Interaction models on sand surface of natural adsorbent with adsorbate Cd$^{+2}$ metal ions in solution with batch operation

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Abstract. The interaction type of metal ion with the adsorbent surface in adsorption operation was evaluated in this study. The binary metal ions in solution was mixed with the sand then shaken in 100 rpm. The kinetics adsorption capacity was than measured with the pseudo order model to evaluate the interaction type from the $r^2$ indicator. The result found that the Cd ions with $r^2 = 0.9656$ and $r^2 = 0.9989$ for first and second order respectively, for black sand and $r^2 = 0.9070$ and $r^2 = 0.999$ for first and second order respectively, for white sand. It was indicated that the interaction type of metal ions on sand surface was occurred together as physical and chemical interaction.

1. Introduction

Heavy metals have ability to harm the physiology and human biological system, if it exceeds the tolerance level; it causes a number of diseases [1,2]. Sand has reported as adsorbent [3,4]. It has used after modified as reported by Gusain et al. (2013) [5] of sands of the Ganges-Varanasi, modified with Fe ion from India, Han [6] of sand modification with FeS from Korea; used naturally as reported by Haryanto [7], with natural sand from Taiwan [8,9], Shi et al. (2014) [10] with the natural sand, Ruba Al-Khali from Saudi Arabia; Thambavani dan Kavitha (2014) [11] of sand from river in Tamil Nadu (Hindi).

The reason to used sand because it has macro-porous and meso-porous structures [12]. Pores contribute a more surface area and a higher selectivity on reaction and adsorption interaction [13]. Charles W, 1994 [14] has reported that sand with porous characteristic creates the intra-particle porosity. Sand as the tetrahedral silica with hydroxyl functional groups on the surface, it can be represented as =Si–OH [15]. The functional interaction with the primary bonding force in inner-sphere complexes is a coordinate-covalent bonding in contrast to electrostatic bonding in outer-sphere complexes [16-18].

There are several purification processes for water contaminated by heavy metals such as: adsorption process [19], coagulation and precipitation chemistry, electro-flotation [19,20], ion exchange and membrane separation [21]. Adsorption process is more efficient and less expensive than other technology entrapment of heavy metals.

Equation (1) uses in measuring the adsorption capacity until it reaches equilibrium; is the amount of metal ion adsorbed in sand at equilibrium ($q_e$). The $q_t$ is the amount of metal ion adsorbed in sand at certain time $t$, when one run on contact time (Equation 2). Equation 3 (%R) is to determine the percentage of metal ion adsorbed removed from water, when using the adsorption operation.
\[ q_e = \frac{(C_0 - C_e)V}{m_{ads}} \]  
(1)

\[ q_t = \frac{(C_0 - C_t)V}{m_{ads}} \]  
(2)

\[ R\% = \frac{(C_0 - C_e)}{C_0} \times 100\% \]  
(3)

Where: \( C_0 \) is the initial metal concentration (mg/L), \( C_t \) is the metal concentration at time \( t \) (mg/L) and \( C_e \) is the metal concentration at equilibrium (mg/L); \( q_e, q_t \) and \( q_r \) is (mg/g). \( V \) is the volume of solution (L) and \( m_{ads} \) is the mass of adsorbent (g) [7,19,22,23,24,25,26].

Adsorption kinetic model can be evidenced by the coefficient correlation \( (r^2) \). First order (4) and second order (5) equations of respectively expressed as follows [1,24,26,27]:

\[ \log(q_e - q_t) = \log q_e - \frac{k_1}{2,303} \times t \]  
(4)

\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_et} \]  
(5)

The aims of this investigation is to apply the pseudo order 1\textsuperscript{st} and order 2\textsuperscript{nd} equations to identify the type of adsorption interaction of metal ion \( \text{Cd}^{2+} \) on two type sand surface base on correlation coefficient \( (r^2) \). The empirical data of adsorption process on single substance of \( \text{Cd}^{2+} \) as adsorbate and sands white and black as adsorbent with batch operation were used.

2. Methodology

Two types sand were used in this study as shown in Figure 1. The white sand Figure 1A was obtained from Pantai Cermin district and the black sand (Figure 1B) from Namorambe district, Sumatera Utara, Indonesia. The size of sand used was 40 mesh. Sand was cleansing then continues to adsorption process. All sand was washed until the washing water has constant pH as the confirmation that sand already has the same condition before used as natural adsorbent.

A. White sand  
B. Black sand

![Figure 1. White and black sand natural adsorbents](image)

In this experiment, Figure 2 shows every section in adsorption process. Section A prepare 50 ppm \( \text{CdCl}_2 \) dissolved by pure water at pH 4.5. Then continue to section B mix 100 ml \( \text{CdCl}_2 \) 50 ppm with 100g sand. Section C, each Erlenmeyer was shacked for 6 hours with 150 rpm revolutions per minute. 0.5 ml samples were taken every 5 minutes to be analyzed by AAS. To confirm the presence of \( \text{Cd}^{2+} \) on sand surface was analyzed by FTRI. SEM was used to identify the sand surface characteristic. Equations 2 and 3 were used to measure the adsorption kinetic. The equations 4 and 5 were used in measure to predict the adsorbent interaction type with adsorbate \( \text{Cd}^{2+} \). Correlation interaction the \( r^2 \) was used to predicts interaction type on both adsorbents surface with contaminant \( \text{Cd}^{2+} \) ion.
3. Result and Discussion

3.1. Adsorption Kinetics

Adsorption kinetics is demonstrated at figure 3. The contact time of adsorption process was conducted for 360 min. The absorption capacity of both adsorbent increased with initial concentration of metal ion Cd 50 ppm. From the results for, in the first 5 minutes, the amount of metal ions Cd$^{2+}$ adsorbed was only 13.66%. Cd$^{2+}$ adsorbed achieves optimum point in the minute-200, where the %R adsorbed was 39.31% for white sand (Figure 3A). For the black sand has optimum point in the minute-200 with the %R 25% as shown in Figure 3B. The adsorption capacity was changes largely in the first 10 minutes. It was lower in comparing the ability of white sand. After some time, the ability of the adsorption capacity starts to decline and relatively constant.

