



Adsorption of copper(II) onto sewage sludge-derived materials via microwave irradiation

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ABSTRACT

The materials with adsorbent properties were produced from urban sewage sludge by two different procedures via microwave irradiation: (1) by one single pyrolysis stage (SC); (2) by chemical activation with ZnCl_2 (SZ). The BET, SEM and FT-IR have been used to evaluate the pore structural parameters and surface chemistry of the adsorbents, respectively. Subsequently they were used for adsorption of Cu(II) from aqueous solutions. The effects of various experimental parameters, such as pH, temperature were investigated in a batch-adsorption technique. The results showed that the adsorption of Cu(II) was maximal at pH 5.0. The kinetic study demonstrated that the adsorption process was followed the second-order kinetic equation. The experimental adsorption isotherm data were well fitted with Langmuir model and the maximum adsorption capacity of Cu(II) were found to be 3.88 and 10.56 mg/g for SC and SZ, respectively, in the solution of pH 5.0. Thermodynamic parameters such as changes in the enthalpy (ΔH^0), entropy (ΔS^0) and free energy (ΔG^0) indicate that Cu(II) adsorption onto SC and SZ is an endothermic and spontaneous process in nature at 15–45 °C. These results indicate that the sewage sludge-derived material via microwave induced ZnCl_2 activation is an effective and alternative adsorbent for the removal of Cu(II) from aqueous solution.

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1. Introduction

The increased attention on the harmful effects of heavy metal ions on human health and the environment over the past few decades has led to a concomitant focus on improved water quality [1]. Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operations and tanners [2]. Copper pollution especially, arises from copper mining and smelting, brass manufacture, electroplating industries and excessive use of Cu-based agro-chemicals. Copper along with arsenic and mercury, is recognized as the highest relative mammalian toxic and continued inhalation of copper containing sprays is linked with an increase in lung cancer among exposed workers [3]. Hence, the removal and recovery of copper from contaminated water and wastewater is important in the protection of the environment and human health.

Many separation methods such as precipitation, chemical reduction, ion exchange, membrane separation, adsorption and biological treatment have been used to remove metal ions from wastewater [4–8]. Adsorption is highly effective and economical method to remove heavy metal ions from aqueous solutions. Acti-

vated carbons, with their high surface area, microporous structure and chemical nature of their surface, are potential adsorbents for the removal of different heavy metals from industrial wastewaters [9,10]. However, activated carbon is a very expensive material. Thus, this kind of treatment may be unaffordable for small-scale industries.

Currently, there are many studies on the development of low-cost adsorbents, namely by using waste materials for that purpose. Wastes reuse and recycle minimize the environmental problems associated with their build-up and reduce the use of noble starting materials. Carbon-like wastes are viewed today with great interest because of their easily obtainable and appreciable economical worth and the possibility of being used in several industrial branches [11–14]. Sewage sludge's potential as a feedstock for producing activated carbon, which arises from its carbonaceous nature, was first recognized by Kemmer et al. [15].

Sewage sludge is produced as a result of wastewater treatment activity and their production is expected to gradually increase through environmental necessity and legal requirements for wastewater treatment. In China, for example, about 30 million tonnes dry solids of treated sewage sludge, commonly known as biosolids, were produced in 2010, which is still increasing in the future. Consequently, its handling and disposal is an issue of particular concern. The decline or loss of the traditional disposal routes for sewage sludge has created a high demand for more cost effective and environmentally benign alternatives. One option which

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exhibits especial promise due to its potential to valorise the sludge is the conversion of the sludge into adsorbents, especially activated carbon.

For preparing activated carbon, conventional heating method is usually adopted, in which the energy is produced by external heating source such as an electric furnace. However, in the external heating, the thermal energy is supplied to the surface of raw material and then transferred inside by heat conduction, and therefore it is difficult to achieve a uniform temperature in the material. Moreover, the processes take at least several hours and consume much energy to achieve the desired activation level under inert atmosphere at high temperature. To solve these problems, microwave heating has been recently gaining attention as a novel method of activated carbon preparation due to its heating rapidly and uniformly [16–19].

In this work, two different materials with adsorbent properties were produced from sewage sludge via microwave irradiation. The main objective of this study was to investigate the feasibility of using these sewage sludge based adsorbents for the removal of copper ions from dilute aqueous solutions. The BET, SEM and FT-IR have been used to evaluate the pore structural parameters and surface chemistry of the adsorbents, respectively. The influence of several operating parameters, such as pH, contact time and temperature on the sorption capacity is investigated. The equilibrium and kinetic data of the adsorption process were then analyzed to study the adsorption isotherms, kinetics, thermodynamics and mechanism of copper ions on the prepared carbons.

