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Study on removal of Cu^{2+} from wastewater by excess sludge

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Abstract. With the social development, the increasing sludge and its subsequent treatment are very severe environmental problems.The adsorption experiments were carried out using different pretreated exess sludge as adsorbent for Cu^{2+} .The sludge of $NaOH$-H_2O_2 treated improve the adsorption capacity which reached 56.12mg/g,however the adsorption capacity of the sludge using $ZnCl_2$-Carbonization treated decrease.Both Langmuir and Freundlich isotherm models fit the adsorption data well with the three types of sludge . The value of R^2 exceeds 0.96 in most cases. Relative to the Pseudo first order kinetic model,the pseudo second orderkinetic model fit the adsorption data more well with the adsorbents. The value of R^2 reached about 1. The maximum adsorption efficiency for optimum pH is about 6. With the increase of adsorption mass, the removal efficiency of sludge increases.For 150mL copper ion solution which concentration was 100 mg/L,the optimum sludge mass corresponds to maximum adsorption efficiency was found to be 1.5g.

1. Introduction
With the rapid development of industrialization and urbanization in China, the problem of heavy metal pollution is becoming more and more serious. Heavy metals can directly enter the atmosphere, water and soil, cause direct pollution of various environmental factors, and also migrate in the atmosphere, water and soil, resulting in indirect pollution of various environmental factors. [1] Heavy metal pollution is persistent and has enrichment effects on organisms. Most of the heavy metals pollution has higher biological toxicity. As the amount of excess sludge increases year by year, it is more urgent to develop recycling and energy saving treatment with economical and efficient methods. Excess sludge is a by-product produced by activated sludge wastewater treatment process. It is an extremely complex heterogeneous body. which composed of organic debris, bacteria, inorganic particles, colloid. [2] Using the adsorption characteristics of excess sludge to adsorb the heavy metal ions in wastewater is economical and efficient. [3,4] It is a good method for waste disposal and sludge utilization.

2. Materials and methods

2.1. . Adsorbent preparation
The excess sludge which has been dewatered through the filter cloth process is taken from the desliming room of the domestic sewage treatment plant. A certain amount of wet sludge is placed in a 105-degree oven and dried to a constant weight and measure the sludge water content. To measure

volatile matter,a certain amount of dryed sludge is put into muffle furnace in a 600degree high temperature for 2 hours.[5]Then, clean the sludge with deionized water several times until the sludge has a clear interface with water. Then, the excess sludge is put into the centrifuge for slurry separation and dried in natural conditions. Finally, the dried sludge is ground in the grinding machine and separated by 200 mesh sieves.

2.2. *Preparation of metal solutions*
The aqueous solutions of metal ions used in the present investigation were prepared by using analytical grade chemicals. Individual stock metal ion solutions of 1000 ppm concentration of Cu^{2+} from $CuCl_2.2H_2O$ was prepared. These stock solutions were used to prepare dilute solutions of these ionsby the dilution with deionized water. The stock solutions were acidified to $4 < pH < 6$ using concentrated HCl in order to prevent the formation of metal hydroxide and to return the metal ion to the dissolve state.

2.3. *Modified treatment of excess sludge*
This part was made in order to enhance the adsorption effect. The modification of excess sludge can be divided into physical and chemical methods. The portion was soaked in $4mol.L^{-1}ZnCl_2$ solution in proportion to 1:2 for 24 hours. The resulted cake is put into Muffle furnace in the temperature of 600 degree for 90 mins. Then, grind through 200 mesh sieves "($ZnCl_2$-Carbonization treated). The other part is soaked in NaOH solution for 12 hours at 60℃ and the solid-liquid ratio is 1: 2. The cake was washed with deionized water until the pH of the wash solution was 7. Then, the cake is soaked with 30% H_2O_2 solution for 12 hours and washed with deionized water and drying, grinding (NaOH-H_2O_2 treated)

2.4. *Measurements*
The heavy metal concentrations were measured with ICP-AES.PH was measured using portable waterproof pH/mv/temperature determinator. The density was measured by weighing acertain volume of the adsorbent. The porosity was observed by Scanning electron microscopy. The specific surface area was measured by static volumetric method. The ash content was measured byburning certain mass of the ash and reweighing the residual ash.

