

Adsorption of Cadmium from Aqueous Solution onto Untreated Gypsum Rock Material: Equilibrium and Kinetics

Zulqarnain Satti ^{1,†}, Mansoor Akhtar ^{2,†,*} , Noreen Mazhar ³, Shifa Ullah Khan ⁴, Naveed Ahmed ¹, Qazi Muhammad Yasir ¹, Muhammad Irshad ^{5,*}, Rashid Pervaiz ⁶, Waqas Ahmad ⁷

¹ School of Geographical Sciences, Northeast Normal University, Changchun, 130024, China

² Faculty of Chemistry, Northeast Normal University, Changchun, 130024, Jilin, China

³ Institute of Chemistry, University of Punjab, Quaid-e-Azam Campus, Lahore-54590, Pakistan

⁴ School of Sino-Foreign Chemical Engineering Liaoning University of Petroleum and Chemical Technology, Fushun, Liaoning, China

⁵ Arid Land Research Center, Tottori University, Tottori, 680-0001, Japan

⁶ Key Lab of Submarine Geosciences and Prospecting Techniques, MOE, College of Marine Geosciences, Ocean University of China, Qingdao 266100, China

⁷ College of Veterinary and Animal Sciences (CVAS), Narowal (Sub-campus), University of Veterinary and Animal Sciences, Lahore

† These authors contributed equally to this paper

* Correspondence: akt100@nenu.edu.cn, mirshad@cuiatd.edu.pk

Scopus Author ID 57191956119

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Abstract: The concentration of heavy metals exceeding from certain limit may cause risk and endanger ecosystems and human health. Water receives a considerable concentration of heavy metals from different anthropogenic and natural sources. A study was carried out to investigate the effectiveness of rock materials on the reduction of Cd from contaminated water. For this purpose, gypsum was applied to the contaminated water. The findings of the present study concluded that the adsorption of Cd was higher in finer rock material rather than coarse material due to the surface area. The finer grains contained a greater surface area than coarse grains. The isotherms of adsorption were constructed according to the mathematical linearization. The best-fitting followed the Freundlich and Dubinin–Radushkevich models, describing multilayer adsorption and chemical interaction, also confirmed by the pseudo-second-order kinetic model. The material removed a greater amount of Cd from contaminated water, especially at an increasing application rate.

Keywords: adsorbent material; cadmium; contaminated water; gypsum.

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1. Introduction

Wastewater has been originating from industries, municipal areas that contain heavy metals. These metals are hazardous for water resources, agriculture, ecosystem, and the human population [1]. The analysis to understand systems and technologies for the removal of heavy metals is crucial to resolve this issue for a sustainable ecosystem. Heavy metals are fairly mobile in the soils and primarily present as an organically bound, exchangeable, and water-soluble species [2]. Most heavy metals produce toxicity, even permit concentrations approximately 0.1–0.3 mg L⁻¹ [3, 4]. Heavy metals have been considered non-biodegradable hence can be accumulated in the living tissues, causing various diseases and disorders. It is

imperative to remove before discharge from the origin. Their harmful effects were brought into consideration when human, and marine life destruction was being noticed, including the aesthetic property of water. Wastewaters need to be treated before discharge into the environment for the protection of numerous species, including humans [5-10]. Basically, adsorption is a mass transfer process in which a substance is transferred from the liquid phase into a solid surface and becomes bound with physical and/or chemical interactions [6, 7]. The higher adsorption capacity and surface reactivity, adsorption using activated carbon can remove metals due to higher surface area such as Ni (II) [11-16] Cr (VI) and Cd (II).

Cd (II) belongs to a group of hazardous heavy metal that exists in the effluent, produced via metal finishing industry [9] (e.g., electroplating), battery industry, and paint industry. Cadmium (Cd (II)), zinc (Zn), copper (Cu), nickel (Ni), lead (Pb), mercury (Hg), and chromium (Cr) are often detected in industrial wastewaters. They originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing, and photographic industries [10, 11]. Adsorption is figured out as the most effective and economical method for Cd (II) containing naturally available material. This material can be efficiently used for the removal of Cd (II) from aqueous solution [17-27]. Adsorption was considered one of the physicochemical treatment phenomena that can be effective in removing heavy metals from the aqueous solutions. According to [13, 32], an adsorbent is cheap or low-cost if it persists abundant in nature. Moreover, it does not require sophisticated instruments and machinery for excavation. Recently, several studies have been conducted on soil heavy-metal pollution from various anthropogenic sources like Industrial wastes [28-38] or mining activity [17, 22].