2. Materials and methods

2.1. Preparation of the adsorbents

Sewage sludge used in this work came from an urban treatment plant in Shanghai, China, where wastewater undergoes an activated sludge biological treatment. In this plant, mixed sludge from the first decantation and the secondary process is anaerobically digested and the resulting material is dried by centrifugation. Dried sludge was milled into powder in a miller and then used as starting material to produce sewage sludge-based adsorbents. The sieved raw material was then divided into two portions. The first portion was soaked in $ZnCl_2$ solution with an impregnation ratio of 1:2 (dry sludge: $ZnCl_2$ wt%). It is important to remark that other relations raw material: $ZnCl_2$ was studied, but the relation 1:2 was chosen because the resultant material presented the best textural characteristics, in particular specific surface area and porosity development. After impregnation, the solution was filtered to take the residual acid for the further process. The mixture of about 10 g was placed in a quartz reactor, and heated in a microwave furnace with 800 W power under a nitrogen flow of 10 mL/min for 10 min. The addition of $ZnCl_2$ initializes the pyrolysis of sewage sludge by its heat carrier properties, and furthermore promotes porosity development in the final adsorbent material due to activation. The as-prepared materials were cooled to room temperature under nitrogen flow. The samples were washed sequentially with 0.5 M HCl, hot water and cold distilled water to remove residual organic and mineral matters, leached with water to pH 6.5–7, then dried at 105 °C and crushed to obtain sewage sludge-based adsorbent finally, which was named SZ. Using the same parent sewage sludge and procedure as above, an adsorbent material (without $ZnCl_2$ impregnation), which was named SC, was also produced.

2.2. Characterization of activated carbon

The specific surface area and pore structural parameters of the samples were determined from the adsorption–desorption

isotherm of nitrogen at $-196\text{ }^\circ\text{C}$ (Micromeritics ASAP2020). The specific surface areas are calculated using BET equation. The total pore volume (V_T) was estimated to be the liquid volume of N_2 at a relative pressure (p/p_0) of 0.95. The micropore area (S_{mic}) and volume (V_{mic}) were obtained using the t -plot method. The mesopore volume (V_{mes}) was the deduction of V_{mic} from V_T . The average pore diameters were estimated from the BET surface area and total pore volume ($D_p = 4V_T/S_{BET}$) assuming an open-ended cylindrical pore model without pore networks [20].

SEM images were recorded to visualize sample morphology. Pore structure and structural changes happening after chemical activation could be also observed. In the present work, the sewage sludge derived materials (SC, SZ) were analyzed by this technique using a Philips XL30 microscope.

Fourier transform infrared (FTIR) spectra were obtained using a spectroscope (Spectrum 1, Perkin–Elmer) at resolution 4 cm^{-1} . Pressed potassium bromide (KBr) pellets at a sample/KBr weight ratio of 1:100 were scanned and recorded between 4000 and 450 cm^{-1} . The pellets were placed in an oven at $120\text{ }^\circ\text{C}$ for 5 h to remove any water present.

2.3. Batch adsorption experiments

The Cu(II) solution was prepared by dissolving $CuSO_4 \cdot 5H_2O$ reagent in doubly distilled water. The effect of pH on the adsorption of Cu(II) was studied in the range $1 < \text{pH} < 6$ (above 6 metal precipitation occurs), which was measured by using a pH meter (FE-20, Shanghai, China). The pH was adjusted by adding a few drops of diluted 0.1 N NaOH or 0.1 N HCl. Initial concentration of Cu(II) was 50 mg/L and the adsorbent dose was kept at 0.20 g. Agitation was provided with a constant agitation speed of 120 rpm. At equilibrium, the Cu(II) concentrations were measured.

In adsorption equilibrium, experiments were conducted by adding a fixed amount of carbons (0.2 g) into 250 mL Erlenmeyer flasks containing 100 mL of different initial concentrations (10–100 mg/L) of Cu(II) solution. The flasks were agitated in an isothermal shaker at 120 rpm $25\text{ }^\circ\text{C}$ for 24 h to reach equilibrium of the solid–solution mixture. A similar procedure was followed for another set of Erlenmeyer flask containing the same Cu(II) concentration without sewage sludge-based materials to be used as a blank. The flasks were then removed from the shaker and the final concentration of Cu(II) in the solution was analyzed using a Unicam model atomic absorption spectrometer (PEAA400, USA). The samples were filtered prior to analysis in order to minimize interference of the adsorbent fines with the analysis. Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium, q_e (mg/g), was calculated from the relationship

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of Cu(II) at initial and equilibrium, respectively. V (L) is the volume of the solution, and W (g) is the mass of dry adsorbent used.

The procedures of kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of Cu(II) were similarly measured.

3. Results and discussion

3.1. Characterization of the adsorbents

Table 1 shows the ultimate and proximate analysis corresponding to the sewage sludge used as starting materials for the production of adsorbents and that corresponding to the products from them obtained. From Table 1, it can be seen that when sewage

Table 1
Ultimate and proximate analysis of sewage sludge raw material used and the products generated.

