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Removal of heavy metals from wastewater using thermally treated sewage sludge adsorbent without chemical activation

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Abstract

Removal of copper as an example of heavy metals from synthetic wastewater by adsorption on sewage sludge adsorbent was studied. The sludge was dried, grinded and thermally treated at various temperatures. Surface morphology and chemical structure of treated sludge were investigated using SEM and FTIR. Parameters studied are initial concentration of copper ions, contact time, sludge dosage, and the heat treatment temperature of the sludge. The removal efficiency of Cu^{+2} increases with increasing sludge dosage. Increasing initial concentration of Cu^{+2} has two opposing effects on the % removal depending on the concentration range used. The maximum removal efficiency was 73%. Experimental data were modeled by using Langmuir and Freundlich isotherms. The data fits Freundlich linear model with R^2 = 0.9585. The mechanism of adsorption of Cu^{+2} by sludge adsorbent was found to take place through a monolayer and heterogeneous surface. Possible applications of the present data in removing copper and other heavy metals from industrial effluents were

1. Introduction

Nowadays water pollution by toxic heavy metals due to the discharge of industrial wastewater without preliminary treatment is a worldwide environmental problem. A lot of industries especially that related to metal processing operations and refineries are considered as dangerous sources of heavy metal emissions. Copper is one of the toxic metals that has harmful effects on living beings, including but not limited to; kidney disease, liver damage, stomach cramps, diarrhea, nausea and vomiting. Copper enters wastewater from many sources such as corrosion of water piping, mining and refining of copper, fertilizer industries, petroleum refining, infiltration and inflow of ground and surface water, etc. Depending on the standards of World Health Organization (WHO), the concentration of copper in drinking water should not exceed 0.05 mg/l, and its concentration in industrial sewage effluent discharge should be less than 3.0 mg/l. Based on the fact of harmful effects of copper on living beings, it should be removed or eliminated from wastewater to match the standards. There are many different technologies involving chemical and physical processes which have been developed previously to eliminate heavy metal ions from wastewater such as chemical precipitation [1,2], adsorption [3,4], ion exchange [5,6], electrochemical technique [7,8], cementation [9-11], membrane processes [12], and solvent extraction [13]. Awual [14] created a novel facial composite adsorbent to improve the detection of Cu (II) and removal from wastewater. The author investigated the effects of several parameters such as initial pH, Cu (II) ions concentration, shaking time, foreign ions. He found the maximum sorption capacity was 176.27 mg/g based on the Langmuir sorption isotherm study. Huang and He [15] investigated the performance of electrosorption in removal of copper ions from wastewater on ordered mesoporouscarbon (OMC) electrode, they found the amount of saturated adsorbed of Cu (II) on the OMC electrosorbent was 56.62 mg/ g at 0.9 V and pH = 4, which is close to 5 times higher than that recorded at open circuit. Siu et al. [16]

studied equilibrium and kinetics of removal of copper from wastewater using ion exchange technique using an iminodiacetate resin. The resin capacity for the copper ions was 2.30 mmol/g. Al-Harahsheh et al. [17] used Fly ash based geopolymer for copper removal, and found that maximum sorption capacity (q_m) occurred at 45 ˚C, reaching a value of 152 mg/g. Mosier et al. [18] carried out experiments to investigate the removal of Cu^{+2} by Microbial biofilms from Chemical Mechanical Planarization (CMP) wastewater. Xu et al. [19] created novel sorbent for the copper removal from waste water, so-called ZnS nanocrystals (NCs). He achieved copper removal efficiency over 99.0 % in one minute. According to his experiments, the saturated adsorption capacity of ZnS NCs sorbent on copper is about 650 mg/g. Bilal et al. [20] studied copper removal from industrial wastewater by waste biomass adsorbents, and conclude bio-adsorbents as agriculture and forest derived have greater potential for removal of Cu^{+2}, and attributed it to cheaper nature, higher uptake, bulk availability and mono to multilayer adsorption behavior.

In another point of view, an increase in amount of sewage sludge generated by wastewater treatment plant as a result of increasing of urbanization and industrialization is considered too as a worldwide problem and requires great attention [21,22]. Approximately 50 percent of the total costs of wastewater treatment are required for final disposal of sludge [23,24]. Reuse of sludge consider as an attractive alternative and best way for final dispose by environmentally friendly way. The idea of reusing solid wastes as adsorbent has been studied by different authors [25,26]. Using sewage sludge is a promising adsorbent since it has low production cost and high environmental sustainability.

Managing the sludge disposal is considered as one of crucial challenges. Water can be discharged to seas, rivers and lakes. Table 1 shows that the treated municipal wastewater represent around 68% of total municipal wastewater. This sludge would add drawback that it tends to accumulate heavy metals and other persistent toxic compounds coming from industrial discharges, traffic related pollution and other commercial activities. Heavy metals are mostly present in sludge because of their hydrophobic nature as they are attached with the solid portion of the wastewater [27].

