficiency of lead (a), copper (b) and cadmium (c)*

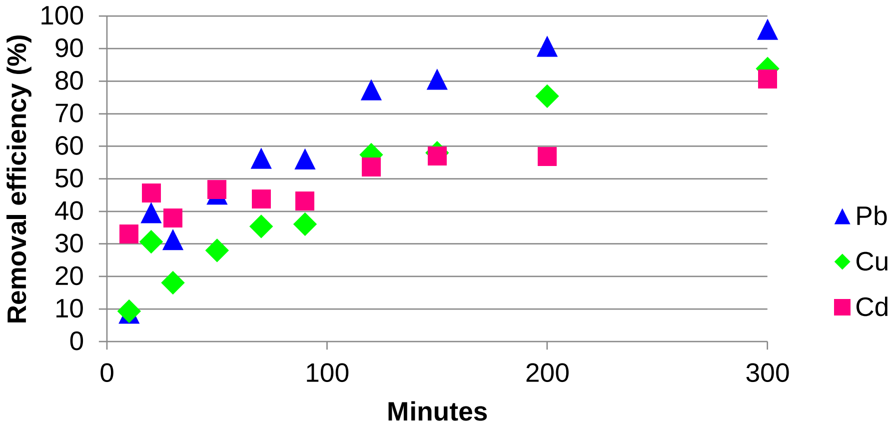

Figure 4. *Kinetics of adsorption efficiency*

Table 1. *Selected factors and levels for the CCRD*

Factors	**Levels**				
	-2	**-1**	**0**	**1**	**2**
A = Contact time (minutes)	45	60	120	180	240
B = Adsorbent dose (g/L)	5	10	15	20	25
C = pH	4	4.5	5	5.5	6
D = Initial concentration (mg/l)					
Pb	3.88	11.14	15.89	17.4	24.12
Cu	4.2	10.6	23.8	26	50
Cd	1.57	3.02	7.38	9.94	13.73
Response: Removal efficiency (% Rem)					

Table 2. *Chemical composition of the clays and zeolite*

Element	**Bentonite**	**Kaolin**	**Zeolite**
SiO_2	62.63%	44.60%	65.91%
Al_2O_3	17.10%	36.09%	10.60%
Fe_2O_3	3.53%	3.43%	3.03%
CaO	2.61%	1.29%	2.52%
MgO	0.61%	0.35%	0.18%
Na_2O	0.99%	0.30%	3.77%
K_2O	0.07%	0.19%	0.14%
TiO_2	0.53%	1.42%	0.17%
P_2O_5	0.03%	0.03%	0.07%
Loss off ignition	11.80%	12.30%	13.60%

Table 3. *Observed and predicted adsorption efficiencies for lead, copper and cadmium with a CCRD*

