Research article

Removal of Cu (II) by calcinated electroplating sludge

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ABSTRACT

Electroplating sludge consists of various heavy metal oxides, which may be utilized as adsorbent to remove Cu (II) present in aqueous environment. This study evaluated the adsorption performance of calcinated electroplating sludge. The adsorption isotherm based on Langmuir equation proved that calcinated electroplating sludge had a higher adsorption performance than raw electroplating sludge, with maximum adsorption capacity 92 mg/g and 76.34 mg/g, respectively. Findings of the conducted kinetic study revealed that both surface adsorption and intra-particular diffusion were involved during the adsorption process. Moreover, the comparison between the experimental and calculated data of equilibrium adsorption capacity demonstrated that the pseudo second-order kinetic equation fitted well with 38.31 mg/g of calcinated sludge and 33.66 mg/g of raw sludge, approximate to real-world data. Furthermore, adsorption mechanism research demonstrated that while OH group plays a vital role in raw sample, Ca^{2+}, in addition to OH group, was involved in ion exchange in calcinated sample.

1. Introduction

Electroplating is the process of plating specific metal onto another by hydrolysis to prevent corrosion or decorative purposes. Hence, the electroplating sludge consists of various heavy metals and is a potential secondary metal; however, without treatment, it can have adverse effects on human health and environment (Chung et al., 2014). Currently, the common technologies used to treat electroplating sludge are landfilling (Li et al., 2015) and brick making (Tang et al., 2014). Nevertheless, the former can contaminate groundwater and soil and cause the leakage of heavy metals (Li et al., 2015), while the latter may lead to the leakage of dangerous volatile heavy metals such as Cu, Fe, Cr, Ni, Mn (Tang et al., 2014). Therefore, a waste product approach utilizes waste as adsorbent for removal of heavy metal present in aqueous environment and can be extremely beneficial to alleviate environmental damage.

Wastewater consists of heavy metals that can destroy the ecosystem by the accumulation through food chain and then act hazardous to human health if discharged directly. To remove heavy metals in aqueous solution, diversified treatment technologies have been examined; such technologies can be chemical technologies, such as precipitation (Bhattacharyya et al., 1979), ion exchange (Hu et al., 2017), or physical technologies such as adsorption (Feng et al., 2009), or even biological technologies (Magdalena

and Małgorzata, 2014) such as using microorganism. However, these methods still have a number of limitations. Most chemical and physical methods involve the use of dangerous chemicals such as acid, alkaline, and other metal and anion ion. Moreover, during the treatment, the high temperature can form vaporized chemicals and affect the environment. Biological methods, although simple and low cost, are time-consuming, which can, in turn, interfere with the economic efficiency of the plant.

Among the physical and chemical methods, adsorption is a convenient method for environmental treatment (Huly and Ali, 2014) and can be used to remove heavy metals in wastewater (Feng et al., 2009). Many research studies have reported that adsorbents such as active carbon (Yongning et al., 2018), silica gel (Hui et al., 2002), metal hydroxide (Asiabi et al., 2017), and composite material (Awual, 2017) have high efficacy in removing heavy metals from wastewater. A commercial adosrbent (such as activated carbon) entails high cost and complicated design. Thus, a natural adsorbent is a suitable alternative choice, though its resources are limited. Therefore, producing low-cost materials with high adsorptive performance has garnered notable attention recently.

Electroplating sludge consists of several heavy metals such as Ca, Fe, Mn, and various metal oxides such as FeO, CaO, which have the potential for adsorption (Asiabi et al., 2017; Wahyuni et al., 2015; Ruijing et al.,

2016). Upon calcination, the heavy metal gets converted to metal oxides and mixed metal oxides, which have high adsorption capacity (Gavin et al., 2004). Even without calcination, the metal oxide (e.g., CaO and Fe_3O_4) existing in the electroplating sludge is also a good choice for adsorption method (Ruijing et al., 2016). Using electroplating sludge as an adsorbent can remarkably save the waste treatment cost for electroplating industry, and plants can use the materials manufactured from electroplating sludge to treat their own wastewater. This method does not involve external chemicals, and thus, there is no risk of forming any by-product that can cause pollution. From the perspective of environmental and sustainable development, it not only mitigates the hazards caused by heavy metal pollution but also utilizes the waste from industry for environmental treatment.