2.5. *Data evaluation*
The adsorbance of bio adsorbent was calculated using the mass balance equation.

$$Q_e = \frac{V.(C_0 - C_e)}{m} \tag{1}$$

where Q_e= the loading capacity of the adsorbent (mg adsorbate/g adsorbent); V = the solution volume in the vessel (l); C_0, C_e= the initial and final concentration of the metal ion (mg/L); m =the mass of the adsorbent added(g)

The removal efficiency $E_r\%$ of the adsorbent on the metal ion is defined as

$$E_r\% = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{2}$$

The adsorption isotherm is a model describing the equilibrium adsorption relationship between adsorbent (solid phase) and metal ion (liquid phase). [6] The Langmuir adsorption model is assumed to be monolayer adsorption. It is considered that the adsorption between adsorbent and metal ion belongs to chemisorption's. The equation is written as follows.

$$Q_e = \frac{Q_{max} b C_e}{(1+bC_e)} \tag{3}$$

where Q_{max} is the maximum metal adsorption capacity under the given conditions; b is a equilibrium constant.

The linear form of Langmuir model is:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \tag{4}$$

The Freundlich equation is an empirical equation describing the adsorption of heterogeneous surfaces. It can be written as:

$$Q_e = K_F C_e^{\frac{1}{n}} \tag{5}$$

where K_F and n are Freundlich constants, which are correlated to the maximum adsorption capacity and adsorption intensity, respectively.

The linear form of Freundlich model can be written as:

$$\log Q_e = \log K_F + \frac{1}{n} \log c_e \tag{6}$$

Pseudo-first order kinetics is a linear relationship between the rate of reaction and the concentration of reactants in the system. [7] The linear form of this model takes the form:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \tag{7}$$

Where Q_t=adsorption capacity of metal ions at t (mg adsorbate/g adsorbent); t=the time; k_1=first-order kinetic adsorption rate constant ($g.mg^{-1}.min^{-1}$).

Pseudo-second order kinetics can be written under the following form:

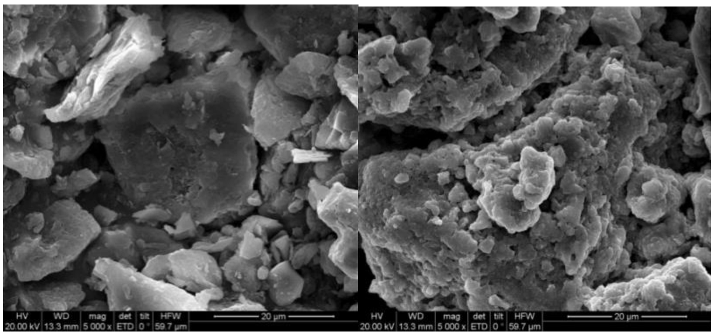
$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{8}$$

Where k_2= second-order kinetic adsorption rate constant ($g.mg^{-1}.min^{-1}$).

3. **Results and discussion**

3.1. Adsorbent characteristics

3.1.1 Comparison and analysis of SEM. The SEM magnified 5000 times of the three types sludge were selected to investigate the change of the surface morphology.



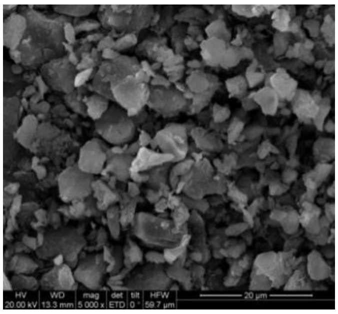


Fig. 1 a. Untreated b. $ZnCl_2$-Carbonization treated c. NaOH-H_2O_2 treated

It is shown in Fig1.a to Fig 1.c that the surface of the untreated sludge is relatively smooth and has less porosity. The $ZnCl_2$-Carbonization treated and NaOH-H_2O_2 treated sludge have more porosity and inhomogeneous structure. It is assumed that the specific surface area of the sludge increased after modification. This change will increase their physical adsorption capacity.