Run	A	B	C	D	A (m)	B (g/L)	C	D (mg/L)			%Rem					
								Pb	Cu	Cd	Pb		Cu		Cd	
											Obs	Pred	Obs	Pred	Obs	Pred
1	-1	-1	-1	-1	60	3	4.5	11.14	10.6	3.02	55.2	53.5	47.9	49.9	35.3	36.7
2	1	-1	-1	-1	180	3	4.5	11.14	10.6	3.02	70.7	69.2	59.8	62.0	53.3	56.0
3	-1	1	-1	-1	60	6	4.5	11.14	10.6	3.02	73.2	71.6	62.4	64.4	49.0	50.4
4	1	1	-1	-1	180	6	4.5	11.14	10.6	3.02	87.9	86.3	88.1	90.3	72.4	75.2
5	-1	-1	1	-1	60	3	5.5	11.14	10.6	3.02	49.6	48.0	41.0	43.1	36.9	38.2
6	1	-1	1	-1	180	3	5.5	11.14	10.6	3.02	66.7	65.2	57.5	59.7	49.3	52.0
7	-1	1	1	-1	60	6	5.5	11.14	10.6	3.02	69.7	68.1	53.2	55.3	52.0	53.3
8	1	1	1	-1	180	6	5.5	11.14	10.6	3.02	86.0	84.4	83.5	85.7	69.8	72.5
9	-1	-1	-1	1	60	3	4.5	17.4	26	9.94	44.5	44.7	28.6	28.6	9.5	8.0
10	1	-1	-1	1	180	3	4.5	17.4	26	9.94	63.5	64.0	33.7	34.9	26.1	27.1
11	-1	1	-1	1	60	6	4.5	17.4	26	9.94	62.6	62.8	43.1	43.1	23.2	21.7
12	1	1	-1	1	180	6	4.5	17.4	26	9.94	80.7	81.2	62.0	63.2	45.3	46.2
13	-1	-1	1	1	60	3	5.5	17.4	26	9.94	39.0	39.2	21.7	21.8	11.0	9.6
14	1	-1	1	1	180	3	5.5	17.4	26	9.94	59.5	60.1	31.4	32.7	22.1	23.1
15	-1	1	1	1	60	6	5.5	17.4	26	9.94	59.1	59.3	33.9	34.0	26.1	24.7
16	1	1	1	1	180	6	5.5	17.4	26	9.94	78.8	79.3	57.4	58.7	42.6	43.6
17	0	0	0	0	120	4.5	5	15.89	23.8	7.38	56.0	57.9	34.5	37.7	31.3	34.2
18	0	0	0	0	120	4.5	5	15.89	23.8	7.38	55.2	57.9	33.3	37.7	30.2	34.2
19	0	0	0	0	120	4.5	5	15.89	23.8	7.38	60.4	57.9	40.5	37.7	36.9	34.2
20	0	0	0	0	120	4.5	5	15.89	23.8	7.38	51.6	57.9	28.3	37.7	25.6	34.2
21	-2	0	0	0	45	4.5	5	15.89	23.8	7.38	44.8	47.9	34.6	31.9	14.5	18.5
22	2	0	0	0	240	4.5	5	15.89	23.8	7.38	79.9	81.1	69.9	65.3	49.0	43.8
23	0	-2	0	0	120	1.5	5	15.89	23.8	7.38	43.0	44.2	29.3	26.5	22.5	20.7
24	0	2	0	0	120	7.5	5	15.89	23.8	7.38	80.2	81.4	69.8	67.0	56.7	54.9
25	0	0	-2	0	120	4.5	4	15.89	23.8	7.38	67.3	68.5	42.1	39.3	33.5	31.7
26	0	0	2	0	120	4.5	6	15.89	23.8	7.38	59.9	61.1	30.7	27.9	32.5	30.7
27	0	0	0	-2	120	4.5	5	3.88	4.2	1.57	83.0	86.3	85.8	76.2	78.2	67.1
28	0	0	0	2	120	4.5	5	24.12	50	13.73	65.2	62.2	40.4	41.4	25.2	27.1
29	0	0	0	0	120	4.5	5	15.89	23.8	7.38	58.9	57.9	38.5	37.7	35.0	34.2
30	0	0	0	0	120	4.5	5	15.89	23.8	7.38	59.2	57.9	38.8	37.7	35.4	34.2
31	0	0	0	0	120	4.5	5	15.89	23.8	7.38	65.0	57.9	47.0	37.7	42.9	34.2
32	0	0	0	0	120	4.5	5	15.89	23.8	7.38	57.2	57.9	36.0	37.7	32.8	34.2