The use of different materials might be beneficial for immobilizing heavy metals in polluted soil. Previously, many studies have been conducted to determine the use of different materials to stabilize heavy metals in soil. In contrast, limited studies recognized the effectiveness of different minerals to reduce their concentrations in polluted water [39-45]. There is a lack of reliable information on the removal of heavy metals from contaminated water by effective rock material. The effectiveness of rock material to ameliorate heavy metals from polluted water was partially identified, and the research question regarding competitive retention of Cd onto these minerals was not properly addressed [46-51]. The aim of the present analysis is to investigate the effectiveness of rock materials for the reduction of Cd from contaminated water. So, it represents sustainable management with high applicability and minimum environmental impact

2. Materials and Methods

The rocks of gypsum (CaSO_4) were sampled from geologic formations (Abbottabad) with a geologic hammer and kept in a polythene bag for laboratory in (NE-SW) direction. Later, rock samples were washed with deionized water and put in furnace around 24 hours (h) at 90 °C for dryness. Powdered rock samples were weighed out as per the specifications of the batch experimentation and kept in a moisture-free environment.

2.1. Chemicals.

The chemicals which were used in this study were Cadmium chloride tetrahydrate (642045, Sigma-Aldrich), NaOH (221465, Sigma-Aldrich), and HNO_3 (225711, Sigma-Aldrich).

2.2. Analysis.

Morphological characterization of the gypsum rocks was obtained via SEM (scanning electron microscopy). The model of equipment was scanning electron microscope FEI Quanta 200, operating at 30 kV.

To characterize the load on the adsorbent's surface, the point of zero charges (pH_{PZC}) of the gypsum rocks was identified. The process involved adding 50 mg of a gypsum rock sample in 50 mL aqueous potassium chloride at 0.05-0.5 mol L⁻¹, with initial pH values ranging from 2.0 to 10.0. Solutions were stirred for 24 h at 200 rpm and 25 °C. At the end of this period, the final pH variation as a function of the initial pH; the point that reached the zero value of pH variation corresponds to the pH_{PZC} [24, 34].

2.3. Adsorption studies.

2.3.1. Effect of the solution's pH and amount of adsorbent mass.

Cd was used in solutions of 10 mg L⁻¹, prepared from CdCl₂ salt utilizing distilled and deionized water. The pH of the solution was adjusted to 5.0, 6.0, and 7.0 using Hydrochloric acid (HCl) and Sodium hydroxide (NaOH), both at 0.1 mol L⁻¹. Cd ion solutions (50 mL) were added to the masses of gypsum rock samples, ranging from 200 to 1,200 mg in 125 mL flasks. Samples were agitated at 200 rpm for 90 min at 25 °C. Thereafter, 10 mL aliquots were removed and centrifuged at 3,000 rpm (629.77 gravity) for 5 min, for the later determination of Cd concentrations in solution by flame atomic absorption spectroscopy. The Cd amount adsorbed was determined using Equation (1):

$$Q_{eq} = (C_0 - C_{eq})/m \quad (1)$$

In which Q_{eq} is the amount of metal adsorbed by adsorbent mass (mg g⁻¹), C_0 and C_{eq} are the initial metal concentration and in the solution equilibrium (mg L⁻¹). V is the solution volume (mL), and m the by-product mass (g).

2.3.2. Effect of contact time.

The optimal contact time for maximum cadmium removal was established. The systems containing adsorbent and Cd solution (10 mg L⁻¹) were stirred at 200 rpm and 25 °C at the time intervals: 60, 120 min.

2.3.3. Adsorption isotherms.

The optimal experimental conditions were adjusted for the construction of isotherms. Herein, 50 mL samples of the aqueous solution of Cd metal at different initial concentrations (10-80 mg L⁻¹ at pH 6.0) were transferred to conical flasks containing 300 mg adsorbent. The system remained in agitation at 200 rpm and 25 °C for 60 min.

