

SLUDGE-ACTIVATED CARBONS FOR COPPER REMOVAL FROM AQUEOUS SOLUTIONS*

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Abstract

In this work, activated carbons (ACs) were prepared using Sewage sludge as starting material. The ACs were pyrolyzed in an inert atmosphere at 550 °C after independent chemical treatment with ZnCl₂ or KOH with ratio of 1:1. The materials were used as adsorbents for removal of Cu(II) from aqueous solutions. The adsorbents were characterized using adsorption/desorption nitrogen isotherm, SEM (scanning electron microscopy). The results showed that copper removal could be linked to surface pH and compounds present on the surface of adsorbent. KOH-treated adsorbent has smaller surface area (186 m² g⁻¹) than ZnCl₂-treated adsorbent (192 m² g⁻¹), however, KOH-treated adsorbent exhibited higher removal of Cu(II). The performance of KOH-treated adsorbent could be attributed to the presence of basic groups on the adsorbent surface. Liu isotherm model gave the best description of the equilibrium data. From the Liu isotherm, the maximum adsorption capacities at 298 K for KOH-treated, ZnCl₂-treated and sewage sludge (without inorganic activation) adsorbents are 31.85, 19.79 and 3.513 mg g⁻¹, respectively. The best desorption experiment was obtained using 1.50 mol L⁻¹ of HNO₃ as eluent. Recoveries of Cu(II) from Cu(II)-loaded adsorbents are 98.9% (ZnCl₂-treated) and 95.5% (KOH-treated).

Keywords: Sewage sludge; Pyrolysis; Adsorption; Isotherm; Heavy metal.

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1 INTRODUCTION

Metal industries generate enormous amounts of wastewaters that contain toxic species. These toxic species are hazardous to the environment and human health [1]. Heavy metals, non-biodegradable and bioaccumulative substances, are the most toxicological relevance species present in the effluents from metallurgical industries [1]. Copper is used in plating, mining and petroleum refining industries that produce a great amount of wastewater and sludge containing a high concentration of copper cations, which have detrimental effects on the water resources [1]. Therefore, it is essential to remove these toxic substances from wastewaters before being disposed into water bodies.

The major methods for removal of toxic substances include membrane filtration, chemical precipitation, ion exchange and adsorption on activated carbon and silica. However, some of these methods are costly [2]. In recent years, many studies have reported the use of low-cost adsorbents for the removal of toxic substances from wastewater [3]. Adsorbents, such as activated carbon, have wider applications in industries for removal of toxic substances. They can be produced from different kinds of carbon sources such as agricultural wastes and woods [2,3].

The usage of wastes for preparing adsorbents for removal of toxic substances from wastewaters has become extremely attractive because it is economical [2,3]. This strategy is beneficial to the environment because valorization of by-products contributes to the minimization, recovery and reuse of waste. Research work focused on the preparation of adsorbents from sewage sludge should be understood within this scenario. The sludge is perhaps the most pressing problem related to water treatment systems at this time, which is on the increase all over the world [4].

Sludge-based adsorbents have been used for removal of heavy metals, pharmaceuticals and dyes [2-4]. Municipal sewage sludge, which is regarded as ecological burden in the society, is a waste produced from numerous domestic and industrial activities. Its accumulation is undesirable and has no economic value. It will be of interest if this waste could be used for constructive purposes.

The aims of this work are to find more effective adsorbents for the removal of heavy metals (such as Cu(II)) and to explore the use of municipal sewage sludge as a raw material, precursor, for production of activated carbons for the removal of Cu(II) from aqueous solutions. Similarly, the recovery of Cu(II) from adsorbents through desorption study was investigated.

2 MATERIAL AND METHODS

2.1 Preparation of sewage sludge derived adsorbents

The raw material used for the preparation of the adsorbents used in this study was the sewage sludge obtained from a municipal wastewater treatment plant in Porto Alegre, RS - Brazil. The sludge was dried at 105 °C for 24 h until the weight loss was constant. The sludge was subsequently crushed with a grinder and sieved to particle size below 250 µm.

The sludge-based adsorbents were prepared using the following procedure: a 50.0 g of powdered sewage sludge, a 50.0 g of inorganic component (KOH) and 10.0 mL of water were properly mixed to obtain a homogeneous paste. The paste was placed in a crucible and dried at room temperature for 24 h. Subsequently, the sample was placed in the pyrolysis furnace under inert atmosphere with gas (argon) exchange

rate at 100 mL min^{-1} to produce carbon adsorbents. The crucibles were heated in the tubular furnace at 10 K min^{-1} up to 823 K for 60 min . The adsorbent was later cooled down to room temperature under inert atmosphere, milled, sieved to particle size $\leq 200 \mu\text{m}$ and stored in an airtight container until use. The carbon adsorbent was named KOH-activated adsorbent.