3.1.2 Comparison and analysis of BET. BET is a key index in the performance of adsorbent. The specific surface area is more conducive to the adsorption. By measuring, the BET using NaOH-H_2O_2 treated, Untreated and $ZnCl_2$-Carbonization treated sludge are 3.0012m^2/g,2.7382 m^2/g and 2.8136 m^2/g respectively. After modification, the specific surface area increased exactly.

3.2. Adsorption isotherms

The adsorption isotherms present the concentration dependent equilibrium distribution towards adsorbate between the adsorbent and the solution at certain conditions. Fig 2 shows the adsorption isotherm of Cu^{2+} ions using the three types of the sludge at 25 ℃.The plot obtained shows that when the initial ion concentration of Cu^{2+} is less than 150mg/L, the loading capacity of the adsorbent, using the three methods above treated excess sludge are basically consistent. It can be seen that treatment of the sludge by NaOH-H_2O_2 seems to improve Cu^{2+} uptake capacity of the sludge when the initial ion concentration is over 150mg/L. But, under the same conditions, the treatment by $ZnCl_2$-Carbonization seems to deactivate the adsorbent and lowers its loading capacity of the metal ions. And the general trend shows that there is a turning point when the adsorption capacity reaches the maximum amount.

In the NaOH-H_2O_2 pretreatment, the adsorption capacity increased significantly, on one hand, could be attributed to an increase in electronegativity, the adsorption of heavy metals is strengthened. In addition, could be attributed to the increase of the adsorbent micropore. [8] On the other hand, $ZnCl_2$-Carbonization treatment was found to reduce the bio adsorption capacity. This behavior could be referred to the fact that the adsorbent is not protected by inert gas when heated in muffle furnace. [9].

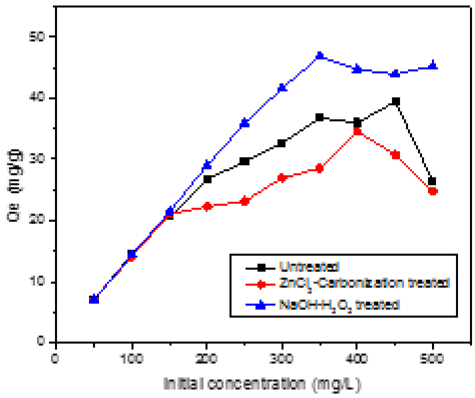


Fig. 2 Adsorption isotherm for Cu^{2+} using the three typesof sludge. Temperature=25 ℃, pH = 6, mixing speed =150 rpm, adsorbent mass = 1g, solution volume = 150 ml, contact time 2 h.

3.3. Adsorption isotherm models

Langmuir and Freundlich models are the most widely used models used to fit the adsorption isotherm data in orderto obtain a linear regression data to predict the maximum adsorption capacity of the adsorbent. [10] Fig 3 shows plots of Langmuir isotherms for the bio adsorption of Cu^{2+} bythe three types of adsorbents. The linear plots of Ce/Q_{max} against Ce show that the adsorption of the Cu^{2+} by the sludge fits well to Langmuir model. The same data were also fit to Freundlich model well as shown in Fig 4. The results are grouped in Table 1. From this one, we can see that NaOH-H_2O_2 treated sludge gives the higher value of Q_{max}. The two model constants for the Cu^{2+} in addition to R^2 values for eachline are shown in Table 1. Italso shows that Q_{max} of $Cu^{2+}$are 29.15,24.54 and 56.12 mg/gwith Untreated, $ZnCl_2$-Carbonization treated and NaOH-H_2O_2 treated sludge, respectively.

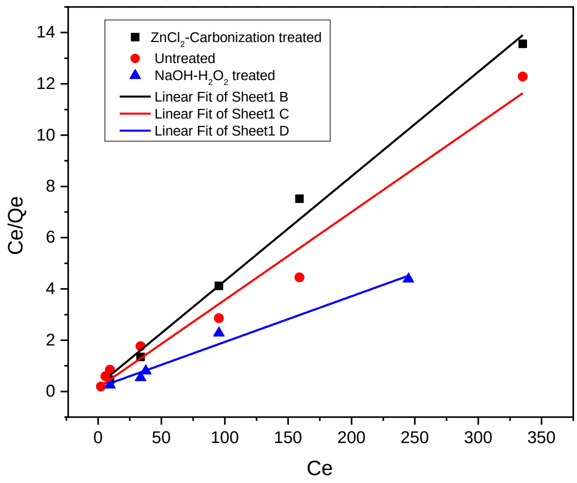


Fig. 3 Langmuir plot of the bio adsorption of Cu^{2+} withthe three types of sludge at 25 ℃

