Highly efficient Cd(II) adsorption using mercapto-modified bentonite as a novel adsorbent: an experimental design application based on response surface methodology for optimization
Ümit Ecer, Şakir Yılmaz and Tekin Şahan

ABSTRACT
We report the optimization with response surface methodology (RSM) for adsorption conditions required for removal of Cd(II) from an aqueous environment with 3-mercaptopropyl trimethoxysilane-modified bentonite (MMB). Central composite design (CCD) in RSM was used to optimize the most significant adsorption variables of initial pH, temperature (°C), initial Cd(II) concentration (C₀, mg L⁻¹) and adsorbent dosage (g). With the quadratic model equation obtained from CCD, the optimum values were determined as initial pH 6.40, temperature 20 °C, C₀ 49.55 mg L⁻¹ and adsorbent dosage 0.17 g. Under optimum conditions, the optimum adsorption amount of Cd(II) was 27.55 mg Cd(II)/g adsorbent and adsorption yield was 94.52%. The obtained results showed that the Langmuir and Dubinin Radushkevich (D-R) adsorption isotherms were more suitable for adsorption equilibrium data. The kinetic studies indicated that the pseudo-second-order kinetic model was fitted to the adsorption kinetic data. Additionally, thermodynamic studies indicated that the adsorption process was spontaneous and exothermic. As a result, MMB can be chosen as an effective adsorbent for treating heavy metals such as Cd(II) in wastewater and removing them from aqueous solutions. Furthermore, it is thought that it will positively contribute to the literature since the adsorbent-adsorbate combination (MMB-Cd(II)) is used for the first time.

Key words | adsorption, bentonite, cadmium, central composite design (CCD), mercapto, response surface methodology (RSM)

INTRODUCTION
The rapid increase in industrial activity in recent years has caused heavy metal pollution in the environment, especially in aquatic systems. This heavy metal pollution is poisonous and these metals are not biodegradable in the environment (Torab-Mostaedi et al. 2015). Heavy metals present in the environment in trace amounts may pose a serious risk to human health and living organism populations. They tend to accumulate in living organisms and can cause significant damage to plants, animals and humans and lethal health problems through food chain transfer. The potential hazards of several toxic heavy metals such as cadmium (Cd), arsenic (As), chromium (Cr), mercury (Hg) and lead (Pb) are well known. Cd is one of the heavy metals that causes environmental pollution. It is toxic to the environment because it is not biodegradable. For all these reasons, it is necessary to remove Cd(II) ions from aqueous solutions. It is broadly distributed in the earth’s crust at an approximate concentration of about 0.1 mg kg⁻¹, and the maximum permissible concentration of Cd(II) in drinking water is 0.005 mg L⁻¹ according to the WHO (World Health Organization) (Alidoust et al. 2015).

Nowadays, there have been many methods developed to remove heavy metals from aqueous environments. Some of these are adsorption (Qin et al. 2017), biosorption (Ecer & Şahan 2018), chemical precipitation (Ahmadi et al. 2014), electrocoagulation (Vasudevan et al. 2010; Vasudevan & Lakshmi 2011; Vasudevan et al. 2011; Vasudevan & Lakshmi 2012b) and reverse osmosis (Ricci et al. 2015) and so on. From among these techniques, adsorption has advantages such as non-hazardous technology, economic
applicability, flexibility in design, regeneration of adsorbents, high selectivity and efficiency and at the same time being environmentally friendly in removing heavy metals from wastewater, which distinguish it from other technologies (Sahan & Öztürk 2014). Considering all these advantages, adsorption is an important technique for the removal of heavy metals. Many adsorbents, such as clays (Yilmaz et al. 2017), activated carbon (Wang et al. 2016), agricultural waste biomass (Garba et al. 2016), sawdust (Semerjian 2010) and biochar (Yu et al. 2018) have been used for Cd(II) adsorption in literature studies. Any clay of volcanic source that includes montmorillonite is called bentonite. It deserves special interest due to its cheap cost and sorption characteristics for adsorption of metals. It has a 2:1 form, occurring as two silicon-oxygen tetrahedral layers and one aluminum–oxygen–hydroxyl octahedral layer. Surface modification can be performed to increase the adsorption capacity of bentonite (Zamparas et al. 2015; Taha et al. 2016). In recent years, surface-modified adsorbents have been increasingly used for heavy metal removal from aqueous environments (Kuo & Lin 2009). The reason for the surface modification of the adsorbents is to achieve higher adsorption capacity and yield for removal of impurities from the aqueous environment. Modification with mercapto containing -SH groups for Cd(II) adsorption is expected to increase the yield. As Cd shows high affinity due to strong linkages with mercapto groups, the efficient removal of Cd(II) can be observed (Özdes et al. 2011; Zamparas et al. 2015).