The aim for this research was to evaluate the efficiency of calcinated electroplating sludge for removing heavy metal Cu (II) in solution. In addition, isotherms and kinetics were modeled to study the ability of these materials. The chemical adsorption was also investigated by characterizing materials.

2. Materials and method

2.1. Chemicals

Electroplating sludge was acquired from zinc electroplating in Thai Nguyen, Vietnam. $CuSO_4.5H_2O$ (97%) from Merck, Germany was selected for assessing the efficiency of raw and calcinated electroplating sludge; HCl (1M), from Merck, Germany was used to control pH; lastly, Whatman filter was used to recover the solution.

2.2. Adsorbent preparation

Raw electroplating sludge was first ground to 0.15 nm and dried at 60 °C for 24 h for gaining constant weight. One part was recovered for adsorption experiment. It has been reported that calcinated materials exhibit the highest efficiency when calcinated at 500 °C (Guilong et al., 2020); therefore, the other part of the ground sludge was calcinated at 500 °C.

2.3. Cu (II) removal by raw and calcinated electroplating sludge in batch mode

The experiment was conducted in shakers at room temperature wherein 200 ml Cu (II) with concentration 250 mg/L was prepared from $CuSO_4.5H_2O$ and poured into glass conical flask. The adsorbent was added to the shaker; the shaking process was performed at 200 rpm at ambient temperature. The sludge was acidic (pH = 4.8) with moisture content 70% and a density 105 g/cm^3. With pH > 4.8, OH^- was required as it could deposit Cu (II). To remove the material, a filter paper was used in the experiment, and a clean solution was recovered and analyzed through AAS equipment. The Langmuir and Freundlich adsorption was applied for fitting the experimental isotherm data. The pseudo first-order second-order kinetic equations were used for fitting adsorption equilibrium adsorption capacity.

2.4. Sample analysis

The concentration of Cu (II) was measured through atomic absorption spectrophotometer (AA – 6800 Shimadzu). To control the pH of the solution, pH meter SI Analytic HandyLab 680 was used. The element composition of material was characterized using X-ray fluorescence (XRF) spectrometer, and the crystal structure was determined using X-ray powder diffraction (XRD) spectrometer.

3. Results and discussion

3.1. Characterization of electroplating sludge and calcinated electroplating sludge

3.1.1. XRF and XRD characterization

Figure 1 shows the XRF of the raw electroplating sludge. It can be seen that the main element composition of the electroplating sludge was Ca, Fe, Cu, and S. The presence of Ca indicates a high potential for adsorption. The crystal structures of the raw electroplating sludge and calcinated electroplating sludge are indicated in Figure 2. After the calcination, Ca transformed to CaO, which can be observed at diffraction peak 52.5° and 62.5°, while there was no CaO peak in raw electroplating sludge.
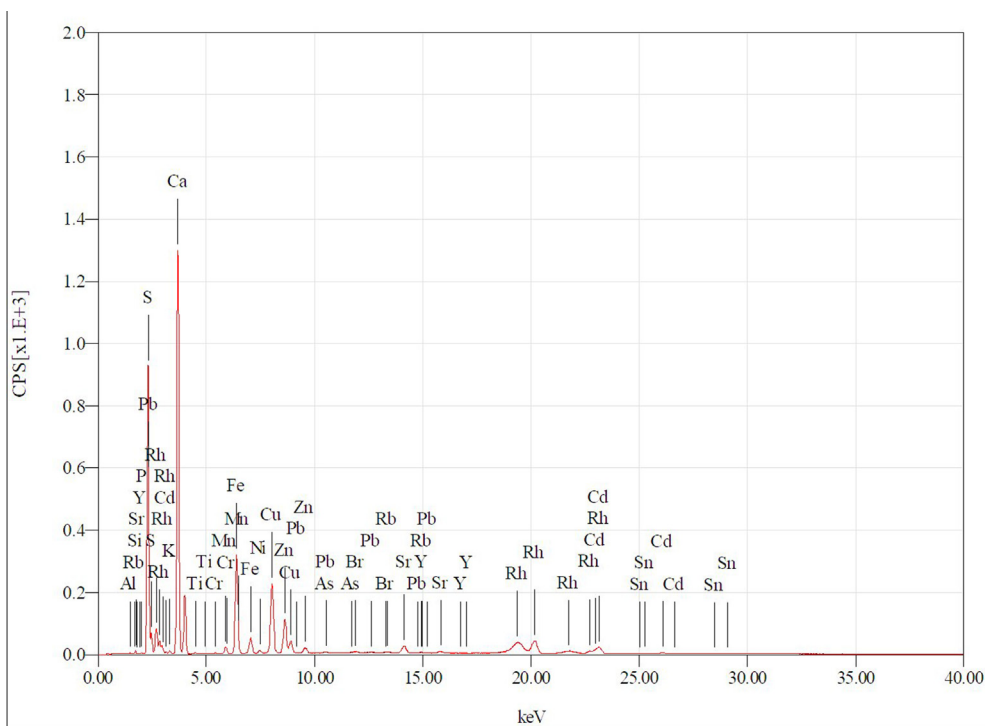