Material	Volatiles (%)	Ash (%)	Fixed carbon (%)	C (%)	N (%)	H (%)	Cl (%)	S (%)
Sewage sludge	45.62	46.41	7.12	37.45	2.90	5.84	0.03	1.32
SC	13.25	67.35	13.64	27.66	1.77	1.16	0.04	0.46
SZ	18.24	35.14	26.56	43.52	1.66	1.68	0.21	0.50

sludge was subjected to pyrolyse to produce SC and SZ materials, most of the organic volatiles were evolved. The SC has a higher percentage of ashes (67.35%) than the SZ (35.14%). The later, which is chemically activated, has 26.56% of fixed carbon and 18.24% of volatile matter, while SC has 13.64% and 13.25%, respectively. Percentages of the other elements (N, H, Cl, S) were analyzed as they could have some effect on the chemical surface of the products, improving adsorption of polar molecules. The Cl content of the SZ was higher than that of the original sludge because of activation with $ZnCl_2$.

Pore characteristic of SC and SZ was determined by N_2 adsorption. The nitrogen adsorption/desorption isotherms of the two sewage sludge-based materials are illustrated in Fig. 1. The both adsorbent materials possessed combination of type I and type II of IUPAC isotherm, indicating simultaneous presence of micropores and mesopores. These isotherms also exhibited a type H4 hysteresis loop, characteristic of slit-shaped pores.

The BET surface area ($377.1 \text{ m}^2/\text{g}$) of SZ is higher than that of the non-activated SC ($48.3 \text{ m}^2/\text{g}$). Thus, activation improved the porosity of the sewage sludge-based material. As Fig. 2 shows, SZ is with a wide pore size distribution. The results suggested that $ZnCl_2$ could significantly enhance the process of pore widening and formation of the mesoporous structure by promoting externally located devolatilization processes [12]. The total pore volumes and pore size of SZ are $0.243 \text{ cm}^3/\text{g}$ and 2.14 nm , while, in the case of the SC, they are $0.089 \text{ cm}^3/\text{g}$ and 2.78 nm , respectively. The low surface area and the porosity of the SC can be attributed first of all to the fact that it was pyrolysed in a flow of inert gas and therefore no activation occurred. Liu et al. [21] compared microwave-induced activation process with the conventional thermal method. They found that the pore structure of the microwave activated carbon was better developed than that of the thermally activated carbon. Moreover, the microwave activated carbon exhibited a slightly higher portion of mesopores than the thermally activated carbons. These should be attributed to the distinct mechanism of microwave heating. The interior part of the carbon can be heated more favorably under microwave radiation, creating a temperature gradient

reducing from the center to the surface [22,23]. As a consequence, the release of tar or volatile matter would be promoted.

The SEM micrographs of SC and SZ are given in Fig. 3. As can be seen from Fig. 3a, there is no enough and successful pore development in the sewage sludge-based char (SC) obtained with microwave-induced pyrolysis without activation. However, there is a good and successful pore development in SZ. The sewage sludge-based material obtained at microwave-induced activation had a regular and highly porous surface, indicating higher surface area.

The FTIR spectra can provide valuable information about functional groups (like carboxyl, hydroxyl, etc.) that are capable of adsorbing metal ions [24]. The FTIR spectra of the activated sludge precursor and the SZ and SC materials were demonstrated in Fig. 4. It was shown that the activated sludge precursor contained more bands than the pyrolysed and activated sewage sludges, and there were only slight differences between the two SZ and SC materials. The broad band at about 3400 cm^{-1} was observed for all samples, which was assigned to the O–H stretching vibration of the hydroxyl functional groups including hydrogen bonding. The intense band at about 2923 cm^{-1} for the activated sludge precursor was attributed to the C–H stretching vibration, which disappeared for the SZ and SC, indicating that the hydrogen element was removed to a large extent. The band at about 1640 cm^{-1} was probably corresponded to the C=O stretching vibration of carbonyl groups belonging to different functional groups [25]. The bands at about 1531 and 1446 cm^{-1} for activated sludge precursor were attributed to $PhNO_2$ and COOH groups vibrations, respectively, which were significantly reduced after microwave-induced pyrolysis or activation. The sharp bands at about 1035 cm^{-1} for the sludge precursor shifted toward higher wave number for SZ and SC, indicating some changes in the C–O–C group in carboxylic and alcoholic groups [26].

3.2. Batch mode adsorption studies

3.2.1. Effect of pH

The effect of pH in the range of 1–6 on the adsorption of Cu(II) onto both SC and SZ was determined and the corresponding vari-

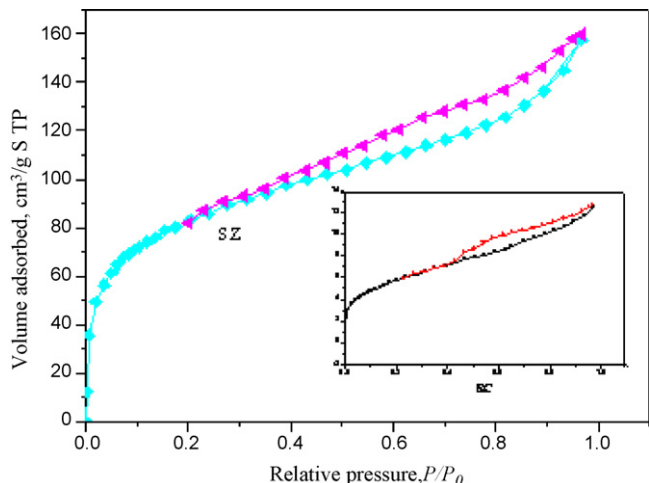


Fig. 1. Nitrogen adsorption/desorption isotherms at 77 K on SC and SZ adsorbents.