Response surface methodology (RSM) combined with central composite design (CCD) is one of the most used optimization techniques in recent years. RSM is a statistical and mathematical algorithm that is used to observe the effect of several parameters affecting the experimental result at the same time. The perfect advantage of using RSM for adsorption is that it decreases the number of experimental replications necessary to evaluate the various parameters and their interactions (Alimohammadi et al. 2017). The statistical design can help to explain the interaction of the various factors and determine the optimum condition of the variables for adsorption. CCD is ideal for consecutive trials and provides a sufficient amount of information for testing lack of fit while not confusing an unusually large number of design points (Ahmadi et al. 2014; Sahan & Öztürk 2014).

In the present study, we investigated the use of MMB for Cd(II) adsorption and optimization using RSM for parameters affecting adsorption yield. Removal of Cd(II) from aqueous solutions was studied under different conditions affecting the yield adsorption. The equilibrium adsorption studies were modeled using Langmuir, Freundlich, and Dubinin Radushkevich (D-R) isotherms, and thermodynamic parameters were investigated. As a result, the new low-cost adsorbent was appraised for its potential application in removal of Cd(II) ions from wastewaters. We believe that this study will add positive value to the scientific literature, as it includes an adsorbent not previously used for Cd(II) adsorption, while at the same time there is a limited number of adsorption studies using mercapto-modified adsorbents in the literature. In addition, the removal of Cd(II) from aqueous media by MMB, which together form a novel adsorbent-adsorbate combination, will make a valuable and original contribution to the literature.

**MATERIALS AND METHODS**

**Preparation of adsorbent**

In this study, raw bentonite (RB) samples obtained from Kütahya region were used. In order to prepare the bentonite as an adsorbent, RB samples were washed with distilled water to eliminate impurities then dried in an oven at 100 °C for 24 h. The dried bentonite was then ground with a grinder and sieved through a 120 mesh sieve to bring it to the desired size (≤125 μm). The RB surface was functionalized with 3-mercaptopropyl trimethoxysilane (MPTMS) agent to increase the affinity of the surface for the Cd(II) ions. For this process firstly, 15 g of RB was treated to 30 mL of toluene (purity ≥99.9%, Merck, Germany) and 15 mL of MPTMS (purity ≥95%, Sigma-Aldrich, Germany) with a condenser on a magnetic stirrer controlled at 60 °C for 6 h with a stirring speed of 800 rpm. At the end of this treatment, the filtrate was filtered with Whatman filter paper. The solid obtained from the filtrate was then treated with toluene to remove undesirable compounds on the bentonite surface, then dried with a drying oven at 100 °C for 4 h and stored in the desiccator until use (Taha et al. 2016; Yilmaz et al. 2017). The process of modification is as shown in Figure 1(a). After the RB was modified, it was used for adsorption of Cd(II) ions from aqueous solutions. The mechanism predicted after the adsorption process is given in Figure 1(b).

**Preparation of Cd(II) solution and batch adsorption studies**

The stock solutions of Cd(II) were prepared from Cd(NO₃)₂·4H₂O (purity ≥98%, Sigma-Aldrich, Germany)
and desired concentrations for the experimental studies were prepared by diluting the stock solution. 0.1 M NaOH and HNO₃ were used in insignificant amounts to adjust the necessary pH value. Batch adsorption experiments were implemented in 250 ml Erlenmeyer flasks including 100 ml of Cd(II) solutions with varying amount of adsorbent and different pH levels. Erlenmeyer flasks were kept on a temperature-controlled magnetic stirrer for the desired adsorption conditions at a fixed contact time of 2 h and fixed agitation speed of 800 rpm. After the adsorption, the solution was filtered with Whatman®-UK filter paper. The concentration of unabsorbed Cd(II) in the remaining solutions was determined by a flame AAS (Atomic Absorption Spectrophotometer, THERMO Solar AA Series spectrometer, USA). The amount of Cd(II) adsorbed by MMB (mg g⁻¹) and the percentage of Cd(II) adsorption were calculated using Equations (1) and (2), respectively.