Table 1, Municipal wastewater production, collection and treatment in countries with the largest urban populations. (Sources: Data from AQUASTAT 2014; GWI 2014)

Country	Municipal wastewater (km^3)			
	Produced	(Year)	Treated	(Year)
India	15.44	2011	4.42	2011
Brazil	9.73	2009	2.51	2009
Egypt, Arab Rep.	7.08	2012	3.71	2012
Canada	6.61	2009	3.55	2009
Germany	5.30	2007	5.18	2007
Italy	3.93	2007	3.9	2007
France	3.79	2008	3.77	2008
Turkey	3.58	2010	2.72	2010
Iran, Islamic Rep.	3.55	2010	0.89	2012
South Africa	3.54	2009	1.92	2009
Spain	3.18	2004	3.16	2004
Pakistan	3.06	2011	0.55	2011
Argentina	2.46	2010	0.29	2000
Colombia	2.40	2010	0.60	2010
Netherlands	1.93	2010	1.88	2010
Australia	1.83	2007	2.00	2013
Saudi Arabia	1.55	2010	1.06	2010
Algeria	0.82	2012	0.32	2012
Iraq	0.58	2012	0.10	2012

Commonly, Industrial waste has higher heavy metals contents than domestic wastewater. Therefore toxic metals such as nickel, chromium, lead, cadmium, mercury may be found in municipal wastewater due to heavy urbanization and the entry of untreated industrial wastewater into the municipal wastewater system [28-30]. Two groups of heavy metals can be classified. The first group includes cadmium, mercury and lead are highly toxic to humans and animals with less toxic effect on plants. The second group comprising zinc, nickel and copper have high toxic effect on plants when present in excess concentration. The latter group has more damaging influence on plants than humans and animals. Heavy metal removal from wastewater by % more than 50 has been achieved using adsorbent of sewage sludge as a preliminary treatment, which will decrease the cost of removal comparing with using commercial activated carbon only for example. And at the same time, disposing the sludge by friendly environmental way and reusing it.

This works aims to study the removal of heavy metals by adsorption using sewage sludge as an adsorbent and Cu^{+2} as an adsorbate example. Adsorption process is one of the most effective techniques can be applied to remove non-biodegradable matters. Adsorption process can be taken place by physisorption or chemisorption process. Adsorbate is attached to the adsorbent physically by Van der Waals forces. The chemisorption can be achieved by chemical bond with the molecules of the adsorbent. Adsorption processes based on physisorption can usually be reversed. Mass transfer of the adsorbate includes mainly four stages (i) convection, (ii) film diffusion (iii) grain diffusion and then (iv) attachment by physical or chemical bonding. Kinetics of adsorption can be controlled mainly by film diffusion and grain diffusion. Adsorbent has an outer and inner surface. The inner surface represents the overall surface of all pores. Pore size and structure play a crucial role in the adsorption capacity.

2. Experimental section

2.1 Materials

Raw sewage sludge has been collected from the final disposal area. Sludge was grinded and thermally treated at three different temperatures, 200, 400, and 600 ˚C. All chemical reagents such as $CuSO_4.5\ H_2O$, HCl, NaOH were in analytical grade. Stock solution was prepared by dissolving $CuSO_4$ in distilled water. Three different initial concentrations of Cu^{+2} were prepared by dilution of the stock solution namely; 50, 100 and 150 ppm. Initial pH of the solution was maintained at 5 by adding either HCl or NaOH. All experiments were conducted at a temperature 25 ± 1 ˚C. Table 2 shows the typical properties of sewage sludge.

Table 2, sewage sludge properties

Element/Parameter	Parameter	Typical %
Proximate analysis	Moisture	5.3
	Volatile matter	50
	Ash	30.772
Ultimate analysis	C	29.75
	H	4.1
	N	4.235
	O	19.7
	S	1.71
	F	0.008
	Cl	0.125

2.2 Apparatus and analysis

A lab scale standard Jar test apparatus was used to conduct the experiments. It consists mainly of six impellers mounted on stainless steel shafts, variable speed motor and six graduated cylinders of 1 L capacity. The impeller is two 90˚ turbine blades of 5 cm diameter and 2 cm height. The impeller rotation speed was ranged from 0 to 200 rpm. During all experiments the rotational speed was maintained at 200 rpm. Surface morphology of thermally treated sludge particles was carried out using JEOL JSM 6490A scanning electron microscope. Images were obtained by secondary electrons at 20 kV, to study micro-structure of treated sludge particles at 200, 400 and 600 ˚C.

Samples were sputter coated with monolayers of gold to enhance the electrical conductivity of sludge particles. Chemical structure was investigated using Fourier Transform Infrared (FT-IR). This analysis was performed using Brukers Alpha FT-IR (Platinium ATR module).HACH DR/3900 spectrophotometer was used for quantitative determination of Cu^{+2} using Phenanthroline method.

Fig. 1 shows different sequence of steps involved in carrying out the present work including sludge treatment, operating conditions and effluent analysis.