The same procedure was used to prepare ZnCl_2 -activated adsorbent (sewage sludge: ZnCl_2 was 1:1). The carbon adsorbents was labeled ZnCl_2 -activated adsorbent.

For comparison, a carbon adsorbent, without inorganic components, with particle size $\leq 150 \mu\text{m}$ was also prepared. This carbon adsorbent was only pyrolyzed and named as sewage sludge (without inorganic activation).

Prior batch adsorption experiments for the three adsorbents, a 10.0 g of adsorbent and 150 mL of 6 mol L^{-1} HCl were placed in a 250 mL boiling flask to complete the chemical activation of the carbon adsorbent (Ribas et al. 2014). The mixture was stirred and refluxed for 2 h (343 K) on a magnetic stirrer. The solid material was adequately washed with deionized water, oven dried at 383 K for 5 h , milled to particle sizes $\leq 150 \mu\text{m}$ and kept until use.

2.2 Characterization of adsorbents

The adsorbents were analyzed using scanning electron microscopy, SEM (JEOL microscope, model JSM 6060).

The N_2 adsorption/desorption isotherms of the adsorbents were carried out using a surface analyzer (Micrometrics Instrument, TriStar II 3020). The specific surface areas were determined using Brunauer, Emmett and Teller (BET) technique.

2.3 Metallic ion solution

A 1000 mg L^{-1} stock solution of Cu(II) was prepared by dissolving suitable amounts of analytical grade of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in deionized water. Working metal solutions ($10.00 - 400.0 \text{ mg L}^{-1}$) were prepared from serial dilution of the stock solution. The pH of solutions was fixed at 6.0 . The Cu(II) concentration was measured using Perkin-Elmer Flame Atomic Absorption Spectrometer.

2.4 Batch adsorption experiments

A 20.00 mL of $10.00 - 400.0 \text{ mg L}^{-1}$ of Cu(II) at pH 6.0 were added to plastic tubes containing 80.0 mg of adsorbent. The flasks were capped, and placed horizontally in a Tecnal shaker, and the system was agitated for 360 min . Afterwards, the flasks were centrifuged using Fanem centrifuge) to separate the adsorbent from the aqueous solutions. The final concentrations of the Cu(II) were determined using FAAS. The amount of Cu(II) removed by adsorbent is given by the Equation 1.

$$q = \frac{(C_o - C_f)}{m} \cdot V \quad (1)$$

Where q is the amount of Cu(II) removed by adsorbent (mg g^{-1}); C_o is the initial Cu(II) concentration, which was in contact with adsorbent (mg L^{-1}); C_f is the Cu(II) concentrations (mg L^{-1}) after the batch adsorption process; V is the volume of Cu(II) solution (L) in contact with the adsorbent; and m is the mass (g) of adsorbent.

2.5 Statistical evaluation of models

The equilibrium data was fitted using nonlinear methods with successive interactions calculated by the Levenberg–Marquardt method. Interactions were computed with the aid of the Simplex method, based on the nonlinear fitting facilities of the Microcal Origin 9.0 software. A determination coefficient (R^2), an adjusted determination coefficient (R^2_{adj}) and the standard deviation (SD) were jointly used to evaluate the suitability of the models [2,3,5]. The standard deviation is defined as a measure of the differences between the theoretical and experimental amounts of metallic ion adsorbed.

The R^2 , R^2_{adj} and SD can be represented by Equations 3, 4 and 5, respectively.

$$R^2 = \left(\frac{\sum_i^n (q_{i,exp} - \bar{q}_{i,exp})^2 - \sum_i^n (q_{i,exp} - q_{i,model})^2}{\sum_i^n (q_{i,exp} - \bar{q}_{i,exp})^2} \right) \quad (2)$$

$$R^2_{adj} = 1 - (1 - R^2) \cdot \left(\frac{n-1}{n-p-1} \right) \quad (3)$$

$$SD = \sqrt{\left(\frac{1}{n-p} \right) \cdot \sum_i^n (q_{i,exp} - q_{i,model})^2} \quad (4)$$

In these equations, $q_{i,model}$ represents individual theoretical q value predicted by the model; $q_{i,exp}$ represents individual experimental q value, \bar{q}_{exp} is the average of experimental q , n represents the number of experiments while p represents the number of parameters in the fitting model [2,3,5].