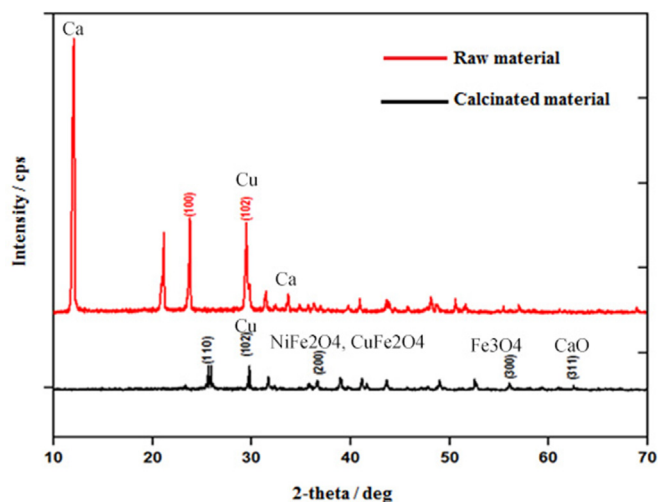**Figure 1.** XRF pattern of the raw electroplating sludge.

Figure 2. XRD patterns of raw and calcinated electroplating sludge.

Furthermore, Cu still remained in calcinated material, although with a lower peak, and demonstrated that the calcination converted Cu from raw material to metal oxides. Moreover, other peaks than CaO and Cu can be seen only in calcinated sludge at diffraction peaks 35.32°, 39.42°, and 56.54° corresponding to $CuFe_2O_4$, $NiFe_2O_4$, and Fe_3O_4; another peak at 43.15° can be observed for both raw and calcinated materials fitted with CuO (Dehghani et al., 2017; Guan et al., 2018; Kostić et al., 2018; Xianhua et al., 2017; Zhang et al., 2016; Zhao et al., 2016). The appearance of this peak may plausibly be the result of conversion of metal in raw electroplating sludge to metal oxide and mixed metal oxides during calcination.

3.1.2. SEM

The raw and calcinated electroplating sludge were also characterized by SEM microscopic image depicted in Figure 3. The surface morphology indicated that after calcination, the calcinated electroplating sludge had
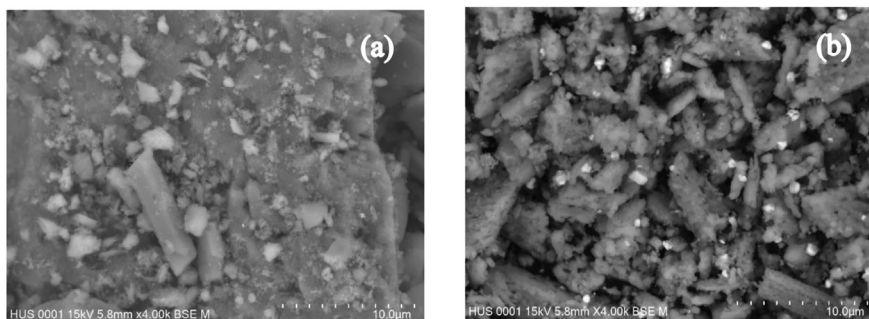
more pores and was rough than the raw electroplating sludge. By this observation, it can be deduced that the adsorption of the calcinated electroplating sludge in the surface is better than the raw electroplating sludge.