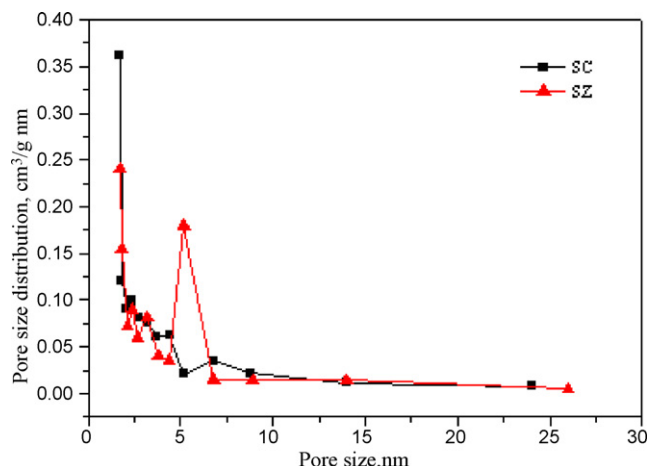


Fig. 2. Pore size distribution of SZ and SC adsorbents.

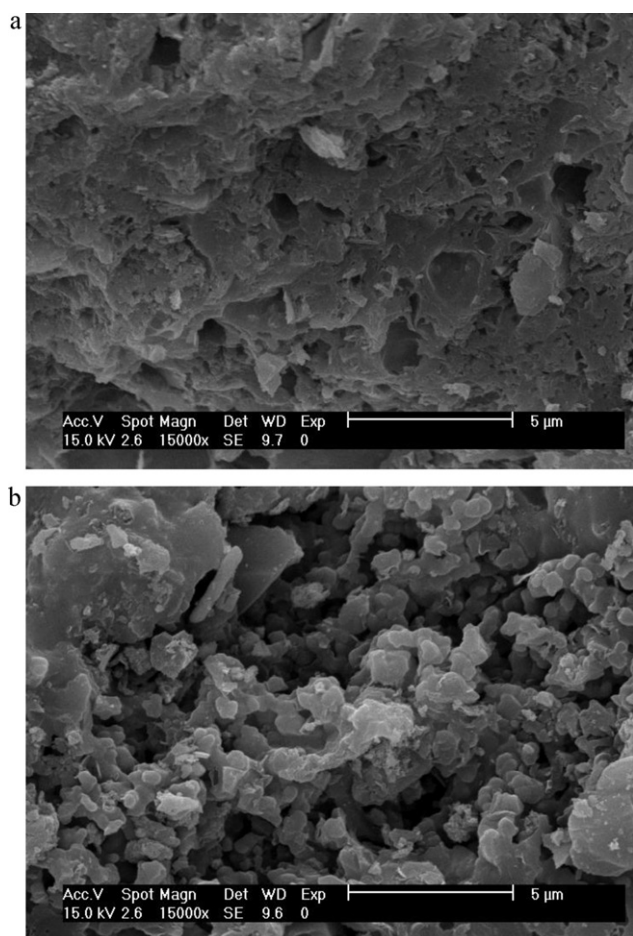


Fig. 3. SEM pictures of SC (a) and SZ (b) adsorbents.

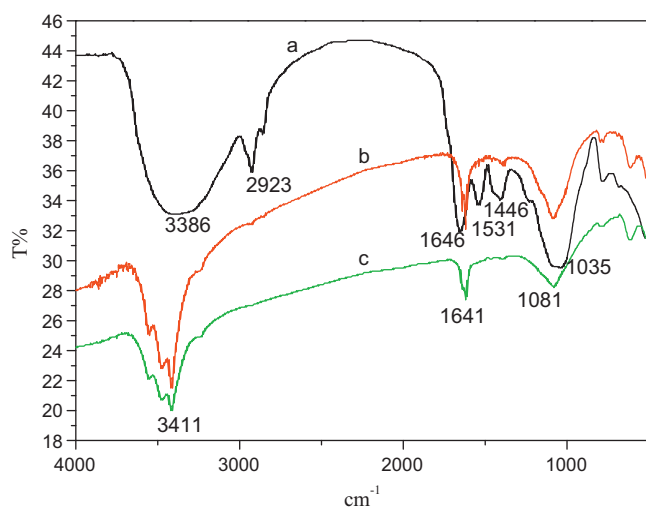


Fig. 4. FT-IR spectra of (a) activated sludge precursor, (b) SC, (c) SZ.