Table 4. *RSM regression coefficients for lead, copper and cadmium*

		Estimate	***Standard error***	***T value***	***Pr(>|t|)***	
Pb	Intercept	2.95E+02	7.71E+01	3.83	0.001341	**
	A	-4.93E-02	1.57E-01	-0.3147	0.756805	
	B	-5.30E-01	1.90E+00	-0.2793	0.783353	
	C	-7.73E+01	2.52E+01	-3.0631	0.00704	**
	D	-5.77E+00	2.66E+00	-2.1727	0.044232	*
	AB	-7.27E-04	2.62E-03	-0.2773	0.784926	
	AC	1.30E-02	2.62E-02	0.4968	0.62572	
	AD	4.87E-03	4.08E-03	1.1932	0.249183	
	BC	2.04E-01	3.15E-01	0.6486	0.525271	
	BD	3.10E-16	4.82E-02	0	1	
	CD	-1.29E-15	4.82E-01	0	1	
	A^2	3.08E-04	2.09E-04	1.4729	0.159049	
	B^2	4.87E-02	2.35E-02	2.071	0.053892	.
	C^2	6.90E+00	2.35E+00	2.9348	0.009254	**
	D^2	1.43E-01	2.51E-02	5.6751	2.74E-05	***
Cu	Intercept	1.65E+01	1.08E+02	0.153	0.88024	
	A	-3.41E-01	2.33E-01	-1.4614	0.16215	
	B	-9.21E-01	2.81E+00	-0.3275	0.74727	
	C	3.46E+01	3.81E+01	0.9061	0.37755	
	D	-2.88E+00	1.60E+00	-1.795	0.09045	.
	AB	1.15E-02	4.11E-03	2.7943	0.01245	*
	AC	3.82E-02	4.11E-02	0.9301	0.36533	
	AD	-3.12E-03	2.54E-03	-1.2269	0.23659	
	BC	-2.31E-01	4.93E-01	-0.4697	0.64456	
	BD	-1.31E-15	2.96E-02	0	1	
	CD	-1.42E-14	2.96E-01	0	1	
	A^2	7.84E-04	3.28E-04	2.3883	0.0288	*
	B^2	9.09E-02	3.66E-02	2.4871	0.02356	*
	C^2	-4.14E+00	3.66E+00	-1.1319	0.27339	
	D^2	4.60E-02	6.14E-03	7.4938	8.78E-07	***
Cd	Intercept	-4.72E+01	1.06E+02	-0.4473	0.6603004	
	A	4.84E-01	2.34E-01	2.0664	0.0543697	.
	B	-6.01E-01	2.80E+00	-0.2146	0.8326278	
	C	3.27E+01	3.78E+01	0.8651	0.3990215	
	D	-8.97E+00	3.97E+00	-2.2611	0.0371558	*
	AB	4.52E-03	4.13E-03	1.0945	0.2890127	

AC	-4.64E-02	4.13E-02	-1.1239	0.2766802	
AD	-3.65E-04	5.93E-03	-0.0616	0.9516205	
BC	1.37E-01	4.96E-01	0.2758	0.7860121	
BD	4.59E-16	7.08E-02	0	1	
CD	-6.73E-15	7.08E-01	0	1	
A^2	-6.56E-04	3.22E-04	-2.036	0.0576376	.
B^2	3.62E-02	3.64E-02	0.9958	0.3333122	
C^2	-2.97E+00	3.64E+00	-0.8169	0.4253053	
D^2	3.74E-01	8.88E-02	4.2088	0.0005903	***

Table 5. *Comparison of optimal operating conditions*

		Operating conditions					
Adsorbent	***Metal***	***Time (minutes)***	***Dose (g/L)***	***pH***	***Initial concentration (mg/L)***	***%Rem***	***Reference***
Ze/Bent/K	Pb	150	25	4.3	4	99.84	Present study
	Cu	150	25	4.3	7	99.67	
	Cd	240	25	4.3	2	61.93	
Ze	Cd	116	5.4	7	25.07	80.77	(Shaban and Abukhadra, 2017)
Bent-SH	Pb	146	14.6	5.1	33	95.08	(Şahan, 2019)
	Cu	146	15.2	4.5	37.9	88.19	
K	Cu	24h	20	5.5	20	65.0	(Al-Makhadmeh and Batiha, 2016)
Ze	Cu	24h	20	5.5	70	99.6	
K	Cd	180	32	6	5	99.2	(Malima *et al*., 2018)
K	Pb	60	10	7	4.66	96.3	(Aggour, Diab, Hegazy, and Elmekkawy Halawia, 2015)
	Cu	60	10	8	4.66	79.5	
	Cd	60	10	7	0.62	91.9	

Bentonite (Bent), Kaolin (K), Zeolite (Ze), Bentonite enriched with SH groups (Be-SH)

Table 6. *Parameters of lead, copper and cadmium adsorption isotherms*

Model	***Parameters***	***Pb***	***Cu***	***Cd***
Langmuir	Qmax (mg/g)	7.27	1.45	0.26
	K_L (L/mg)	0.03	0.15	0.68
	R_L	0.10 - 0.58	0.05 - 0.59	0.07 - 0.70
	R^2	0.987	0.981	0.999
Freundlich	K_F(mg/g).(L/mg)^(1/n)	0.24	0.41	0.15
	N	1.09	3.30	6.09
	R^2	0.986	0.968	0.987

***Table 7**. Parameters of kinetic models*

Model	Parameters	Pb	Cu	Cd
PFO	Qe	1.46	1.32	0.22
	k1	0.01	0.01	3.45E-03
	R^2	0.942	0.899	0.843
PSO	Qe	1.93	1.80	0.39
	k2	5.60E-03	3.90E-03	0.06
	R^2	0.950	0.918	0.625