3.2. Evaluation of the adsorption capacity of raw and calcinated electroplating sludge

3.2.1. Effect of time

Figure 4 describes the result of Cu (II) removal of raw and calcinated electroplating sludge. It is evident that both adsorbents exhibited a high adsorption performance, and the calcinated electroplating sludge had a higher efficiency. After 15 min, the Cu (II) remaining in the solution was only 24.53% with raw electroplating sludge and 8.64% with calcinated electroplating sludge. The value of equilibrium adsorption capacities of raw and calcinated electroplating sludge were 33.63 mg/g and 38.34 mg/g, respectively after over 240 min of adsorption. The percentage of Cu (II) in the solution after shaking for 240 min was only 0.15%, while the remaining Cu (II) experimented with raw electroplating sludge was 8.8%. On the basis of this result, it can be concluded that the calcinated electroplating sludge exhibited higher adsorption performance than raw electroplating sludge.

3.2.2. Effect of pH

Adsorption efficiency of raw and calcinated electroplating sludge were tested with pH. Figure 5 depict the concentration of Cu (II) with pH 2, 3, 4, and 4.8 (pH of initial solution) at equilibrium. An assessment with pH > 5 by adding OH⁻ was also conducted in this study; however, in this case, Cu (II) deposited immediately. With pH = 2, the remaining concentration of Cu (II) upon shaking with raw electroplating sludge was 257 mg/L, which was higher than the initial concentration of Cu (II) (250 mg/L); for calcinated electroplating sludge, it was about 172 mg/L. The phenomenon was caused by the appearance of high ion H⁺ in solution, Cu in material, observed in XRD and XRF dissolved Cu (II), and hence increased the concentration of Cu (II) in solution. The remaining Cu (II) in the solution with calcinated electroplating sludge was lower because of the formation of mixed metal oxides of Cu such as $CuFe_2O_4$ and CuO (Figure 2). However, in high-pH solutions, the adsorbents exhibited high adsorption performance; raw electroplating

Figure 3. SEM image of (a) raw electroplating sludge and (b) calcinated electroplating sludge.
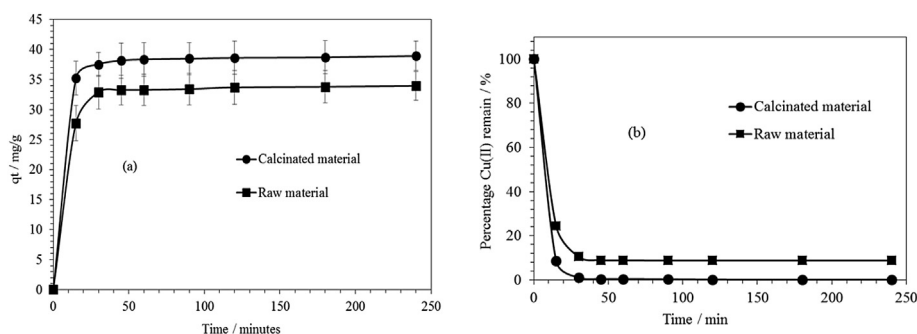

Figure 4. (a) Adsorption capacity and (b) percentage of Cu remaining in solution of raw electroplating sludge and calcinated electroplating sludge at pH = 4.8 and initial concentration = 250 mg/L.
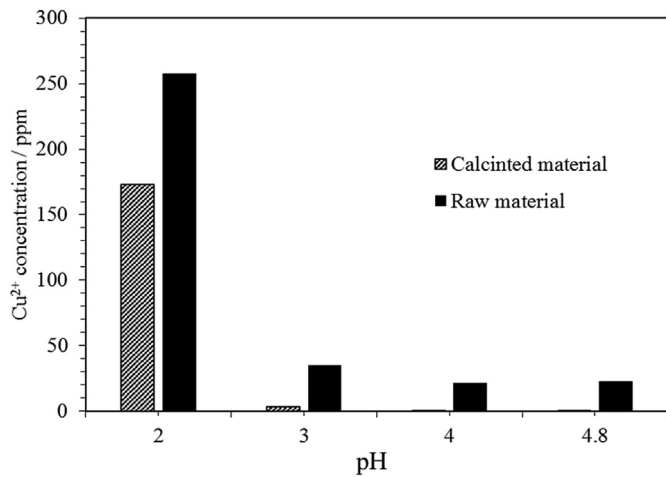
Figure 5. Concentration of Cu (II) remaining in solution after shaking for 2 h at different pH levels of raw and calcinated electroplating sludge; initial concentration = 250 mg/L, shaking speed = 200 rpm in ambient temperature.
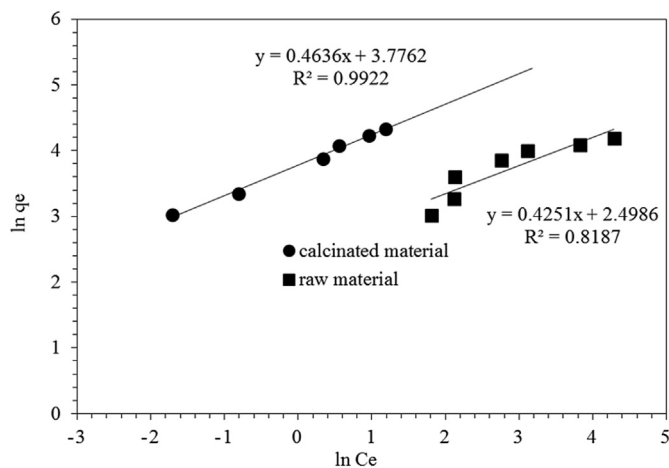