ations of q_e (mg/g) are shown in Fig. 5. As it can be seen, SZ has larger capacity to adsorb the Cu(II) here studied than SC. As it was previously said, this may be related to the higher surface area of SZ and to the chemical modification introduced by the activation step. The adsorption capacity of Cu(II) increased up to pH 5.0 and then decreased at pH 6.0 for both the sewage sludge-based adsorbents. The effect of pH may be explained in relation to the interaction of

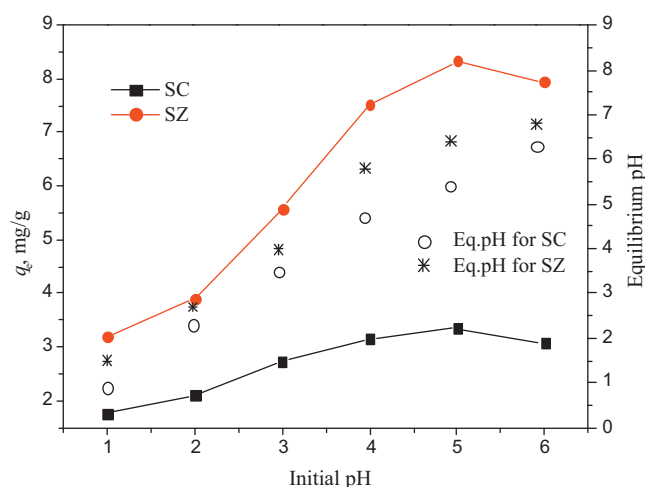
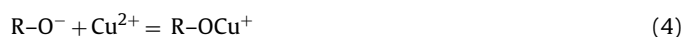
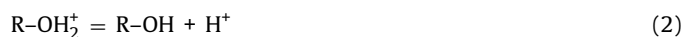


Fig. 5. Effect of pH on the adsorption of Cu(II) onto SC and SZ adsorbents.

Cu(II), $\text{Cu}(\text{OH})^+$ and $\text{Cu}(\text{OH})_2$ with surface functional groups present in SC and SZ adsorbents as follows:



where R- represents the surface sites of sewage sludge-based adsorbents; R-OH_2^+ , R-OH , R-O^- represent protonated, neutral, and ionized surface hydroxyl functional groups; R-OCu^+ and $\text{R-OCu}(\text{OH})$ are formation of the bonding complexes. It can be seen that at lower pH values, H^+ competes with the Cu ions for the active surface sites and, moreover, the less functional groups, i.e., R-O^- are ionized (deprotonated) in this region, and it is difficult that they form Cu complexes. Previous study also demonstrated that in the pH-effect experiments, the copper adsorption onto carbon was mainly due to the formation of metal-surface complex RO-Cu^+ shown in Eq. (4) [27]. Comparison of solution pH during the experiments in Fig. 5 shows that the final pH is much higher than the initial pH. This observation gives important supportive evidence of a strong adsorption of hydrogen ions by the SC and SZ adsorbents (R-OH_2^+). As the pH increased above 5.0, the precipitation of Cu(II) as copper hydroxides could be seen, which restricted the true adsorption studies [28]. Therefore, an optimized pH of 5.0 is taken for all the adsorption experiments for both SZ and SC. The effect of pH on the adsorption capacities of SC and SZ adsorbents is in agreement with the previously reported results for adsorption of Cu(II) from aqueous solutions by modified barks [29], grape seed and chestnut shell activated carbons [30], hazelnut husk activated carbons [28], wheat shell [31] in the literature.

3.2.2. Effect of contact time on adsorption

The influence of contact time on the removal of Cu(II) by SZ and SC is presented in Fig. 6. A fast adsorption kinetic was observed and the adsorption equilibrium can even be reached within the contact time of only about 60 min. Both pseudo-first-order and pseudo-second-order kinetic models were used to correlate the adsorption data [32].

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

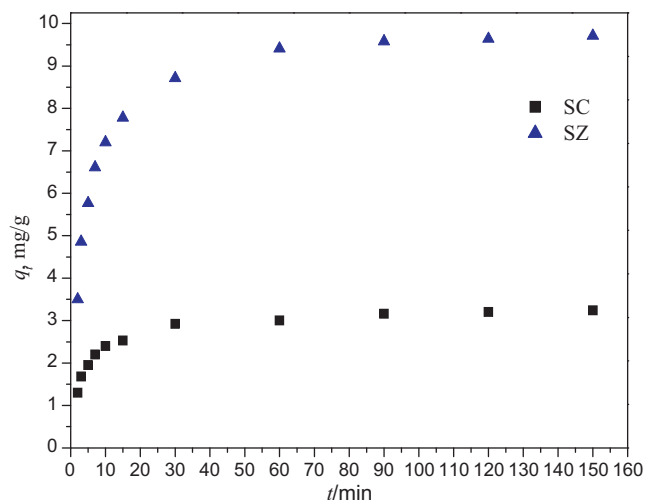


Fig. 6. Effect of contact time on Cu(II) adsorption onto SC and SZ at 25 °C.