2.4. Desorption.

The adsorbent material used in the adsorption isotherms was separated from the aqueous solutions via filtration method, washed in distilled and deionized water, and dried at 70 °C for 36 h. The adsorbent mass was obtained and placed in contact with 40 mL of hydrochloric acid solution at 0.1 mol L⁻¹ and then stirred at 200 rpm around 1 hour.

3. Results and Discussion

3.1. Adsorbent characterization.

The adsorbent capacity of the sample has been shown in Figure 1, with the magnification of 10,000. However, the irregular and heterogeneous nature of gypsum are clearly seen, which favors the adherence of metal ions in the aqueous solution.

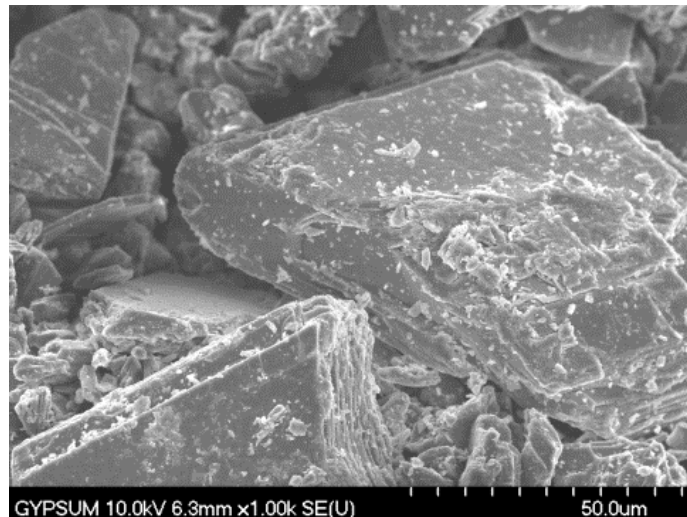


Figure 1. Scanning electron micrograph of the gypsum adsorbent enlarged 10,000 fold.

The outcome of pH_{PZC} determination for gypsum adsorbent material is shown in (Figure 2), confirming the data obtained by also performed the pH_{PZC} test [25].

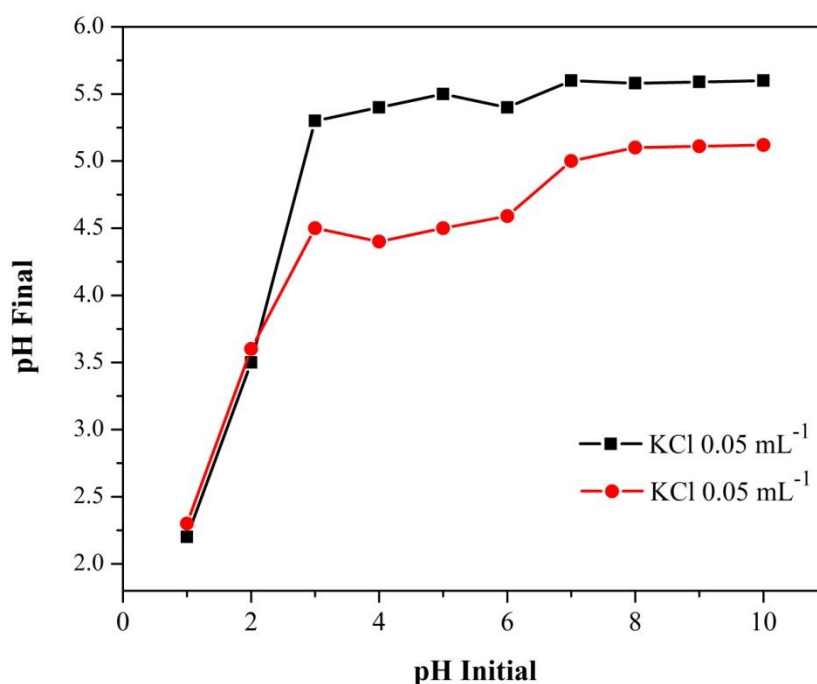


Figure 2. Experimental data for determining the pH_{PZC} for gypsum adsorbent material.