Figure 6. Freundlich isotherm for the adsorption of Cu (II) with raw electroplating sludge and calcinated electroplating sludge.

sludge had adsorption efficiency about 86% and 91% at pH 3 and 4, and the same for calcinated material was 98% and 99%, respectively. In summary, in a low-pH solution, the leaching of metal occurred. Furthermore, calcinated electroplating sludge not only enhanced the adsorption efficiency but also reduced the leaching of metal in a low-pH solution.

3.3. Adsorption isotherm

To study the adsorption isotherm of the materials, the Langmuir and Freundlich isotherm models were used in this research. First, the concentration of Cu (II) was modified to 100 mg/L, 150 mg/L, 200 mg/L, 250 mg/L, 300 mg/L, 350 mg/L, and 400 mg/L and shaken with 1g raw and calcinated electroplating sludge, respectively. Subsequent to that, the data from the experiment were used for calculating the value of model.

The Langmuir equation can be written as follows:

$$\frac{C}{q_e} = \frac{1}{q_{max}K_L} + \frac{C}{q_{max}} \tag{1}$$

With q_e is adsorption capacity at equilibrium (mg/g), C is remaining concentration of Cu (II) in solution (mg/L) after the adsorption process, q_{max} is maximum adsorption capacity, and K_L is Langmuir constant.

The Freundlich equation can be written as:

$$ln q_e = ln K_F + \frac{1}{N_F} ln C \tag{2}$$

where q_e is adsorption capacity at equilibrium (mg/g), C is concentration of Cu (II) remained in solution (mg/g) after the adsorption process, K_F is the Freundlich constant related to the adsorption capacity, and $1/N_F$ is intensity of adsorbent.

The Langmuir isotherm and Freundlich linear are shown in Figures 6 and 7, it can be observed that the data of Langmuir model fitted with the experiment more than the Freundlich model. The acquired correlation coefficients (R^2) with the former for both raw and calcinated materials were close to 1, while Freundlich isotherm only showed high correlation coefficients (R^2) for the calcinated electroplating sludge. On the basis of this result, it can be concluded that there is a high possibility for the adsorption of Cu (II) on the surface to be homogeneous and monolayer adsorption and the adsorption sites to be on the surfaces of material (Ghasemi et al., 2014). Table 1 further indicates that the maximum adsorption capacity of the calcinated electroplating sludge (91 mg/g) is higher than the raw electroplating sludge (76.34 mg/g). The higher efficiency of calcinated electroplating sludge could be caused by the in-

Table 1. Parameters of isotherm models for Cu (II) adsorption with raw electroplating sludge and calcinated electroplating sludge.

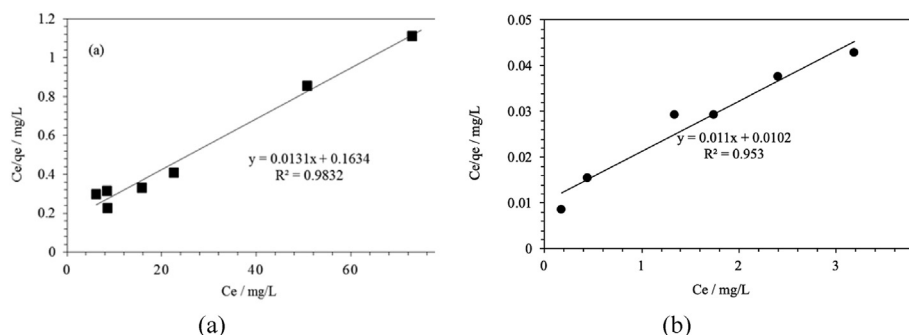| Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_F (L/mg)	R^2
Calcinated electroplating sludge	91.00	1.077	0.9530	2.1570	43.65	0.9922
Raw electroplating sludge	76.34	0.080	0.9832	2.3524	12.17	0.8187

Figure 7. Langmuir isotherm for the adsorption of Cu (II) with (a) raw electroplating sludge and (b) calcinated electroplating sludge.