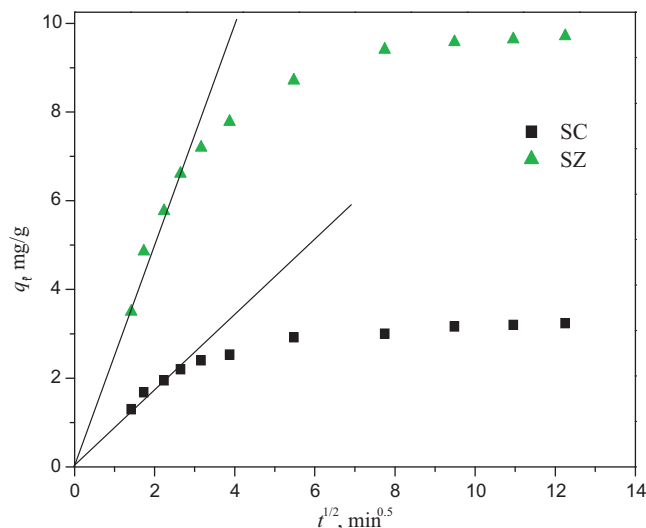


Fig. 7. Intra-particle diffusion plot for Cu(II) adsorption onto SC and SZ carbons.

where q_t (mg/g) is the amount of solute adsorbed per gram of adsorbent over a time period t (min), k_1 (1/min) and k_2 (g/mg min) are the kinetic parameters to be determined. The kinetic parameters are determined and listed in Table 2. Higher correlation coefficients of the pseudo-second-order model and the calculated q_e values close to the experimental data indicated that Cu(II) adsorption onto both SZ and SC can be approximated more favorably by the pseudo-second-order model than the pseudo-first-order one. This reveals that the limiting stage of the process is more the mechanism of adsorption than the mass transfer from the solution to the surface of the adsorbent [33]. It was also more likely to reflect that the adsorption behavior might involve the valency forces through sharing electrons between metal ions and adsorbents [34,35]. About the values of k_2 , as it may be seen in Table 2, the higher values were obtained for SZ than for SC, which displayed the faster adsorption kinetics. In many cases, the pseudo-second-order kinetic model provided better results for the adsorption of Cu(II) onto activated carbons from various biomasses [36,37].

In general, the adsorption process may be described as a series of steps: mass transfer from fluid phase to the particle surface across the boundary layer, diffusion within the porous particle, and adsorption itself onto the surface. Considering the pseudo-second-order model cannot identify the diffusion mechanism, intraparticle diffusion model based on the theory proposed by Weber and Morris [38] was then tested as:

$$q_t = k_i t^{1/2} \tag{8}$$

where k_i is intraparticle diffusion rate constant (mg/g min^{0.5}). It is obtained from the slope of the straight line of q_t versus $t^{1/2}$. As shown in Fig. 7, the plot of the square root of time versus the uptake (q_t) for the initial adsorption results in a linear relationship

passing through origin, implying that the rate-limiting step of the adsorption may be due to the intraparticle diffusion [39,40].

3.2.3. Adsorption isotherms

The capacity of an adsorbent can be described by its equilibrium sorption isotherm, which is characterized by certain constants whose values express the surface properties and affinity of the adsorbent. To analyze the validity of the adsorption data Langmuir and Freundlich adsorption models were run as discussed below.

The Langmuir isotherm equation, which is the most commonly used for monolayer adsorption on to a surface with a finite number of identical sites, is represented by the following Eq. (9):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{9}$$

where C_e is the equilibrium concentration of metal ions (mg/L), q_e is the amount of metal ions adsorbed (mg/g), q_m is the maximum adsorption capacity of metal ions (mg/g), and K_L is the Langmuir adsorption equilibrium constant (L/mg) related to the affinity of the binding sites [41].

The Freundlich isotherm equation, the most important multi-layer adsorption isotherm for heterogeneous surfaces, is described by the following Eq. (10):

$$q_e = K_F C_e^{1/n} \tag{10}$$

where K_F ((mg/g)(L/mg)^{1/n}) and n are the Freundlich adsorption isotherm constants, which are indicators of adsorption capacity and adsorption intensity, respectively [42].

Graphic presentations of the adsorption isotherms of Cu(II) onto SC and SZ at 25 °C are illustrated in Fig. 8. The values of isotherm constants are presented in Table 3. The results indicate that the Langmuir isotherm fits better than the Freundlich isotherm under

Table 2 Kinetic parameters for the adsorption of Cu(II) onto the SZ and SC at 25 °C.

Type of the adsorbents	SC	SZ
First-order kinetics		
k_1 (1/min)	0.0134	0.0276
R^2	0.8581	0.9386
Second-order kinetics		
k_2 (g/mg min)	0.1101	0.0290
q_2 (mg/g)	3.47	9.88
R^2	0.9918	0.9918
Intraparticle diffusion		
k_p (mg/g min ^{0.5})	0.6978	2.4028
R^2	0.9695	0.9735

Table 3 Adsorption isotherm constants for the adsorption of Cu(II) onto SZ and SC at 25 °C.