\[
Q_e = \frac{(C_0 - C_e)V}{m} \\
\%\text{Adsorption} = \frac{(C_0 - C_e)}{C_0} \times 100
\]

where \(C_0\) and \(C_e\) are the initial and equilibrium adsorbate concentration (mg L⁻¹), respectively, \(Q_e\) is the amount of adsorbed Cd(II) at equilibrium (mg g⁻¹), \(V\) is the volume of solution used in experimental runs (L), and \(m\) is mass of the added adsorbent (g).

**Experimental design and optimization**

The optimum conditions for the maximum value of Cd(II) adsorption with MMB was determined by means of three-levels (−1, 0, and +1) and four variables. The experimental series and levels of independent variables with coded and un-coded values for Cd(II) adsorption are given in Table 1. The obtained experimental results were examined using Design Expert 7 trial version. An experimental design model was improved with CCD for connection between results experimentally obtained and predicted by the model. Generally, the second order quadratic model equation is given by Equation (3).

\[
\gamma_p = \beta_0 + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \beta_{ii} x_i^2 + \sum_{i=1}^{4} \sum_{j=i+1}^{4} \beta_{ij} x_i x_j
\]
where $y_p$ is the predicted response value, $X_1$ and $X_2$ represent the independent variables and $\beta_0$, $\beta_i$, $\beta_{ij}$ are regression coefficients of the developed model which are constant, linear, quadratic and interaction coefficients, respectively.

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$y_o$ and $y_p$ are observed and predicted responses, respectively.
RESULT AND DISCUSSION

Analyses for characterization of adsorbent

MMB characterization was already reported in our previous work (Sahan et al. 2018). From the results obtained in the previous work, EDX analysis showed that the presence of the sulfur peak on MMB was characteristic evidence for the mercapto (-SH) groups. From XRD results, the diffraction signal intensity was relatively decreased since the crystal lattice structure was covered by amorphous organic groups, which could be attributed to the formation of silanol groups on the surface of the bentonite and methoxy groups attached to the Si-O matrix. The Fourier transform infrared (FTIR) spectra showed that there is a weak band which was not observed for RB at 2,559 cm⁻¹, indicating that this was attributed to -SH stretching vibration. Moreover, the characteristic peak observed at 2,931 cm⁻¹ was due to methoxy groups (-OCH₃) in the MPTMS. It can be said that the modification of RB with the MPTMS agent was successful. In addition, thermogravimetric analyses (TGA) of RB and MMB were performed with approximately 4–5 mg samples by heating between 50 and 1,000 °C at 10 °C min⁻¹, under an argon flow rate of 100 mL min⁻¹ using a Setaram Labsys Evo Gravimetric Analyzer (TGA/DSC 1,600 model, France). The thermogravimetric curves for RB and MMB are shown in Figure 2. The curves show that MMB undergoes more weight loss than RB. RB showed a total mass loss percentage of 25.34 wt% in the temperature range of 50–1,000 °C. It can be said that the mass loss occurring from 50 to 400 °C is due to desorption of water molecules adsorbed on the surface. At higher temperatures, the mass loss may be attributed to the dehydroxylation of the clay sheets. On the other hand, the total weight loss of MMB observed in the range of 50–1,000 °C is about 57 wt%. The first loss of MMB is assigned to loss of water molecules. Then, a further mass loss of 21.75 wt% was observed between 300 and 450 °C and is associated with the decomposition of organic components consisting of -SH (3.70 wt%). The weight losses at higher temperatures than 450 °C for MMB are attributed to the dehydroxylation of silicate layers as in the case of RB. The results from TGA show that the surface of the bentonite clay was successfully modified by the MPTMS agent.

CCD results obtained for Cd(II) adsorption

Statistical analysis with CCD was chosen to show that it forms a well-established model of the adsorption process. In this study, four important parameters, initial pH (X₁), temperature (°C) (X₂), initial concentration (C₀, mg L⁻¹) (X₃) and adsorbent amount (g) (X₄) (Table 1) were used. The parameters shown in Table 1 are coded with three levels, which are -1, 0 and +1, respectively. The number of experiments to be completed for four variables was calculated as 30 (=-2 k + 2k + 6), where k is the number of independent variables. These 30 experiments are given in Table 1 together with the obtained responses. Both actual (un-coded) and coded values of quadratic model equations obtained with CCD are given in Equations (4) and (5), respectively. Linear, quadratic coefficients and their interaction can be seen in both equations.