Table 2. Comparison of maximum adsorption capacities of calcinated electroplating sludge with other adsorbents.

Adsorbent	q_{max} (mg/g)	Reference
Raw electroplating sludge	76.34	This study
Calcinated electroplating sludge	91	This study
Cellulose	64	Liu et al. (2002)
KGMP	10	Say et al. (2003)
Chitin	58	Abdelkader et al. (2016)
Chitosan	67	Abdelkader et al. (2016)
PEG-dimethacrylate-methacryloyl-amido-histidine	48	Chen et al. (2016)
$CaCl_2$-pre-treated Algerian bentonite	55.476	Ouakouak et al. (2020)
Hematite	7.205	Wang et al. (2008)
Beidellite	25.3	Oncel (2008)
Natural kaolinite	4.42	Potgieter et al. (2006)
Natural palygorskite clay	30.7	Sheikhhosseini et al. (2013)

crease of many oxides in the structure, which makes the surface of this material more porous than the raw electroplating sludge.

3.4. Comparison of material manufactured from electroplating sludge with other absorbent

Maximum adsorption capacities of adsorbents made from electroplating sludge for the Cu (II) removal were compared with adsorbents used in previous research studies. The results are encapsulated in Table 2. Comparing with natural origin adsorbents such as natural kaolinite, natural palygorskite clay, both raw and calcinated electroplating sludge materials exhibited markedly higher adsorption capacity. Even the synthesized adsorbents such as PEG, KGMP could not compete with the adsorbents from the electroplating sludge.

3.5. Kinetic study

To predict the adsorption rate of the material, the research used pseudo first-order and second-order kinetic equations (Al-Degs et al., 2006). Pseudo-first-order kinetic equation is expressed as follows:

$$\log(q_e - q_t) = logq_e - \frac{k_1}{2.303}t \qquad (3)$$

where q_e is the amount of Cu (II) adsorbed at equilibrium, q_t is the concentration of Cu (II) which was adsorbed at time t, and k_1 is the rate constant of pseudo first-order kinetic equation.

The pseudo second-order kinetic equation can be written as:
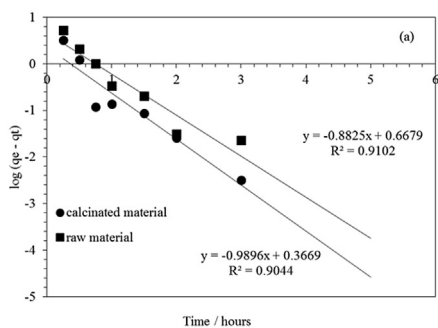
$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \qquad (4)$$

Table 3. Kinetic constants for the adsorption of Cu (II) with raw electroplating sludge and calcinated electroplating sludge.

Adsorbent		Calcinated electroplating sludge	Raw electroplating sludge
First-order kinetics	$q_{e,cal}$ (mg/g)	2.33	4.66
	K_1 (hour^{-1})	2.28	2.03
	R^2	0.90	0.91
Pseudo second-order kinetics	$q_{e,cal}$ (mg/g)	38.46	34.13
	K_2 (g.mg^{-1}.hours^{-1})	22.5350	0.78
	R^2	1	0.9999
$q_{e,exp}$ (mg/g)		38.31	33.66
K_{id} (mg/g.hour$^{0.5}$)		0.19	0.44
Intercept y		37.99	32.91

Where q_t and q_e are the amounts of Cu (II) adsorbed at time t and at equilibrium, respectively, and k_2 is the second-order rate constant. Another crucial factor worth mentioning in the current context is the intra-particle diffusion. The rate constant of intra-particle diffusion (k_{id}) is given by the following equation (Kalavathy et al., 2005; Singh et al., 2006):

$$q_t = k_{id}t^{0.5} + y \qquad (5)$$

where q_t is amount of Cu (II) adsorbed at time t, k_{id} is the initial rate of intra-particular diffusion (mg/g hour$^{0.5}$), and y is the intercept of linear.