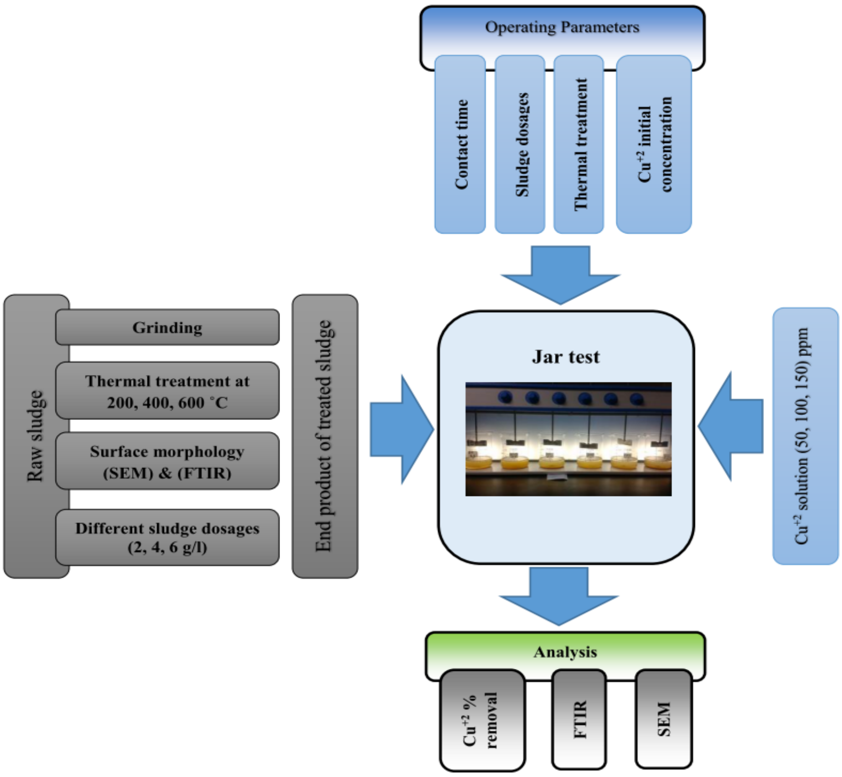

Fig. 1, Schematic presentation of the different steps of the experimental work.

The % removal of Cu^{+2} was calculated by using the equation (1):

$$\% \, removal = \left(\frac{C_o - C}{C_o}\right) \times 100 \qquad (1)$$

where C_o and C are initial and final concentrations of Cu^{+2} respectively.

3. Results and discussion

Removal of Cu^{+2} from aqueous solution was studied under various conditions such as contact time, initial concentration of Cu^{+2}, adsorbent dosage, sludge treatment temperature.

To study the effect of contact time on the removal efficiency of Cu^{+2}at different initial concentrations, samples of the solutions were analyzed at different time intervals, the % removal of Cu^{+2} increased with increasing contact time with a decreasing rate. The % removal was rapid and on increasing contact time the % removal increased slowly. This may attributed to the fact that at initial stages all active sites on the adsorbent surface were vacant and solute concentration gradient was high and the ratio of adsorbate molecules to the adsorbent molecules and to the available surface area is low. Also on increasing contact time the driving force between the bulk of the solution and the liquid-adsorbent interface decrease with a consequent decrease in the rate of removal [31,32].

Fig. 2 shows the effect of initial concentration of Cu^{+2} on the % removal at different adsorbent dosages and different sludge treatment temperatures.

The % removal of Cu^{+2} increases with increasing initial concentration of Cu^{+2} passes through maximum at 100 ppm and then decreases. Previous studies showed that initial concentration of dissolved ions has two opposing effects namely [32-36]; (i) increasing initial concentration leads to increasing the bulk concentration and increasing the concentration difference between the solution bulk and the interface with a consequent increase in the driving force for ions transfer and increasing the rate of removal. (ii) increasing initial concentration leads to increase the inter-ionic attraction and decreasing the diffusion of ions to the adsorbent surface with a consequent decrease in the rate of Cu^{+2}transferfrom the solution bulk to the adsorbent surface [37]. As the concentration of metal ion increases, rapid saturation of the adsorbent and more surface sites are covered at a constant adsorbent dose consequently the adsorbent capacity gets exhausted due to non- availability of the surface sites [38]. Under the present range of operating parameters it seems that the first effect is predominant in the concentration range from 50 – 100 ppm and the second effect is predominant in the concentration range 100 – 150 ppm. Fig. 2 also shows the effect of sludge dosage on the% removal of Cu^{+2}. The data show that within the present range of parameters studied and for a given initial concentration of Cu^{+2} the % removal increases with increasing sludge dosage and increasing sludge treatment temperature, this may be attributed the fact that with increasing the adsorbent dose the surface area and the active adsorption sites for bonding the heavy metal ions will increase[39,40]. Increasing the adsorbent dosage has two opposing effects namely; (i) the number of available adsorption sites increases by increasing the adsorbent dose and it therefore results in an increase in the % removal. (ii) the inter-particle interaction, such as aggregation, resulting from high adsorbent dose, would lead to a decrease in the total surface area of the adsorbent and on an increase in diffusional path length [41].