Analysis of variance (ANOVA) is the most reliable method for evaluating the quality of the applied model. ANOVA results are shown in Table 2. The significance of the coefficients was assessed taking into account the F and p-values in the ANOVA table. A p-value lower than 0.0001 implies that the model is significant. Using this method of analysis, it is possible to compare between the independent variables and the response. The R² value obtained as 0.93 shows that 93% of the variance in the response is clarified by the model.

![Figure 2](https://iwaponline.com/wst/article-pdf/78/6/1348/504516/wst078061348.pdf)
The relevance of the model was found by using diagnostic plots, which are presented in Figure 3. The points on the plot obtained are not very scattered, indicating that data transformation is not necessary (Figure 3(a)). For this reason, the results show that the prediction of the experimental data obtained from the quadratic model is adequate. It is generally essential to inspect whether the results obtained resemble the actual system (Ahmadi et al. 2014; Yilmaz et al. 2017). If the model does not resemble the reality, it will give incorrect information for the optimization and investigation of the predicted response for the model. The residuals are very important in evaluating model qualification (Chen et al. 2017). The residuals are indiscriminately distributed in the range of ±1.5 in Figure 3(b). It can be concluded that the experimental data fit with the predicted ones evaluated from Equation (4).

![Figure 3](https://iwaponline.com/wst/article-pdf/78/6/1348/504516/wst078061348.pdf)

**Figure 3** | (a) Relationship between actual and predicted Cd(II)% removal, (b) studentized residuals versus predicted Cd(II)% removal.

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**Table 2** | Analysis of variance (ANOVA) for Cd(II) adsorption using CCD

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<th>F value</th>
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</table>

R² = 0.93.
Effects of process variables on adsorption capacity

Initial pH is one of the most effective independent parameters for adsorption capacity. Figure 4(a) shows three-dimensional simultaneous effects of initial pH and temperature on the Cd(II) adsorption capacity of MMB adsorbent. Removal of Cd(II) ions increased with an increase from 2.0 to 6.5 in the initial pH of the Cd(II) solution. The active binding sites on the surface of MMB become negatively charged with the increase in initial pH and electrostatic attraction occurs among positive Cd(II) ions and groups with negative charge on MMB. This result can be shown as the reason for the increase in Cd(II) adsorption. The removal of Cd(II)% reduced when the initial pH was above approximately 6.5. Almost all of the Cd(II) ions in solution were adsorbed by MMB when the initial pH value was approximately 6.5. The reduction in Cd(II) adsorption onto MMB adsorbent with initial pH above 6.5 can be attributed to the change in surface charge and separation of functional groups on MMB. One of the most important reasons for this is that Cd(II) ions can be precipitated as Cd(OH)₂ solid that does not dissolve at high pH.

The point of zero charge (pH_{PZC}) is one of the important parameters that defines the sensitivity of pH, one of the parameters affecting adsorption, and affects the adsorption properties of the active center species and the surfaces. The total surface charge at pH_{PZC} is neutral. Adsorption of anions is advantageous at pH < pH_{PZC}, while the adsorption of cations is advantageous at pH > pH_{PZC}. According to the method used for pH_{PZC} in the literature, it was identified as 5.42 (Şahan et al. 2018). In the present study, the optimum initial pH value was found to be 6.40 (see heading 3.3). Since this value is greater than pH_{PZC}, the MMB surface is more enriched with negative charges because of the deprotonation of surface sites and optimum adsorption is possible (Mall et al. 2006; Torab-Mostaedi et al. 2013; Şahan & Öztürk 2014).

Figure 4(a) also shows that the removal of Cd(II) reduces with increasing temperature in the range of 20–35 °C. The kinetic energies of the metal particles

![Graphs showing effects of process variables on adsorption capacity](https://iwaponline.com/wst/article-pdf/78/6/1348/504516/wst078061348.pdf)
increase with the increasing temperature of the solution, so the desorption rate can increase at higher temperatures. However, a slight increase in Cd(II) removal was observed when the temperature was increased from 35 °C to 50 °C. The increase in Cd(II) adsorption with temperature may depend on the reduction in the thickness of the border layer surrounding the sorbent, therefore the mass transfer strength of adsorbate in the boundary layer decreases. Low temperatures are favorable for Cd(II) adsorption. This result demonstrated that the removal of Cd(II) was comparatively favored at low temperatures and the removal process was exothermic between 20–35 °C (Sekar et al. 2004).