Type of the adsorbents	SC	SZ
Langmuir		
q_m (mg/g)	3.88	10.56
K_L (L/mg)	0.2965	0.4115
R^2	0.9970	0.9905
Freundlich		
K_F ((mg/g)(L/mg) ^{1/n})	1.072	3.40
n	2.86	3.32
R^2	0.9691	0.9549

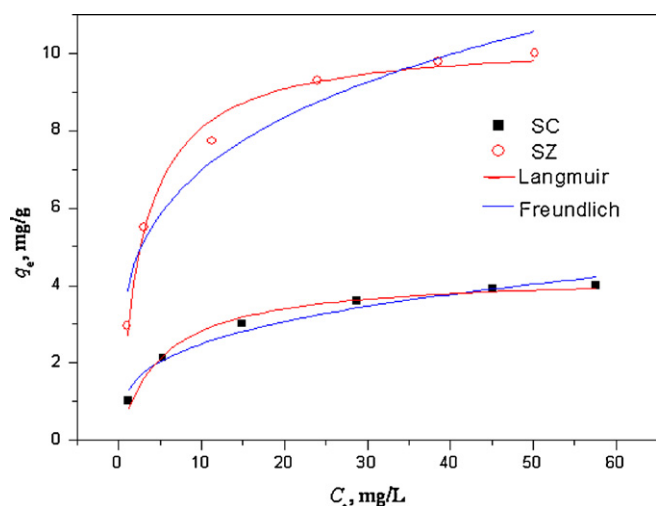


Fig. 8. Adsorption isotherm for the adsorption of Cu(II) onto SZ and SC carbons at 25 °C.

the concentration range studied, which may be due to homogeneous distribution of active sites onto SZ and SC surface, since the Langmuir equation assumes that the surface is homogenous. Moreover, the n values in Table 3, all between 1 and 10, indicate heterogeneity of the adsorbents and favorable adsorption [43]. The maximum adsorption capacity obtained from the Langmuir isotherm was 10.56 and 3.88 mg/g for SZ and SC, respectively, at 25 °C and pH 5. This suggests that Cu(II) could be more easily adsorbed on SZ.

A comparison of the maximum Cu(II) adsorption capacity, q_m , of SZ with those of other low cost adsorbents reported in the literature is given in Table 4. It can be seen that the differences in Cu(II) adsorption capacities are due in part to variation in properties of the adsorbents such as specific surface area, structure, functional groups, etc. Other than the adsorbent properties affecting the adsorption, the solution matrixes such as pH, temperature, and the presence of competing cations would also influence on the adsorption to various degrees. The adsorption capacity of SZ is relatively low when compared with other sewage sludge carbon in reference [2], the different performance can be explained in term of the heterogeneous nature of sludges [48]. Although, the adsorption capacity of SZ is not the highest one, it can be obtained cheaply in large quantities.

3.2.4. Effect of temperature

Fig. 9 shows the Cu(II) adsorption uptake, q_e (mg/g) on SZ and SC at initial concentration of 50 mg/L. The Cu(II) adsorption uptake was found to increase with increasing solution temperature from 15 to 45 °C, indicating the endothermic nature of the adsorption reaction. The enhancement in the adsorption capacity might be due to the chemical interaction between adsorbates and adsorbent, creation of some new adsorption sites or the increased rate of intraparticle diffusion of adsorbate molecules into the pores of the adsorbents at higher temperatures [49]. Senthilkumar et al. [50] also noted similar observations and they suggested that the increase in adsorption capacity with increase in temperature might be due to the possibility of an increase in the porosity and in the total pore volume of the adsorbent, an increase of number of active sites for the adsorption as well as an increase in the mobility of the adsorbate molecules.

In order to gain insight into the mechanism involved in the adsorption, thermodynamic parameters of free energy change (ΔG^0 , kJ/mol), enthalpy change (ΔH^0 , kJ/mol) and entropy change (ΔS^0 , J/mol K) were used to describe thermodynamic behavior of

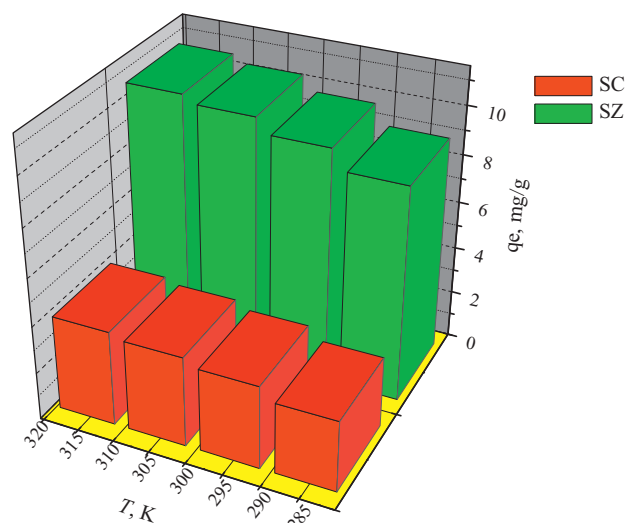


Fig. 9. Effect of solution temperature on Cu(II) uptake.