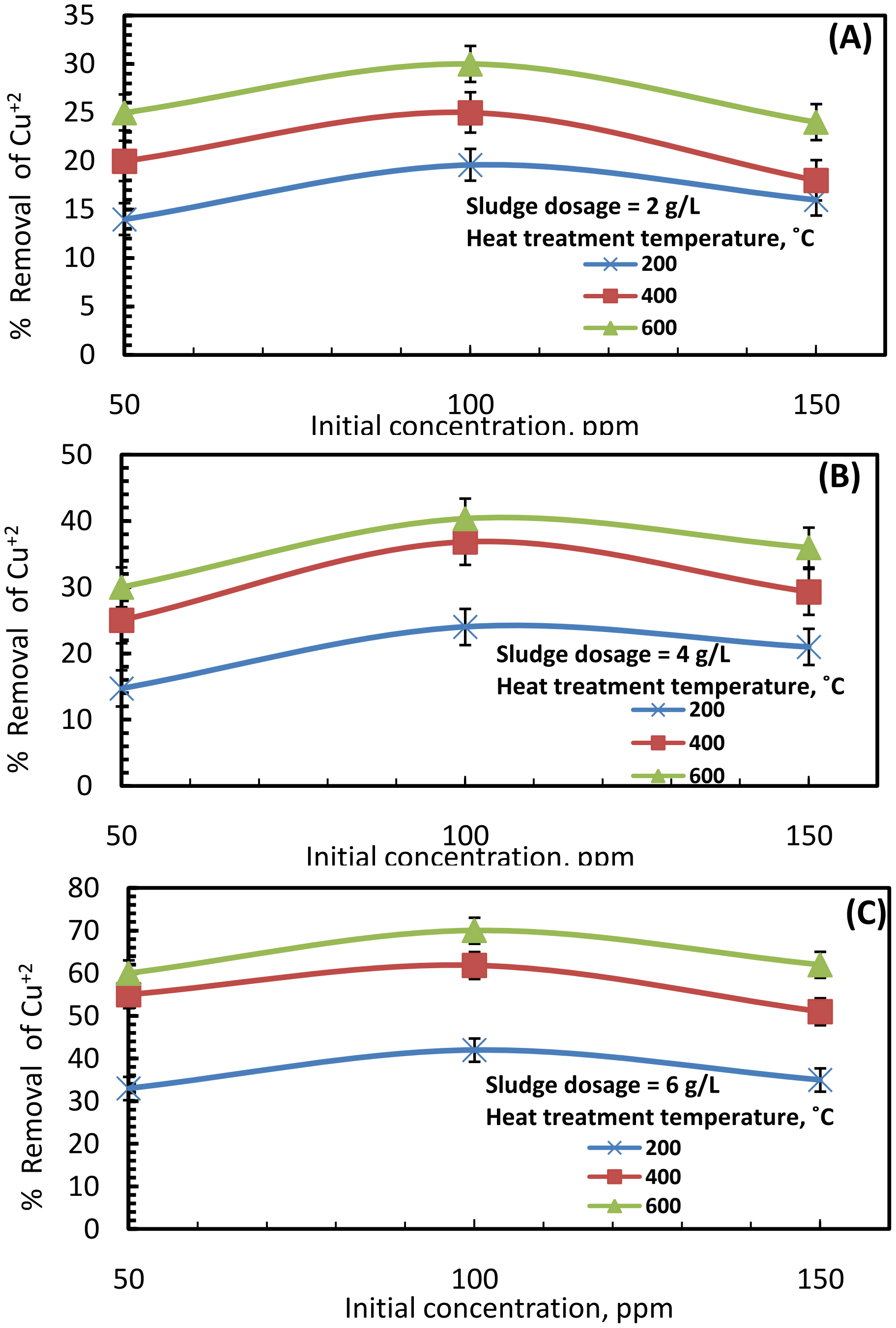

Fig. 2, Effect of initial concentration of Cu^{+2} on the % removal at different adsorbent dosages and different sludge treatment temperatures.

The data on Fig. 2 shows that the first effect predominates within the present range of sludge dosages used (2 – 6 g/L). Despite the increase in the sludge dosage increased the % removal but the adsorption density with decreases with increasing the adsorbent dosage, this may be because of unsaturation of adsorption sites through the adsorption process [42].

To study the effect of heat treatment temperature, the sludge after drying and grinding was treated at three different temperatures namely; 200, 400 and 600 ˚C for 3 hours holding time. Mass losses of sludge increased with increasing temperaturewith a formation of little pores and structural changes. The weight losses are mainly due to dehydration, organic and inorganic materials decomposition [43].

Fig. 2 shows that the maximum removal of Cu^{+2} was achieved with sludge samples treated at 600 ˚C at different sludge dosages (2, 4, and 6 g/L). In order to explain the effect of sludge treatment temperature on the % removal of Cu^{+2}, the sludge samples were analyzed by SEM analysis at the three temperatures 200, 400 and 600 ˚C respectively before and after adsorption. Surface morphology of heat treated sludge particles was analyzed by SEM. Fig.3 (a, b and c) shows the surface morphology of treated sludge particles at 200, 400 and 600 ˚C respectively. Ash is mainly found in compact or spherical shapes of different size. Some unshaped fragments refer to remaining volatile carbon [44]. Therefore it is noticed that the unshaped fragments are found mainly in the treated sludge at lower temperature 200 ˚C. Fig.3 (c) also display partially developed morphology with more roughness and some micro-holes on the surface.