2.6 Equilibrium models

Langmuir, Freundlich and Liu models, as shown in Equations 9, 10 and 11, respectively, were used to analyze equilibrium data.

$$q_e = \frac{Q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (9)$$

$$q_e = K_F \cdot C_e^{1/n_F} \quad (10)$$

$$q_e = \frac{Q_{max} \cdot (K_g \cdot C_e)^{n_L}}{1 + (K_g \cdot C_e)^{n_L}} \quad (11)$$

Where q_e represents the amount adsorbate adsorbed at the equilibrium (mg g^{-1}); Q_{max} represents the maximum adsorption capacity of the adsorbent (mg g^{-1}); K_L represents the Langmuir equilibrium constant (L mg^{-1}); C_e represents equilibrium dye concentration (mg L^{-1}); K_F represents the Freundlich equilibrium constant [$\text{mg g}^{-1} (\text{mg L}^{-1})^{-1/n_F}$]; n_F is a dimensionless exponent of the Freundlich equation; K_g represents the Liu equilibrium constant (L mg^{-1}); and n_L represents a dimensionless exponent of the Liu equation.

2.7 Desorption experiments

Desorption studies help to elucidate the mechanism of adsorption, regeneration of adsorbent, and recovery of adsorbate from the spent adsorbent apart from protecting the environment from solid waste disposal problems. Batch desorption studies were

carried out by agitating a 20.0 mL of 100.0 mg L⁻¹ Cu(II) solution with 80.0 mg of carbon adsorbent for 240 min. The liquid phase was separated from the solid phase. Then, metallic loaded adsorbents were agitated with a 20.0 ml of aqueous solutions (0.10-1.50 mol L⁻¹ HCl or 0.10-1.50 mol L⁻¹ HNO₃) for 1 h.

3 RESULTS AND DISCUSSION

The scanning electron microscopy (SEM) images of the sludge-based adsorbents are given in Figures 1a, b and c. As shown in Figure 1a, there is no enough and successful pore development in the adsorbent obtained with pyrolysis without chemical activation. However, the chemical activation with KOH and ZnCl₂ (Figures 1b and c) increases the roughness compared to the untreated sample (Figure 1a). The sludge-based adsorbents obtained by chemical activation have a regular and highly porous surface, indicating higher surface area that is responsible for higher amount of Cu(II) adsorbed from aqueous solutions.

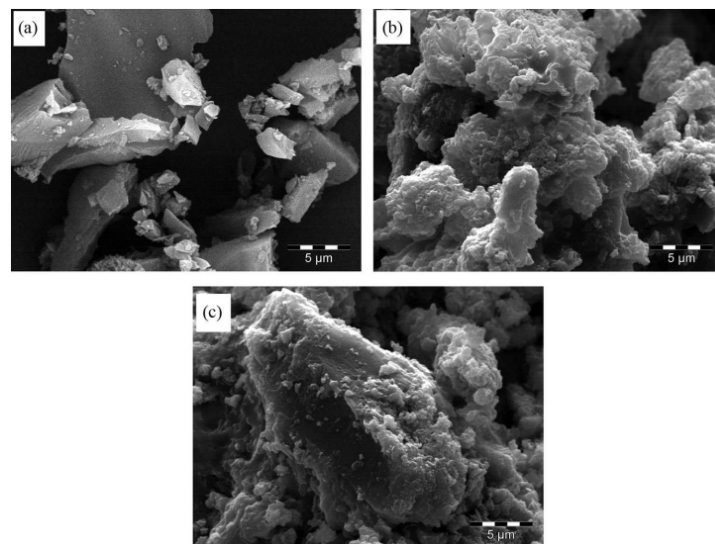


Figure 3. Scanning electron micrographs of (a) sewage sludge without activation; (b) ZnCl₂-treated sludge; and (c) KOH-treated sludge.

The textural properties such as surface area and pore volume of sewage sludge and adsorbents are shown in Table 1. The surface area of pyrolyzed materials without chemical treatment and with chemical treatment (ZnCl₂ and KOH), under N₂ at 550 °C and hold time of 60 min, were evaluated. The values of specific surface areas of ZnCl₂-activated and KOH-activated adsorbents are similar. The specific surface areas of the chemically treated adsorbents are much higher than that of sewage sludge (without inorganic activation) – an indication that chemical activation improved the textural characteristics of ZnCl₂-activated and KOH-activated adsorbents.

Table 2. Textural properties of adsorbents.