the adsorption of Cu(II) onto SZ and SC. These parameters were calculated from following equations:

$$\Delta G^0 = -RT \ln K_d \quad (11)$$

$$\ln K_d = \frac{\Delta S_0^0}{R} - \frac{\Delta H^0}{RT} \quad (12)$$

where R is the universal gas constant (8.314 J/mol K), T is the solution temperature (K) and K_d (q_e/C_e) is the distribution coefficient [51]. Thus, a plot of $\ln K_d$ versus $1/T$ should be a straight line (not shown). The observed thermodynamic values are given in Table 5. The negative values of ΔG^0 indicate the feasibility and spontaneity of the adsorption process. The high positive values of ΔH^0 confirm the endothermic nature of the overall adsorption process. The ΔH^0 values showed that the adsorption process of Cu(II) onto both sewage sludge-based adsorbents were taken place via physical adsorption. It may be suggested that electrostatic interaction between adsorption sites and the metal ion is the major mechanism responsible for the Cu(II) adsorption process. The positive value of ΔS^0 suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent and an affinity of the adsorbent.

3.2.5. Metal desorption

Desorption studies help to elucidate the mechanism of adsorption and to regenerate the adsorbent, as to well as recover Cu(II) from the spent adsorbent apart from protecting the environment from solid waste disposal problems. Regeneration of SZ saturated with Cu(II) was performed at 25 °C by using 0.1 N HNO₃ as regenerant, and the regeneration efficiency for Cu(II) was 59%. The fact that only partial or incomplete Cu(II) desorption shows that chemisorptions, physisorptions and ion-exchange mechanisms are operative in the adsorption process. Only the Cu(II) ions that are adsorbed by physisorption and ion-exchange are desorbed and the Cu(II) ions that are removed by complex formation are not desorbed.

The relative price of the material produced in the present study is very much lower than that of commercial activated carbons. The sewage sludge is available free of price, and after considering expenses like transport, chemicals, electrical energy and processing cost, the cost of SZ material would be approximately 550RMB/t. The cost of the activated carbon used for water treatment in our country is around 6000RMB/t.

Table 4
Comparison of adsorption capacity of various adsorbents for Cu (II).

Adsorbent	pH	Temperature (°C)	Adsorption capacity (mg/g)	BET (m ² /g)	References
Sewage sludge carbon/char	4.0	25	30.7/6.7	472/60	[2]
Cassava peel activated carbon	5.0	25	52	1567	[44]
Hazelnut husk activated carbon	5.7	18	6.64	1092	[28]
Rubber wood sawdust carbon	6.0	30	5.73	1673	[45]
Wheat shell	5.0	25	10.84	–	[31]
Sawdust	6.29	23	8.45	–	[46]
Pomegranate peel	5.8	26	1.32	–	[47]
Sewage sludge-derived adsorbent	5.0	25	10.56	377	This study

Table 5
Thermodynamic parameters calculated for the adsorption of Cu(II) onto SC and SZ adsorbents.

Adsorbent	ΔG^0 (kJ/mol)				ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
	288 K	298 K	308 K	318 K		
SC	–21.3	–22.7	–24.1	–25.4	14.5	0.125
SZ	–23.8	–25.2	–26.6	–28.3	19.8	0.151

4. Conclusions

The two materials with adsorbent properties were produced from urban sewage sludge by two different procedures via microwave irradiation: (1) by one single pyrolysis stage (SC); (2) by chemical activation with ZnCl₂ (SZ). The sewage sludge-based adsorbents prepared with microwave demonstrated similar surface chemical properties. The SZ showed higher development of the BET surface area and larger volume of pores than the SC. Further, both SZ and SC had high ratio of mesopore, which was mainly resulted from the rapid heating associated with microwave irradiation. The materials prepared from sewage sludge can be effectively used as adsorbent for the removal of Cu(II) from aqueous solutions. The solution pH played a significant role in influencing the capacity of an adsorbent toward Cu(II). An increase in the pH of solutions led to a significant increase in the adsorption capacity of both adsorbents. The pseudo-first-order and pseudo-second-order kinetic models were used to analyze the data obtained for Cu(II) adsorption onto SC and SZ. The results indicated that the pseudo-second-order equation provided the better correlation for the adsorption data. The Langmuir and Freundlich isotherm models were used to express the sorption phenomena of Cu(II) to the prepared adsorbents. The experimental adsorption isotherm data were well fitted with Langmuir model and the maximum adsorption capacity of Cu(II) were found to be 3.88 and 10.56 mg/g for SC and SZ, respectively, in the solution of pH 5.0. The positive ΔH^0 value indicated that the adsorption process was endothermic in nature.

Based on all results, it can be also concluded that the sewage sludge-derived material (SZ) via microwave induced ZnCl₂ activation is an effective and alternative adsorbent for the removal of Cu(II) from an aqueous solution because of its considerable adsorption capacity and cost-effective renewable sources.

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