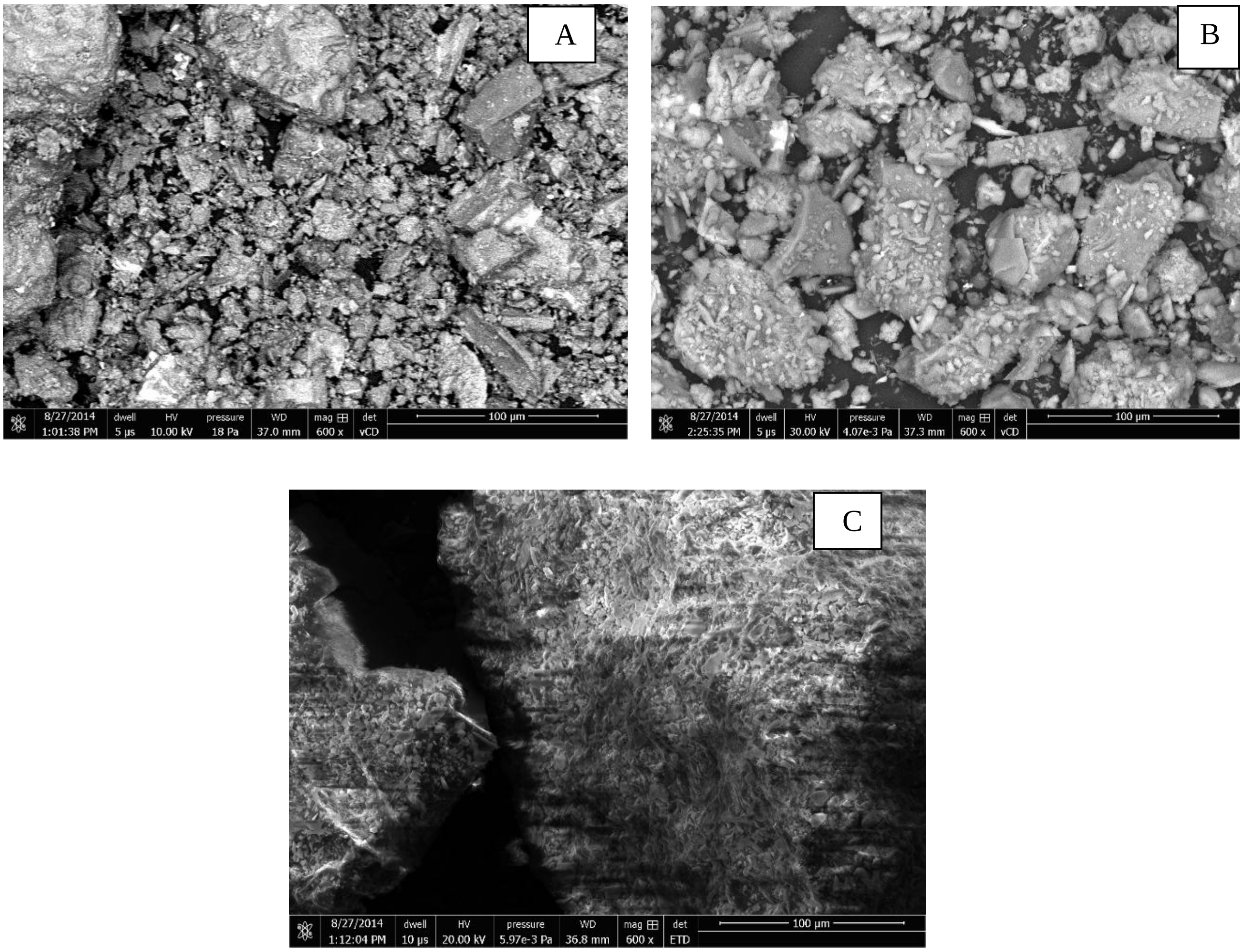

Fig. 3, SEM analysis of sludge samples at different treatment temperatures (A: 200 ˚C, B: 400 ˚C, C: 600 ˚C).

It give a high potential for pollutants to be adsorbed and attached on the adsorbent surface and consequently has higher adsorption capacity in the adsorption process [45]. Fig. 4 (a & b) shows the surface of loaded adsorbent of heat treated sludge at 200 and 600 ˚C. It is noticed that sludge surface has less porosity after adsorption. This can be attributed to the heavy impregnation of iron onto the adsorbent surface [46]. The concentration of adsorbate can be found more on treated sludge at 600 than 200 ˚C. This can be attributed to the high adsorption capacity of treated sludge at 600 ˚C [47].