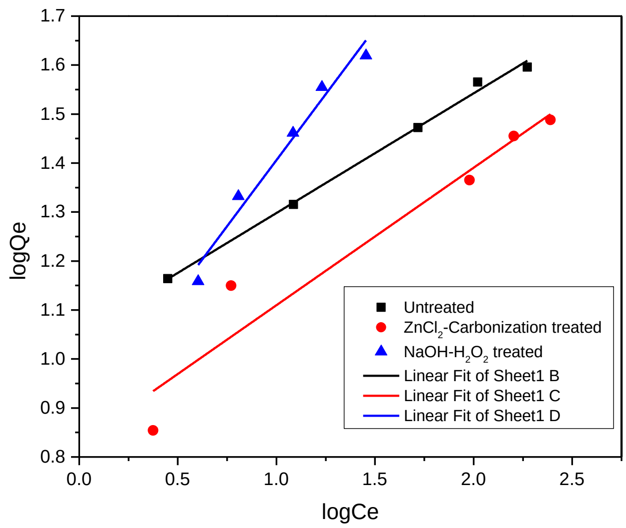


Fig. 4 Freundlich plot of the bio adsorption of Cu^{2+} withthe three types of sludge at 25 ℃.

Table 1. Linear regression data for Langmuir and Freundlich isotherms for the bio adsorption of the Cu^{2+}, with the three types of sludge

Ion	Type of sludge	Langmuir parameters			Freundlich parameters		
		Q_{max}	K_L	R^2	K_F	n	R^2
Cu^{2+}	Untreated	29.15	0.24	0.9724	11.314	4.09	0.9948
	$ZnCl_2$-Carbonization treated	24.54	0.17	0.9899	6.74	3.56	0.914
	$NaOH-H_2O_2$ treated	56.12	0.12	0.9722	7.3629	1. 856	0.9632

3.4. Kinetic model

The adsorption kinetics analysis can better describe the adsorption mechanism. [11] The results of Pseudo first order kinetics and Pseudo second order kinetic are showed in Table 2that the adsorption of the three adsorbents using Untreated, $ZnCl_2$-Carbonization treated, $NaOH-H_2O_2$ treated fits well to Pseudo second order kinetic and the correlation coefficient R^2 reached over 0.9990. The calculated experimental values are very close to the theoretical values. Because of Pseudo second order kinetic model is based on the chemical adsorption model, it can be concluded that the adsorption process has the occurrence of chemisorption. [6].

Table 2. Pseudo first order kinetics and Pseudo second orderkineticisotherms for the bio adsorption of the Cu^{2+} withthe three types of sludge.

Ion	Type of sludge	Pseudo first order kinetics			Pseudo second orderkinetic		
		Q_e	K_1	R^2	Q_e	K_2	R^2
Cu^{2+}	Untreated	14.144	0.1824	0.7369	14.497	0.044	0.9996
	$ZnCl_2$-Carbonization treated	13.249	0.0858	0.9136	14.285	0.0105	0.9990
	$NaOH-H_2O_2$ treated	13.214	0.3576	0.2145	12.987	0.0968	0.9997

3.5. Effect of pH

Hydrogen ion concentration in the adsorption solution has a great impact on the adsorption behavior of metal ions from aqueous solutions. Hydrogen ions can affect the solubility of metal ions, replace some adsorption sites of some cations in the adsorbent. [12] For these reasons, the PH values of solution were within the range of 3—8. To observe the effect of pH, Cu^{2+} solution is adjusted to different pH values. From the experimental data,it can be observed in Fig 5 that the three types of adsorbent all have an optimum value of pH. In the range of 5.5-6.5, the removal efficiency of the three types sludge reached a maximum. The maximum removal efficiencies of Cu^{2+} of the Untreated, $ZnCl_2$-Carbonization treated and the $NaOH-H_2O_2$ treated sludge were 96.23%,94.10% and 97.82%. As it is represented on Fig. 5 the $NaOH-H_2O_2$ treated sludge has a higher removal efficiency than other two types sludge. At low values of PH, the mobility of the hydrogen ions is higher the metal ions and it reacts with active sites earlier than metal ions. At high values of pH, the metal ions are easy to form precipitation of hydroxides.