Adsorbent amount is a significant parameter because it reflects the optimum capacity of the material used as the adsorbent (Mathialagan & Viraraghavan 2002; Yilmaz et al. 2017). In this study, the adsorbent amount was studied between 0.01 g and 0.50 g. When the adsorbent amount increases from 0.01 to 0.20 g, the Cd(II)% removal rapidly increased and reached its maximum value (Figure 4(b)). Since removal of Cd(II)% by MMB at the amount of 0.20 g of adsorbent reached the optimum level approximately, more than 0.20 g of adsorbent does not cause any change in the adsorption of Cd(II) ions. The adsorption of Cd(II)% is significantly increased by increasing the amount of adsorbent, indicating that there is more surface area for Cd(II) ions in the solution due to the increase in active regions on MMB.

C₀ is a significant parameter for the removal of heavy metal ions from the aqueous environment because the increasing C₀ causes an increase in the driving forces of heavy metal ions from solution to the active adsorption sites. In addition, the mass transfer strength of the metal ions between the solid adsorbent and the aqueous solution phases can be attenuated with increasing C₀. As shown in Figure 4(c), the adsorption capacity increased rapidly at the beginning by increasing initial Cd(II) concentrations from 5 to 50 mg L⁻¹ and then equilibrium was reached at about 50 mg L⁻¹. If C₀ is higher than 50 mg L⁻¹, the pores on the surface of the adsorbent are insufficient to absorb more metal and the non-adsorbable ions remain in the solution, so the Cd(II) adsorption gradually decreased above 50 mg L⁻¹ of MMB adsorbent (Wang et al. 2016).

Many studies have been carried out on the multi-component adsorption of metal ions since these effects have great significance both in industry and in ecological conservation. Consequently, an artificial wastewater sample that resembles real industrial wastewater was prepared to analyze Cd(II) adsorption capability with competitive adsorption for industrial applications. Artificial wastewater with multiple metals containing 82.5 mg L⁻¹ Cd(II), 70 mg L⁻¹ Zn(II) and 4.2 mg L⁻¹ Cu(II) metal ions was prepared and the required number of experiments were carried out under optimum conditions. The medium Cd(II) removal yield was 85.03% while it was 77.31% and 91.63% for Zn(II) and Cu(II), respectively, (Figure 5). It can be said that MMB is an advantageous and potential adsorbent for wastewater containing Cd(II) and other heavy metal ions.

Determination of optimum adsorption conditions

In order to detect the optimum value for Cd(II) removal yield of the studied parameters, the level of each parameter was selected to maximize range and response (% removal). The program we used offered us some solutions. The point that gave the best response was selected as the maximum solution. The optimum values were determined as pH 6.40, temperature 20 °C, C₀ 49.55 mg L⁻¹ and adsorbent dosage 0.17 g. The maximum amount of Cd(II) adsorbed under optimum conditions is 27.54 mg Cd(II) g⁻¹ MMB and adsorption yield was calculated to be 94.52%. It was observed that model predictions of Cd(II) removal yields are a good fit with experimental investigations. Some experiments were carried out to determine the adsorption capacity of RB under these optimum conditions. Adsorption yield for RB was obtained as 54%. These results show us that the adsorption efficiency is significantly increased as a result of the modification.

The comparison between the material used as adsorbent for Cd(II) removal in our study and some of the other materials used in the literature is shown in Table 3. It was determined that the MMB used in this study is convenient for Cd(II) adsorption from aqueous solutions. When the results are evaluated, it is observed that MMB has a higher adsorption efficiency compared to other adsorbents. In addition, MMB has a great potential for adsorption of

![Figure 5](https://iwaponline.com/wst/article-pdf/78/6/1348/504516/wst078061348.pdf)
Cd(II) from aqueous media due to its being naturally abundant, easily modifiable and cheap.