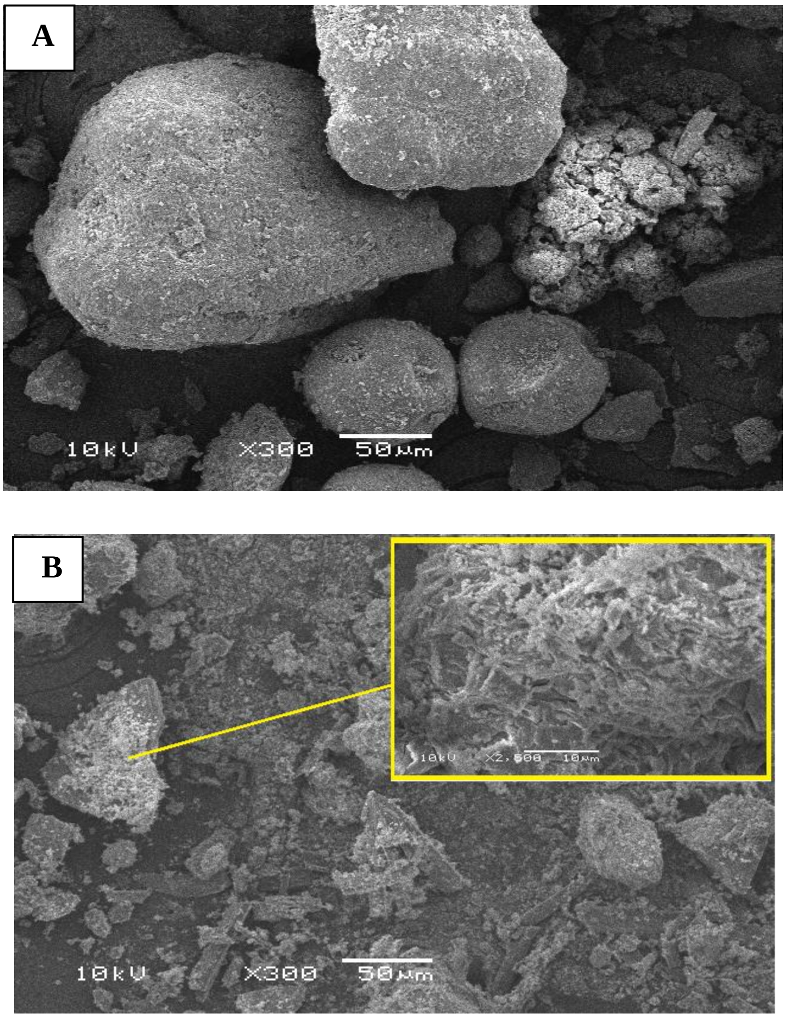

Fig. 4, SEM of sludge after adsorption process (A) Treated sludge at 200 ˚C (B) Treated sludge at 600 ˚C.

Also FTIR spectra show visible changes during heating of sludge, which are related to surface structure. Fig.5 shows detailed spectra evolution with heating for selected wavenumber ranges.

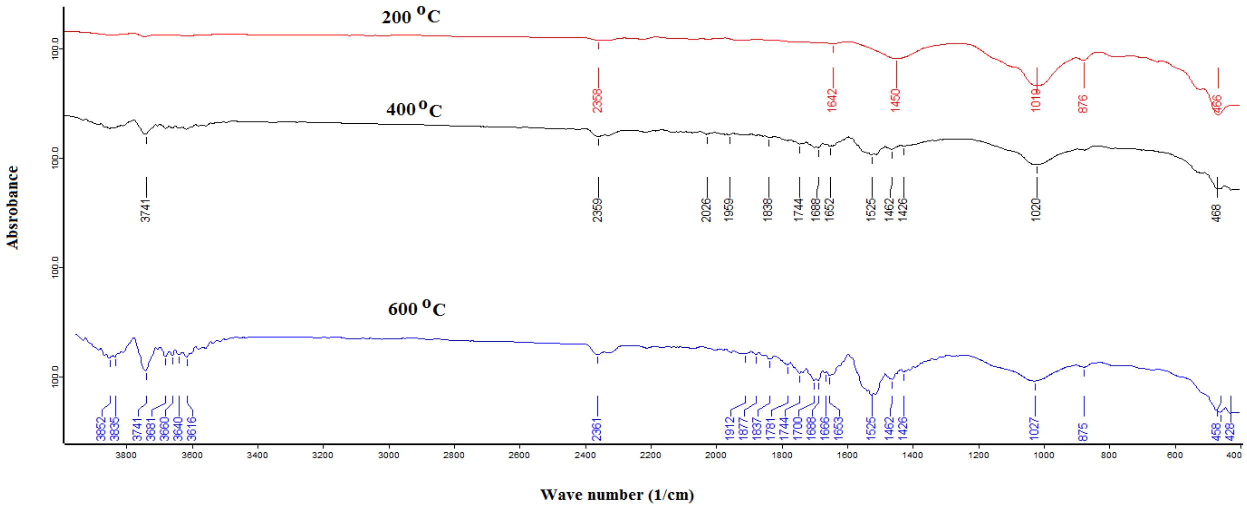

Fig. 5, FTIR spectra of sludge samples at different treatment temperatures.