![Figure 3. Adsorption kinetic of Cd ion on white sand (A) and black sand (B).](image)

The adsorption equilibrium can be achieved by measuring the contact time between the adsorbent with the adsorbate Cd$^{2+}$. For the white sand, adsorption capacity continues to increase to adsorb Cd$^{2+}$ ion until the time of 300 minutes with the concentrations of adsorbate Cd$^{2+}$ consecutively: 25.35%, 29.22%, 31.44%, 34.55%, 35.41%, 37.51 %, 38.35%, 38.61%, 38.89%, and 38.96%. After 100 minutes interaction, adsorption of Cd$^{2+}$ by white sand had approached a constant point. This show, that the adsorption process has achieved an equilibrium state. The equilibrium time is to find out when an adsorbent already reached saturation so that the adsorption process has been completed [11]. For the black sand, the equilibrium time was after 80 minutes.

In this investigation, the data of adsorption kinetics of Cd ion on white sand and black sand are empirically derived using models pseudo first order (Equation 4) and pseudo second order (Equation 5). This modelling is required to describe and evaluate adsorption mechanism and identify an average rate of adsorption on the adsorbent sands for single solution [1]. The models can also be used to categorize whether during the adsorption process chemical reactions and physical interaction occur or not in the adsorbent based on the correlation coefficient. The ($r^2$) correlation coefficient obtained by plotting the data of adsorption capacity (qt) versus time using the above equation.
3.2. Pseudo First Order
The equation of Pseudo First Order have value of $r^2 = 0.907$ and $r^2 = 0.9606$ for white and black sand respectively as shown in Figure 4. Figure 5 shows the equation of Pseudo second order for white (A) and black (B) sand. The results have value of $r^2 = 0.999$ for white sand and $r^2 = 0.9989$ for black sand. These show that modeling of pseudo first and second order makes the data more representative adsorption interaction.

![Figure 4](image1.png)

**Figure 4.** Pseudo First Order model with Cd$^{2+}$ 50 ppm and speed 150 rpm

3.3. Pseudo Second Order
From the results of theoretical calculations, the correlation coefficient ($r^2$) for first order is lower than second order as shown at Figure 4 and 5. The equation of first order and second order, each has the value of correlation coefficient ($r^2$) related quite similar. From these data it can be determined that the adsorption process was involving a chemical interaction (chemisorption) and physical interaction (physical sorption) between the adsorbate and adsorbent on the surfaces occur together [1,24,26,27].

![Figure 5](image2.png)

**Figure 5.** Second Order Pseudo with Cd$^{2+}$ 50 ppm and speed 150 rpm

Cleanse Sand (A) and contaminated sand (B) was confirmed of the changing the effect of adsorption on sands surface by using FTIR as shown in Fig. 6. Galo et al. (2004) [28] have reported the range wavenumber (cm$^{-1}$) for Si-OH is in the range 500 to 1000. As shown in Figure 6 within the wavenumber range FTIR analysis, the interaction of on sand surface to interact with Cd$^{2+}$ after and
before contaminated of the white sand. In this study, the interaction of Cd\textsuperscript{2+} with functional Si-OH on sand surface have confirmed as shown on variation of wavenumber in the range 500 to 1000 (cm\textsuperscript{-1}). Figure 7 shows the surface characteristic the white sand with 1500x magnitude. The SEM image shows the porous characteristic of sand. The surface characteristic of white sand with ability to interact with Cd ion is about 40 ppm. The possible diffusion adsorbed metal ion goes to inter particle area on adsorption operation. It is impact to the interaction on sand surface with porous characteristic as chemical and physical interaction on sand surface.

A. Cleansed sand
B. Contaminated sand

**Figure 6.** FTIR confirmation cleansed white sand (left) and contaminated white sand (right)

**Figure 7.** SEM surface of white sand

4. Conclusions
The adsorption capacities of the white sand were higher than black sand. The investigation was to apply the pseudo order 1\textsuperscript{st} and order 2\textsuperscript{nd} base on the adsorption kinetic empirical data for both sand types. It was obtained the trend similar on correlation coefficient (r\textsuperscript{2}). The results found that the Cd\textsuperscript{2+} ions with r\textsuperscript{2} = 0.9070 and r\textsuperscript{2} = 0.9656 for first order for white and black sand respectively. For the second order found that the r\textsuperscript{2} = 0.999 and r\textsuperscript{2} = 0.9989 for white and black sand respectively. The result was indicated that the interaction type of Cd\textsuperscript{2+} ions on sand surface was occurred together as physical and chemical interaction. Analyze with using BET is needed to confirm the difference pore size area of both sand types that impact to adsorption capacity of white sand higher than black sand.
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