3.2. Adsorption study.

3.2.1. Effect of solution pH and adsorbent mass.

The study revealed that solutions at pH 6.0 had a higher percentage of Cd ion removal than at the other pH values. (Figure 3) confirms that the pH_{PZC} was pH 5.5, and showing

adsorbent behaved in this condition as a negatively charged species. In the literature, pH 6.0 values extensively reported in Cd adsorption [26].

The influence of the adsorbent mass on the Cd adsorption (Figure 3) shows the masses higher than 500 mg, accordingly. The percentage of adsorption was constant due to the fact that a large number of sites in the adsorbent surface are available during the early stage. Thereafter, the remaining sites are difficult to occupy due to the formation of aggregates and repulsive forces between the ions in the solid and those which are free in solution [26]. Thus, in the account of present outcomes, the adsorbent mass used in subsequent studies was 500 mg.

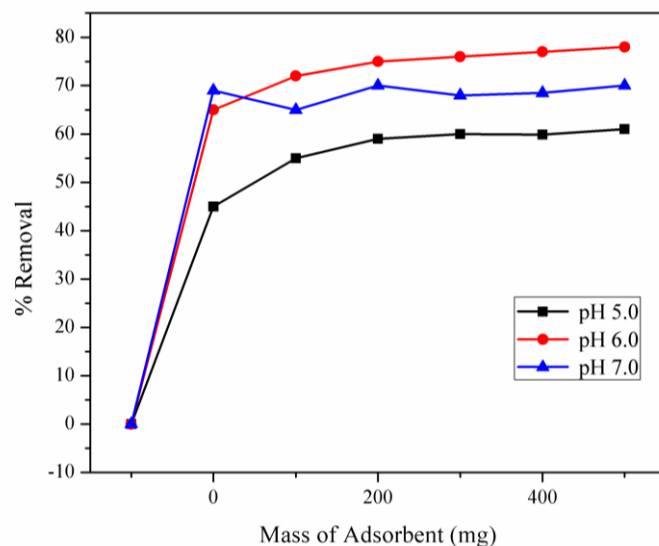


Figure 3. Percentage of Cd removal gypsum material depending on the variation of adsorbent mass and solution pH (C_0 : 10 mg L⁻¹, 90 min, 200 rpm 25 °C).

3.2.2. Effect of contact time.

The kinetics of adsorption of Cd on adsorbent material was analyzed using four models [38]. The pseudo-first-order model (Equation (2)) illustrates that the adsorption rate is proportional to the number of sites unoccupied by the solutes [27].

$$\log(Q_{eq} - Q_t) = \log Q_{eq} - K_1 \times t / 2.303 \quad (2)$$

in which Q_t is the amount adsorbed at time t (min) given in mg g⁻¹, K_1 is the speed constant for pseudo-first-order (min⁻¹).

Unlike the pseudo-first-order model (Equation (2)), the pseudo-second-order model predicts the adsorption of chemical nature [25].

$$\frac{t}{Q_t} = \frac{1}{K_2 \times Q_{2eq}} + \frac{1t}{Q_{eq}} \quad (3)$$

where K_2 is the speed constant of pseudo-second-order (g mg⁻¹ min⁻¹).

The Elovich model (Equation 4) describes the kinetics of chemisorption behaviors [27]

$$Q_{eq} = A + B \ln t \quad (4)$$

where A represents the initial speed of chemisorption, and B is related to the extent of surface coverage and the chemisorption activation energy.

Although the intraparticle diffusion model was shown a higher value for the coefficient of determination (R^2 0.904) than the pseudo-first-order (0.807) and Elovich models (0.870),

the pseudo-second-order model demonstrates a better fit by having Q_{eq} experimental values (0.902) similar to the Q_{eq} calculated (0.890) and the R^2 value (0.998) around 1.

The kinetic study regarding question reinforces involving bibliographic study performed by the absorbency of divalent metals on various adsorbents was comprehensively described by the pseudo-second-order model, which indicates that the speed mechanism control is based on chemical adsorption [26, 28].