The result of the kinetic research is depicted in Figure 8 and Table 3. It can be seen clearly that the pseudo second-order kinetic equation fitted better than pseudo first-order kinetic equation; the former had extremely high R^2 value of 0.9999 with raw material and 1 with calcinated material. The $q_{e,cal}$ value further validated the superiority of pseudo second-order kinetic equation. The data acquired from calculation of equilibrium adsorption capacity from this equation were approximately the same as that attained from the experiment, i.e., 34.13 mg/g with 36.66 mg/g of raw electroplating sludge and 38.46 mg/g with 38.31 mg/g of calcinated electroplating sludge, while the value calculated using pseudo first-order kinetic equation was far lower than the real data from experiment.

The intra-particular diffusion linear is illustrated in Figure 9, and the value of k_{id} is shown in Table 3. Initially, the plot was a curve, and gradually transitioned to linear; the curve in initial stage represented boundary layer diffusion, and the linear plot represented intra-particular diffusion (Ghasemi et al., 2014; Jihyun et al., 2008). Therefore, it can be concluded that during adsorption, both surface adsorption and intra-particular diffusion were involved (Ghasemi et al., 2014; Jihyun et al., 2008). In addition, the intra-particle diffusion coefficient (k_{id}) of raw material is higher than calcinated material, while the value of intercept y in the intra-particular diffusion is linear, which indicates the
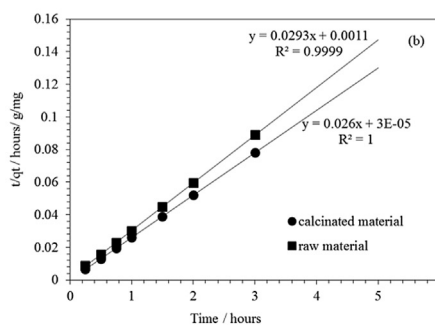

Figure 8. (a) Pseudo first-order kinetic and (b) pseudo second-order kinetic equation for adsorption of Cu (II) with raw electroplating sludge and calcinated electroplating sludge.
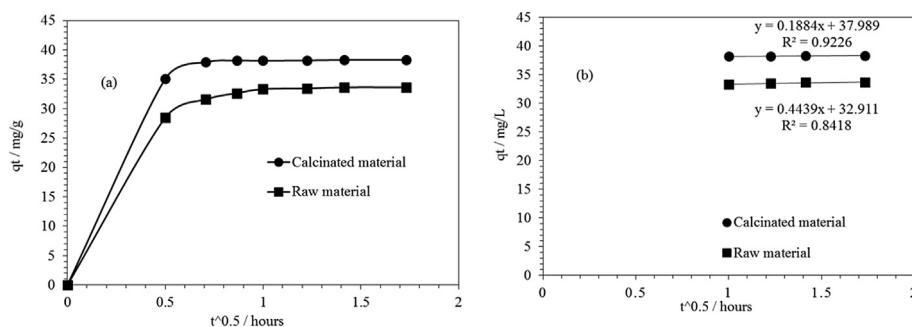
Figure 9. (a) Intra-particular diffusion kinetic and (b) Intra-particular diffusion kinetic linear for adsorption Cu (II) of raw electroplating sludge and calcinated electroplating sludge.
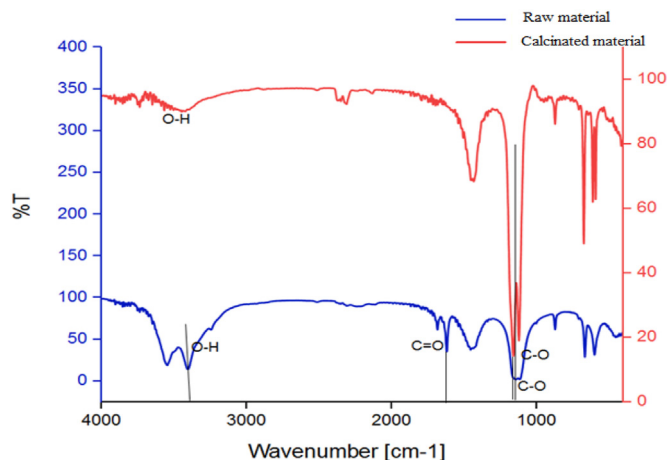