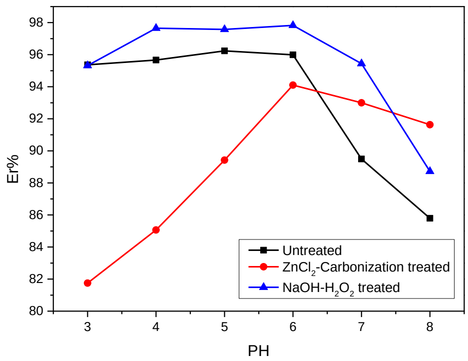


Fig. 5 Effect of pH on the adsorption of Cu^{2+} ions onto various types of sludge. Temperature = 25 ℃, mixing speed = 150rpm, adsorbent mass = 1g, solution concentration=100mg/L, solution volume= 150ml, contact time 2h.

3.6. *Effect of adsorbent mass*

The effect of varying the sludge mass on theCu^{2+} ions is represented in Fig 6. The sludge mass in this study varied from 0.3 to 3.0. It is shown in Fig 6 that the removal efficiency of three types adsorbent increase as the sludge mass increase. For this phenomenon, the result is that binding sites increase as the sludge mass increase. Forexample, the removal efficiency of$NaOH$-H_2O_2 treated sludge contacted with 100 mg/l Cu^{2+} solution increases from 75.7% to 98.58% as the mass increases from0.3 to 1.5 g. But, with the increase of sludge mass, the speed of removal efficiency is slowing down. As is represented in Fig 6. the three types of sludg, using $NaOH$-H_2O_2 treated, Untreated and $ZnCl_2$-Carbonization treated respectively have different maximum removal efficiency:98.58%,96.39% and 97.65%. These results indicate that this sludge has a large potential as a bio adsorbent for metal ions since the removal efficiency with small amounts of this adsorbent exceeds 96%.

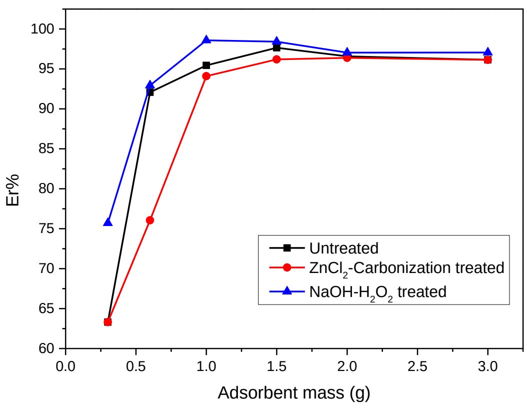


Fig. 6 Effect of sludge mass on the adsorption of Cu^{2+}ions onto three typesofsludge. Temperature = 25 ℃, pH = 6, mixing speed = 150 rpm, solution concentration=100mg/L, solution volume =150 ml, contact time 2 h.

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4. Conclusion

Based on experimental results the following conclusions can be drawn:

(1) Excess sludge can be easily applied as acheap bio adsorbent for removing heavy metal ions from aqueous solution suchas Cu^{2+}.

(2) The adsorption capacity of the sludge was improved by treating the sludge with NaOH and H_2O_2.Although theadsorption capacity of the sludge using $ZnCl_2$-Carbonization treated decreased, the structure more stable and easier to separate from water.

(3) The experimental adsorption data of the three types sludge fit to the Langmuir and Freundlich models well.

(4) Pseudo second order kinetic model was found fit the experimental adsorption dataof the heavy metal onto the treated and untreated sludge.

(5) Increasing the adsorbent mass can improve the removal efficiency of the adsorbents. And there isan optimum value of the pH equal to 6 at which the removal efficiency for the three sludge reach the maximum.

(6) This study will be subjected of further investigations inlabs.

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