A broad band at 3616 cm^{-1} corresponds to O‒H stretching vibrations. These functional groups may represent compounds such as alcohols and carboxylic acids found in the sample. The peak at 1653 cm^{-1} is due to the Amide I band. C=O stretching vibrations from other functionalities are found at the left of the 1700 cm^{-1} peak. They refer to fatty acid carboxylic groups. The band at 1525 cm^{-1} may be due to N-H bending, which is characteristic of the Amide II band. C=C aromatic skeletal vibrations can also be found between 1653 and 1500 cm^{-1} and may exist in the sample due to lignin structures41. In the interval between 1400 and 1525 cm^{-1}, vibration of CH_2 groups and O‒H bending vibrations for alcohols and carboxylic acids cause a variety of peaks. Consequently, a broad band around 1426 cm^{-1} is detected. Band at 1027 cm^{-1} has been assigned by several authors to polysaccharides. Peak at 873 cm^{-} can be assigned to inorganic carbonates, particularly calcium carbonate. Spectrum below 875 cm^{-1} could be result of aromatic structures, amine and amide groups. In this study, an attempt has been made to detail the FTIR spectra of sewage sludge and chars regarding the changes experienced by the solid fraction through heat treatment within the entire temperature range (200-600 ˚C), while being aware of its obvious limitations. In general, organic functional groups found in sewage sludge tend to decrease with increasing temperature [48]. Also some structural changes in the solid matrix can be discerned.

4. Adsorption isotherm

The performance of an adsorbent can be studied by adsorption isotherm data, which can be obtained by a series of experimental tests. Several isotherm models are commonly used in modeling the adsorption data, such as Freundlich and Langmuir [48-51]. The Freundlich isotherm is based on power function equation (2):

$$q_{eq} = K_F . C_{eq}^{n_F} \tag{2}$$

q_{eq} : Equilibrium loading in mg/g
C_{eq} : Equilibrium concentration in mg/L
K_F : Freundlich constant in mg/g
n_F :Freundlich exponent

The Freundlich exponent n_F has a decisive influence on the profile of the adsorption isotherm. Fig. 6 gives a qualitative representation of the profiles of three isotherms with different Freundlich exponents.

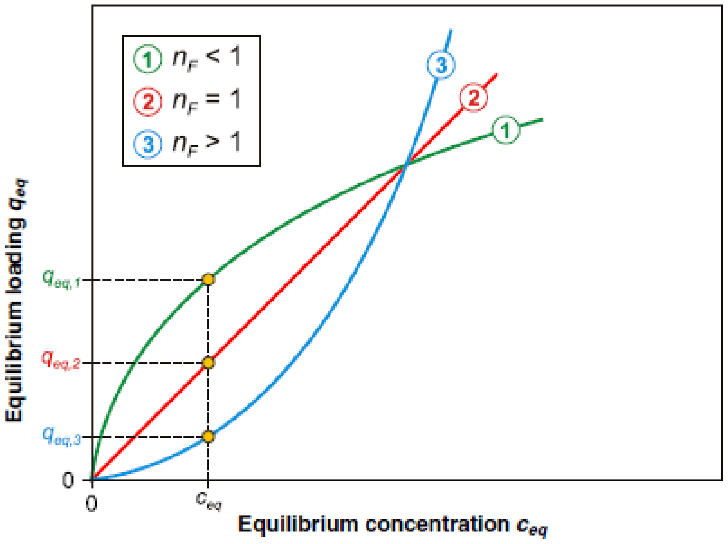

Fig. 6, Effect of n_F on the isotherm curve

In the field of water treatment, it is usually aiming for very low equilibrium concentrations. In this case, the equilibrium concentration corresponds to the maximum permitted adsorbate concentration in the treated water. Upon reaching the equilibrium concentration c_{eq}, isotherm 1 reaches a significantly higher loading than compared to isotherm 3. In the case of isotherm 1 the adsorbent's capacity is therefore utilized much better. This means that much less adsorbent is required to reach the equilibrium concentration c_{eq} than would be needed in the case of isotherm 3. As such, in the case of Freundlich exponents < 1 is a favourable isotherm curve. Accordingly, in Freundlich exponents > 1 there is an unfavorable curve. The Freundlich exponent therefore allows us to express how well a substance can be adsorbed. Where: the smaller the Freundlich exponent, the better the adsorbate can be adsorbed.

The linear forms of the Freundlich and Langmuir isotherms are given in equations (3) and (4) respectively:

$$\ln q_e = \ln K_F + \frac{1}{n_F}\ln C_{eq} \tag{3}$$

$$\frac{C_e}{q_e} = \left[\frac{1}{q_m K_L}\right] + \frac{C_e}{q_m} \tag{4}$$

Fig. 7 shows linear fitting of Freundlich and Langmuir adsorption isotherms of the sewage sludge adsorbent by linear analysis. The data suggests that Freundlich isotherm model generates a satisfactory fit to the experimental data, while Langmuir isotherm model cannot.

In the field of water treatment it is usually aimed for very low equilibrium concentrations. In this case, the equilibrium concentration corresponds to the maximum permitted adsorbate concentration in the treated water. As such, in the case of Freundlich exponent n < 1 is a favorable isotherm curve. For the present experimental data n is 3.9 which confirms favorable isotherm at higher concentrations of Cu^{+2}.