Figure 10. FTIR spectra of raw electroplating sludge and calcinated electroplating sludge.

electroplating sludge was OH^- exchange with Cu to form H^+ (Guilong et al., 2020), and the main path of calcinated electroplating sludge was between Ca^{2+} and Cu^{2+}, and with a small contribution of OH^- group through reaction (1), (2). Figure 11 demonstrates the adsorption mechanism under question.

$$M - OH + Cu^{2+} \rightarrow 2(M - O)Cu + H^+ \qquad (1)$$

(Calcinated electroplating sludge) $- Ca^{2+} + Cu^{2+} \rightarrow$ (Calcinated electroplating sludge) $- Cu^{2+} + Ca^{2+}$ $\qquad (2)$

4. Conclusion

Both raw and calcinated electroplating sludge showed high adsorption performance with Cu (II). After 4 h of adsorption process, the Cu (II) remaining in the solution was 8.8% with raw electroplating sludge and 0.15% with calcinated electroplating sludge. However, at low pH, raw sludge was easy-to-leak heavy metal to solution. This phenomenon also occurred with calcinated sludge, with lower amount, because of the
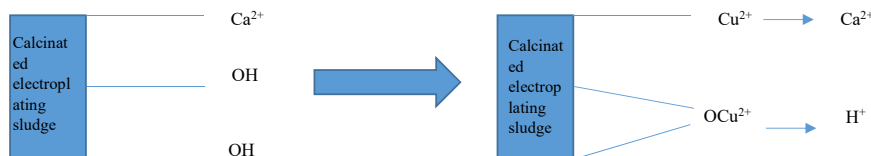

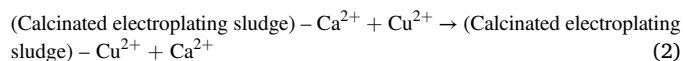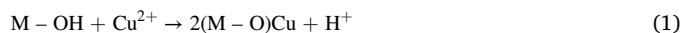**Figure 11.** Adsorption mechanism of raw and calcinated electroplating sludge.

boundary layer effect and implies that the calcinated electroplating sludge had higher tendency for surface adsorption than raw electroplating sludge (Jihyun et al., 2008).

3.6. Adsorption mechanism

XRD spectra in Figure 2 reveals that the raw electroplating sludge consists of high amount of Ca metal. By calcinating, Ca metal was converted to ion metal Ca, which plays a vital role in Cu adsorption by ion exchange mechanism (Guilong et al., 2020). To further study about the adsorption mechanism of raw and calcinated electroplating sludge, Fourier transform infrared spectroscopy (FTIR) was used, and this result is illustrated in Figure 10. It can be seen that subsequent to calcination, the OH^- group that could be from hydroxide, was decreased, while the lattice vibration, such as $M - O - M$ and $O - M - O$ vibration was observed at approximately 500 cm^{-1} adsorption peak (Guilong et al., 2020). Moreover, at band between 1,000 cm^{-1} and 1,500 cm^{-1}, the rise of $C = O$ group and C–O also was observed.

It can be concluded that after calcination, the amount of O–H group decreased; however, it increased the amount of metal ion, C–O and $C = O$ group. In exchange ion mechanism, the main path of raw

conversion of metal to mixed metal oxides. Both the raw and calcinated electroplating sludge fitted well with the Langmuir equation with high value of R^2. Findings of kinetic analysis revealed that the adsorption eventuated with pseudo second-order kinetics. Moreover, intra-particular diffusion plot proved that the adsorption process consists of both surface adsorption and intra-particular diffusion, and during the adsorption process, calcinated electroplating sludge easily adsorbed Cu (II) in the surface than raw electroplating sludge. Besides the physical aspect, the ion exchange was involved in the adsorption process. OH^- exchange was main path in raw sample, while both OH^- group and Ca^{2+} ion play a vital role in calcinated material. With a high ability of adsorption, electroplating sludge can be utilized for environmental treatment and open a new approach to recycle pollutant to friendly environmental adsorbent.

Declarations

Author contribution statement

Tran Thi Huong & Le Thi Vinh: Performed the experiments; Contributed reagents, materials, analysis tools or data.

Tran Quang Minh: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Pham Thi Thuy & Nguyen Manh Khai: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Le Van Trong: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Funding statement

Data availability statement

The data that has been used is confidential.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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