Properties	KOH-treated adsorbent	ZnCl ₂ -treated adsorbent	Sewage sludge (without inorganic activation)
Specific surface area (m ² g ⁻¹)	186	192	25.5
Total pore volume (cm ³ g ⁻¹)	0.112	0.158	0.070

The disparities in textural properties could be linked to differences in the methods of impregnation. Ros et al. [6] reported that dry bleeding using KOH could increase the efficiency and the surface area better than the impregnation done by humid method. Similarly, the same researchers reported that different surface areas found in literature could be related to different types of raw materials used (sewage sludge), and that raw materials with higher carbon content might produce adsorbents with higher surface areas [6,7].

3.1 Chemical activation with ZnCl₂

ZnCl₂ is one of the most effective chemical activation reagents for sewage sludge [6,7]. In these studies the highest specific surface area was achieved by the chemical activation with ZnCl₂. These authors reported surface area up to 647 m² g⁻¹, however, in this work the surface area is 192 m² g⁻¹. The characteristics of the sewage sludge utilized might be a significant factor for explaining the large surface area achieved [7]. The diversity of optimum activation conditions is reflected in the variety of mechanisms by which ZnCl₂ can develop porosity. ZnCl₂ is generally believed to act as a dehydrating agent and as a tar formation suppressant [4].

3.2 Chemical activation with KOH

KOH is an effective activating reagent for production of activated (Ros et al. 2006; Gasco et al. 2005). The highest surface areas reported in the literature are 1882 m² g⁻¹ and 1686 m² g⁻¹ [6,7]. However, in the present work the surface area is 186 m² g⁻¹ (Table 1) – low values compared with literature values. A possible explanation for the discrepancy in these values could be traced to pyrolysis conditions under which the samples were produced [4-7]

3.3 Equilibrium studies

An adsorption isotherm describes the relationship between the amount of adsorbate removed by the adsorbent and the adsorbate concentration left in the solution. There are many equations for analyzing equilibrium data of experimental adsorption. The parameters of these equilibrium models provide useful insights into the adsorption mechanism, the surface properties and affinity of the adsorbent.

Figure 4 and Table 2 present respective curves and fitting parameters adsorption isotherms of Cu(II) onto Sewage sludge (without inorganic activation), KOH-treated and ZnCl₂-treated adsorbents.

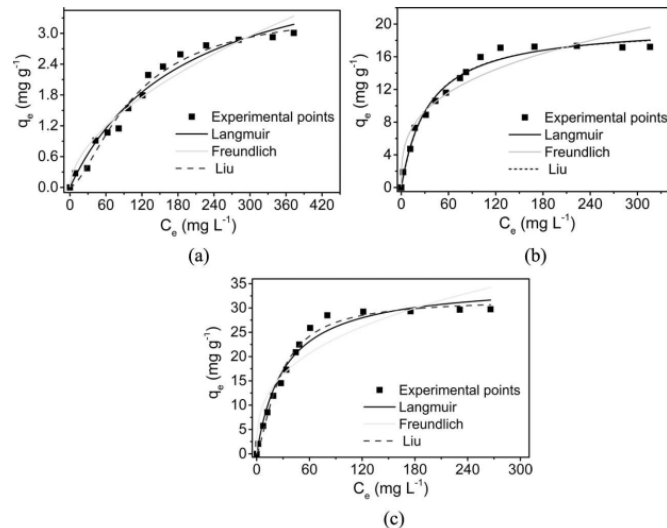


Figure 4. Langmuir, Freundlich, and Liu adsorption isotherm models for Cu(II) removal by (a) sewage sludge without activation; (b) ZnCl₂-treated sludge; and (c) KOH-treated sludge.

Table 2. Isotherm parameters for Cu(II) adsorption using sewage sludge (without inorganic activation), KOH-treated and ZnCl₂-treated adsorbents. Conditions: temperature, 25 °C; pH 6.0; contact time, 4 h; adsorbent mass, 80.0 mg.

	Sewage sludge (without inorganic activation)	KOH- treated	ZnCl ₂ - treated
Langmuir			
Q _{max} (mg g ⁻¹)	4.797	35.44	20.01
K _L (L mg ⁻¹)	0.00525	0.03125	0.02891
R _{Adj}	0.9715	0.9768	0.9848
SD (mg g ⁻¹)	0.1760	1.6257	0.7544
Freundlich			
K _F (mg g ⁻¹ (mg L ⁻¹) ^{-1/n_F})	0.1186	5.151	3.195
n _F	1.775	2.948	3.173
R _{Adj}	0.9398	0.8861	0.9239
SD (mg g ⁻¹)	0.2557	3.605	1.629
Liu			
Q _{max} (mg g ⁻¹)	3.513	31.85	19.79
K _g (L mg ⁻¹)	0.009427	0.03747	0.02954
n _L	1.542	1.421	1.031
R _{Adj}	0.9807	0.9866	0.9836
SD (mg g ⁻¹)	0.1449	1.2356	0.7276