**Adsorption equilibrium study**

**Langmuir isotherm**

The Langmuir adsorption isotherm describes the uptake as consisting of a homogeneous surface with monolayer adsorption without interaction among adsorbed molecules (Langmuir 1918). The non-linear and linear form of the Langmuir isotherms may be symbolized as Equations (6) and (7).

\[
Q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e} \quad (6)
\]

\[
\frac{1}{Q_e} = \frac{1}{q_{\text{max}} K_L C_e} + \frac{1}{q_{\text{max}}} \quad (7)
\]

where \( C_e \) is the equilibrium metal ion concentration (mg L\(^{-1}\)), \( K_L \) is the Langmuir equilibrium constant (L mg\(^{-1}\)), \( Q_e \) is the amount of Cd(II) ions adsorbed on MMB at equilibrium (mg g\(^{-1}\)) and \( q_{\text{max}} \) is the monolayer maximum adsorption capacity (mg g\(^{-1}\)).

\[
R_L = \frac{1}{1 + K_L C_0} \quad (8)
\]

The value of \( R_L \) shows the nature of the Langmuir isotherm. It is considered to be a favorable process when it is between 0 and 1. The \( R_L \) value was calculated as 0.034 (Equation (8)). This result indicates that the adsorption process is favorable (Kamaraj et al. 2017; Pandiarajan et al. 2018).

**Freundlich isotherm**

The Freundlich equation suggests that as the concentration held in the solution increases, it increases the concentration of adsorbate on the surface (Freundlich 1906). The Freundlich isotherm model assumes heterogeneous adsorptive energies on the adsorbent surface and can be written as:

\[
Q_e = K_f C_e^{1/n} \quad (9)
\]

\[
\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (10)
\]

where \( K_f \) is a Freundlich constant indicating adsorption capacity (L g\(^{-1}\)) and \( 1/n \) is an experimental parameter related to the adsorption density.

**D-R isotherm**

The D-R model is useful for determining whether adsorption is due to a physical or chemical process. The D-R isotherm describes the characteristic adsorption curve belonging to the porous construction of the adsorbent (Dubinin & Radushkevich 1947). The test conclusions are more successful at high and medium resolution concentrations of porous and non-porous solids. It is defined in non-linear and linear form in Equations (11) and (12), respectively.

\[
q_e = q_m e^{-B_D c^2} \quad (11)
\]

\[
\ln q_e = \ln q_m - B_D c^2 \quad (12)
\]

where \( q_m \) is the maximum monolayer adsorption capacity (mg g\(^{-1}\)), \( q_e \) is the adsorbed metal ion amount at equilibrium.

---

**Table 3** Comparison of the adsorbent used in our study with some adsorbents used in literature

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Initial Cd(II) concentration (mg L(^{-1}))</th>
<th>Cd(II) adsorption amount (mg g(^{-1}))</th>
<th>Cd(II)% removal</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesized nanozeolite</td>
<td>200</td>
<td>171.2</td>
<td>78.86%</td>
<td>Pham et al. (2016)</td>
</tr>
<tr>
<td>Perlite</td>
<td>1</td>
<td>0.42</td>
<td>55%</td>
<td>Mathialagan &amp; Viraraghavan (2002)</td>
</tr>
<tr>
<td>Granular activated carbon</td>
<td>27</td>
<td>3.47</td>
<td>78%</td>
<td>Wang et al. (2016)</td>
</tr>
<tr>
<td>Egyptian Na-activated bentonite</td>
<td>100</td>
<td>3.14</td>
<td>90.63%</td>
<td>Taha et al. (2016)</td>
</tr>
<tr>
<td>Maghemite (γ-Fe(_2)O(_3)) nanoparticles</td>
<td>50</td>
<td>1.75</td>
<td>24.5%</td>
<td>Ahmadi et al. (2014)</td>
</tr>
<tr>
<td>Turkish illitic clay (TIC)</td>
<td>50</td>
<td>11.25</td>
<td>78%</td>
<td>Ozdes et al. (2011)</td>
</tr>
<tr>
<td>Modified plantain peels</td>
<td>120</td>
<td>10.44</td>
<td>99.43%</td>
<td>Garba et al. (2016)</td>
</tr>
<tr>
<td><em>Pinus halepensis</em> sawdust</td>
<td>5</td>
<td>5.36</td>
<td>97.7%</td>
<td>Semerjian (2010)</td>
</tr>
<tr>
<td>Shoe waste</td>
<td>305</td>
<td>396.32</td>
<td>94.66%</td>
<td>Iqbal et al. (2016)</td>
</tr>
<tr>
<td>Maize tassel-magnetite nanohybrid</td>
<td>44.6</td>
<td>52.05</td>
<td>97.26%</td>
<td>Guyo et al. (2015)</td>
</tr>
<tr>
<td>Grapefruit peel</td>
<td>50</td>
<td>42.09</td>
<td>85.56%</td>
<td>Torab-Mostaedi et al. (2013)</td>
</tr>
<tr>
<td>Mercapto-modified bentonite</td>
<td>49.55</td>
<td>27.55</td>
<td>94.52%</td>
<td>This study</td>
</tr>
</tbody>
</table>
(mg g⁻¹) and $B_D$ is the activity factor related to mean energy of adsorption (mg² J⁻²). $\varepsilon$ is the Polanyi potential and can be calculated from Equation (13).