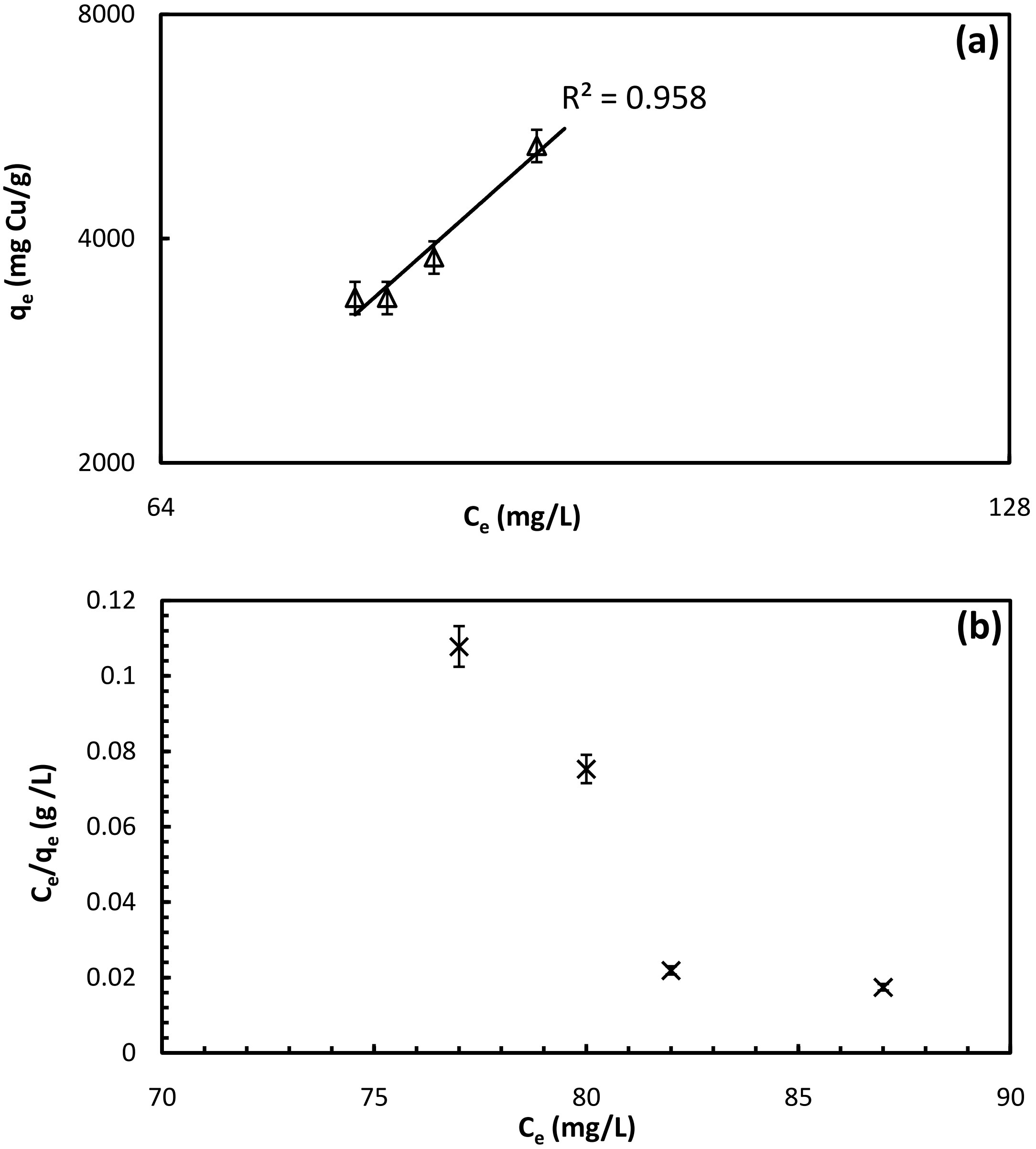

Fig. 7, linear fitting of isotherm models for the adsorption of Cu^{+2} by treated sludge (Sludge treatment Temp = 600 ˚C; dosage: 6 g/L; contact time: 150 min; pH: 5.0; at room temperature and agitation speed: 200 rpm) (a) Freundlich, (b) Langmuir

Conclusions

The main objectives of this work was to find a low cost material (sludge) used as heavy metals adsorbent, and minimize the cost of heavy meals elimination using commercial adsorbent by using sewage sludge. The sludge showed reasonable removal of Cu^{+2} and the % removal increased with increasing sludge dose and the temperature at which sludge was treated. The process is considered a friendly environmental for sludge reuse.

SEM analysis confirmed that sludge treatment at temperature 600 ˚C produce smallest particle size and in turn larger surface area which enhance the adsorption process.

FTIR spectra showed that organic functional groups found in sewage sludge tend to decrease with increasing treatment temperature.

The present experimental data fitted well Freundlich linear isotherm model with an exponent of 3.9 for Cu^{+2} which confirms a favorable isotherm for high concentrations of Cu^{+2}. The mathematical correlation obtained by the modeling analysis is important for operational design and applicable practice of the adsorption systems.

To minimize the total cost of heavy metals removal from wastewater using any commercial adsorbent like activated carbon, the treated sludge can be used as preliminary treatment process that will eliminate the initial concentration of heavy metals and in turn decrease the dose of followed commercial adsorbents.

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