The values of standard deviation of the Freundlich model are 0.2557, 3.605 and 1.629 mg g⁻¹ for Sewage sludge (without inorganic activation), KOH-treated and ZnCl₂-treated adsorbents, respectively. The standard deviation values for Langmuir model are 0.1760, 1.6257 and 0.7544 mg g⁻¹ while standard deviation values for Liu model are 0.1449, 1.2356 and 0.7276 mg g⁻¹ for Sewage sludge (without inorganic activation), KOH-treated and ZnCl₂-treated adsorbents, respectively. Based on the values of standard deviation, the equilibrium of adsorption of Cu(II) on three

adsorbents, is best described by Liu isotherm model. The Liu isotherm model shows lower values of standard deviation – an indication that the experimental amounts adsorbed by the adsorbents are closer to those calculated the Liu model.

The maximum adsorption capacities obtained from the Liu isotherm are 31.85, 19.79 and 3.513 mg g⁻¹ for KOH-treated, ZnCl₂-treated and sewage sludge (without inorganic activation) adsorbents, respectively.

Although KOH-treated adsorbent has lower surface area than ZnCl₂-treated adsorbent, but KOH-activated adsorbent has greater efficiency for the removal of Cu(II) than ZnCl₂-activated adsorbent. This observation could be linked to the presence of basic groups (especially OH group) on the surface of KOH-activated adsorbent [6-8].

3.4 Desorption studies

Regeneration of adsorbents saturated with Cu(II) was performed at 25 °C using 0.10-1.50 mol L⁻¹ HCl and 0.10-1.50 mol L⁻¹ HNO₃ as eluents. The regeneration efficiencies for Cu(II) using 1.50 mol L⁻¹ HCl are 92.4% and 96.7% for KOH-treated and ZnCl₂-treated adsorbents, respectively. For 1.50 mol L⁻¹ HNO₃, the corresponding efficiencies are 95.5% and 98.9% (Table 3).

Table 3. Desorption of Cu(II) from KOH-treated and ZnCl₂-treated adsorbents. Conditions: temperature, 25 °C; contact time, 1 h; adsorbent mass, 80.0 mg; and using 0.1-1.5 mol L⁻¹ HCl and HNO₃.

Eluent	KOH-treated adsorbent	ZnCl ₂ -treated adsorbent
	%Recovery of Cu(II)	
HCl (mol L ⁻¹)		
0.10	27.8	31.4
0.25	37.6	44.5
0.50	53.6	58.6
1.00	69.5	74.2
1.50	92.4	96.7
HNO ₃ (mol L ⁻¹)		
0.10	34.8	39.3
0.25	49.6	53.7
0.50	61.9	67.1
1.00	87.7	92.4
1.50	95.5	98.9

To investigate re-utilization of the regenerated adsorbents, the regenerated adsorbents were employed for metal uptake in a new cycle of adsorption. It was observed that the adsorption capacity was ca. 56% of the original adsorbents, indicating that adsorbents produced from sewage sludge could be a good alternative adsorbent for Cu(II) removal from aqueous solutions.

4 CONCLUSION

In this work, activated carbons were produced from urban sewage sludge using three different procedures: (1) one single pyrolysis stage (sewage sludge without inorganic

activation); (2) chemical activation with ZnCl_2 (ZnCl_2 -activated adsorbent) and (3) KOH (KOH-activated adsorbent). The sewage sludge-based adsorbents show different surface properties. The ZnCl_2 -activated adsorbent has higher surface area and larger pore volume than other two adsorbents, however, KOH-activated adsorbent has higher capacity for removal of Cu(II) from aqueous solutions. The isothermal data were fitted to Liu, Langmuir and Freundlich isotherms models to understand the adsorption process of Cu(II). The data were best described by Liu model and the maximum adsorption capacities of Cu(II) are 31.85, 19.79 and 3.513 mg g^{-1} at 298 K for KOH-activated, ZnCl_2 -activated and sewage sludge (without inorganic activation) adsorbents, respectively. About 99% of the Cu(II) was desorbed from Cu(II)-loaded adsorbent using 1.50 mol L^{-1} of HNO_3 . The regenerated adsorbents were re-utilized for Cu(II) uptake. It can be inferred that KOH-activated and ZnCl_2 -activated sewage-sludge adsorbents are effective and alternative adsorbents for removal of Cu(II) from an aqueous solutions because of their cost-effective and considerable adsorption capacities.

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