$$\varepsilon = RT\ln(1 + \frac{1}{C_e})$$ (13)

where $\beta$ gives an indication of the mean adsorption free energy $E$ (kJ mol⁻¹) which can be calculated using the following correlation (Equation (14)).

$$E = \frac{1}{\sqrt{-2B_D}}$$ (14)

If the value of $E$ is between 8–16 kJ mol⁻¹, the adsorption mechanism is chemical ion exchange. If this value is less than 8 kJ mol⁻¹, the adsorption process is physical (Sahan & Öztürk 2014; Kamaraj et al. 2018). The $E$ value was calculated to be 0.707 kJ mol⁻¹. This shows that Cd(II) adsorption is of a physical nature.

Figure 6 shows the linear isotherm plots. The isotherm parameters and their correlation coefficients $R^2$ acquired from these isotherm models are given for comparison in Table 4. When the correlation coefficients are considered, Langmuir and D-R equations are better than the others.

In addition, the non-linear isotherms including Langmuir, Freundlich, D-R, Langmuir-Freundlich (L-F), Redlich-Peterson (R-P), Toth and Khan have also been applied to the adsorption data (Figure S1, available with the online version of this paper). The L-F isotherm model assumes that adsorption energy is heterogeneously distributed onto the surface of the adsorbent. This model converts to the Langmuir isotherm at high adsorbate concentration and the Freundlich isotherm at low concentration. The R-P isotherm is a hybrid isotherm featuring both Langmuir and Freundlich isotherms, which incorporates three parameters into an empirical equation. Therefore, the mechanism of adsorption is a mix and does not follow ideal monolayer adsorption. Additionally, this isotherm is applicable in either homogeneous or heterogeneous systems because of its versatility. The Toth isotherm is an empirical modification of the Langmuir equation with the aim of reducing the error between experimental data and the predicted value. It is clear that when $n = 1$, this equation converts to the Langmuir isotherm equation. Consequently, the parameter $n$ defines the heterogeneity of the adsorption system and if it deviates further away from 1, then the system is said to be heterogeneous. The Khan isotherm model is a general model suggested for the pure solutions. The parameters of non-linear adsorption isotherm models were evaluated by using the Solver in Microsoft Office Excel. The non-linear equations of L-F, R-P, Toth and Khan

![Figure 6](https://iwaponline.com/wst/article-pdf/78/6/1348/504516/wst078061348.pdf)
and the parameters of all non-linear isotherm models are given in Tables S1 and S2, respectively (available online).

**Kinetic studies**

The adsorption kinetic studies are very important to determine the effect of Cd(II) adsorption at the different time intervals. Three kinetic models including the pseudo-first-order (Lagergren 1898), pseudo-second-order (Ho & McKay 1999) and Weber-Morris (Weber & Morris 1965) were tested to obtain kinetic data for Cd(II) adsorption onto MMB. The linearized forms of these models are as follows:

\[
\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\]

(15)

\[
t = \frac{1}{q_t} \left( \frac{k_2 q_e^2}{k_2 q_e^2 + q_e} \right)
\]

(16)

\[
q_t = k_d t^{0.5} + C
\]