3.2.3. Adsorption isotherms.

To interpret the experimental data, four linearized isotherm models were employed. The Langmuir model (Equation (5)) suggests the adsorption on a uniform surface composed of a finite number of sites containing monolayer adsorption[27]

$$\frac{C_{eq}}{Q_{eq}} = \frac{1}{q_m \times b} + \frac{C_{eq}}{q_m} \quad (5)$$

in which q_m is related to the maximum capacity of adsorption and b or the Langmuir equilibrium constant K_L is related to the adsorbent–adsorbate interaction forces.

Unlike the Langmuir model, the Freundlich model (Equation (7)) describes multilayer adsorption, and it applies to heterogeneous surfaces [27].

$$\log Q_{eq} = \log K_f + \left(\frac{1}{n}\right) \times \log C_{eq} \quad (6)$$

in which K_F is related to the adsorption capacity and n to the intensity of adsorption and the adsorbent–adsorbate interaction.

The Dubinin–Radushkevich isotherm (D–R) (Equation 7) is applied to determine the adsorption energy and distinguish if the process is physical or chemical [26].

$$\ln Q_{eq} = \ln Q_d - B_d \times \varepsilon^2 \quad (7)$$

in which Q_d is the maximum capacity of adsorption (mol g^{-1}), B_d expresses the adsorption energy ($\text{mol}^2 \text{J}^{-2}$), which is linked with the average power of sorption (E) ($E=1/\sqrt{-2B_d}$). ε is the Polanyi potential ($\varepsilon=RT\ln(1+1/C_{eq})$ in which R is the universal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$), and T is the temperature (K).

Table1. Parameters of the mathematical models of Langmuir, Freundlich, and Dubinin–Radushkevich for Gypsum adsorbent material.

Parameters	Gypsum material
<i>Langmuir</i>	
$q_m(\text{mg g}^{-1})$	18.332
b or $K_L (\text{L mg}^{-1})$	0.025
R^2	0.908
<i>Freundlich</i>	
$K_F (\text{L g}^{-1})$	0.552
N	1.118
R^2	0.941
<i>Dubinin–Radushkevich</i>	
$Q_d (\text{mol g}^{-1})$	4.4×10^4
$E (\text{kJ mol}^{-1})$	8.034
R^2	0.934

The D–R and Freundlich models demonstrate the adsorption process for both adsorbents with R^2 values (Table 1). This suggests that the adsorption is influenced by the

adsorbent surface heterogeneity, with more than one type of active site interacting with the metal, which indicates that the adsorption occurred in multilayers [29].

Regarding parameter n , both adsorbents showed adsorption intensity, the obtained n value was greater than 1, representing beneficial and favorable adsorption [27], and mentioned (Table 1) for better understanding. The E values were greater than 8 kJ mol^{-1} , which proves that both adsorbents have a chemical interaction with the metal. Also, the values of b , which represents the interaction power, were higher in the carbon (0.094 mg L^{-1}) than the biosorbent (0.028 mg L^{-1}), which confirms the superior results of the E value for the commercial adsorbent.

3.3. Desorption.

The proportion of Cd ion adsorption on the gypsum material was 76%, including adsorbed amount around 79% of the ions were recovered in the desorption. These differences in adsorption and desorption between the two adsorbents can be explained with greater interaction (b) and adsorption intensity (n) Table 1 with the metal under consideration. These percentage values of desorption can be accepted satisfactory for possible reuse of the adsorbent material during new stages of adsorption [30].

4. Conclusions

Overall, the characterization of the gypsum material showed a favorable structure for adsorption. The better adsorption of Cd ions was found in solutions with pH 6.0, confirming the pH dependence on the adsorption process with the value of 5.5 in the determination of pH_{PZC} in the present study. The interaction of the gypsum material with the metal ions pointed to chemisorption due to the best kinetics fit with the pseudo-second-order model. The value of the average energy of sorption (E) of D–R greater than 8 kJ mol^{-1} . Furthermore, we concluded that the removal of Cd moieties which did not undergo any treatment could be used as a potential Cd adsorbent. It is an effective tool in the remediation of environmental compartments contaminated by toxic heavy metals. We further recommend analyzing the behavior of the mineral materials, subsequently investigating the adsorption capacity with industrial effluents for different categories of metals.

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Conflicts of Interest

The authors declare no conflict of interest.

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