(17)

where \(q_t\) and \(q_e\) (mg \(g^{-1}\)) are the adsorbed amount at time \(t\) and equilibrium, \(k_1 (\min^{-1})\) and \(k_2 (\text{mg} \cdot \text{min}^{-1} \cdot \text{g}^{-1})\) are the rate constant of pseudo-first and second order, respectively, \(k_d (\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5})\) is the intraparticle diffusion rate constant and \(C\) is the thickness of the boundary layer (Kamaraj et al. 2016). From the results based on Figure S2 and Table S3 (available online), it can be concluded that the pseudo-second-order model is more suitable for kinetic data because of higher \(R^2\). In addition, the theoretical \(q_e\) value (31.35 mg \(g^{-1}\)) obtained from the pseudo-second-order model is fairly close to the experimental \(q_e\) value (27.54 mg \(g^{-1}\)). The Weber-Morris model was employed to explain how Cd(II) ions are transferred from the solution to the MMB surface (Vasudevan & Lakshmi 2013). The obtained results indicated that %Cd(II) adsorption onto MMB might be controlled by intraparticle diffusion as well as film diffusion because the line does not pass through the origin.

**Thermodynamic parameters for Cd(II) adsorption**

The thermodynamic parameters including free energy change (\(\Delta G^\circ\)), enthalpy change (\(\Delta H^\circ\)) and entropy change (\(\Delta S^\circ\)) have great value to evaluate the naturalness and the heat change of the adsorption processes. These coefficients for Cd(II) adsorption can be calculated using the van’t Hoff Equation (Equation (21)).

\[
K_C = \frac{C_A}{C_S}
\]

(18)

\[
\Delta G^\circ = -RT \ln K_C
\]

(19)

\[
\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ
\]

(20)

\[
\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}
\]

(21)

The thermodynamic parameters obtained from Figure 7 for the adsorption of Cd(II) on MMB at the examined temperatures are presented in Table 5.

The negative \(\Delta G^\circ\) values of Cd(II) adsorption at diverse temperatures (20–35 °C) confirm that the adsorption processes are natural and spontaneous. The values of \(\Delta G^\circ\) increased with an increase in temperature, which verifies that the applicability and naturalness of adsorption increases at lower temperatures (Lakshmi & Vasudevan 2013; Taha et al. 2016). The negative value of \(\Delta H^\circ\) suggests the exothermic nature of Cd(II) adsorption. The negative \(\Delta S^\circ\) value characterizes a decrease in randomness at the solid/liquid interface during the adsorption of Cd(II) on MMB (Semerjian 2010; Kamaraj et al. 2015).

**Table 4 |** Langmuir, Freundlich and D-R isotherm constants for Cd(II) adsorption on MMB

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>D-R Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(q_{\text{max}}) (mg (g^{-1}))</td>
<td>68.97</td>
<td>n 2.55</td>
<td>53.32 (mg (g^{-1}))</td>
</tr>
<tr>
<td>(K_L) (L (mg^{-1}))</td>
<td>0.285</td>
<td>(K_f) 21.04</td>
<td>(B_D) 1.0E-06 (mol^2 \cdot j^{-2})</td>
</tr>
<tr>
<td>(R_L)</td>
<td>0.034</td>
<td>(R^2) 0.95</td>
<td>(E) 0.707 (kJ \cdot mol^{-1})</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.99</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 7 | Plot of \(\ln K_C\) vs. \(1/T\) for the prediction of thermodynamic parameters of Cd(II) adsorption.
CONCLUSION

The current study indicates that MMB can be used as an efficient adsorbent for removal of Cd(II) from wastewater. CCD was employed to rate the effects of parameters on the removal efficiency of Cd(II) ions. The optimum conditions for maximum Cd(II) adsorption were pH 6.40, temperature 20 °C, initial metal ion concentration 49.55 mg L⁻¹ and adsorbent dose 0.17 g for MMB. In optimum conditions, the amount adsorbed and the maximum removal yield were calculated to be 27.54 mg g⁻¹ and 94.52%, respectively. The results obtained for the adsorption of Cd(II) ions from aqueous solutions were tested with some isotherm equations and it was determined that Langmuir and D-R adsorption isotherms are more compatible than the others. Moreover, the kinetic data fitted very well with the pseudo-second-order model. The results based on the Weber-Morris kinetic model showed that the step controlling the adsorption rate was not only the intraparticle diffusion but also film diffusion. Thermodynamic studies showed that the adsorption process was spontaneous and exothermic. As a result, MMB can be chosen as an effective adsorbent for treating heavy metals from wastewater and removing them from aqueous environments.

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REFERENCES


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