



Recycling Of Sewage Sludge To Prepare An Effective Adsorbent To Treat Selected Heavy Metals - Contaminated Water

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Abstract

The introduction of more stringent legislation limiting the disposal and use of sewage sludge, combined with an increase in its production and the loss of previously recognized disposal routes, has sparked a search for alternate applications for sewage sludge. The conversion of sludge into adsorbents is one of the promising technologies give a more stable treatment of sludge. In a batch mode adsorption, adsorbent created by recycling sewage sludge was employed as a sustainable and low-cost material to remove iron and copper ions from simulated polluted aqueous solutions. A laboratory test was done to determine the influence of a variety of operational parameters on metals adsorption, including the acidic function (pH), agitation speed, adsorbent dosage, agitation period, and initial concentration at room temperature. The maximum removal efficiency was 98.91 and 98.22 % for Fe and Cu respectively at optimum factors: pH=4, agitation time =250 rpm, agitation time=180 min, adsorbent dose=1.5 g and initial concentration=50 (mg/l) for each metal .The isotherm system was studied using the three most popular models, Freundlich, Langmuir, and Temkin models. The results of the isotherm models showed the Langmuir model isotherm gave an obvious preference with the high correlation coefficient $R^2=0.933$ for Fe and $R^2= 0.927$ for Cu. In this way sewage sludge, which pollutes the environment and is costly to treat, may be recycled in a useful and economic way to achieve the lowest heavy metals concentration level.

keywords : sewage sludge ; iron , copper , adsorption , isotherms model.

1. Introduction

Increased human activity and rapid industrialization has led to the release of many hazardous substances into water resources that has put aquatic ecosystem and environment at risk [1]. Heavy metal ions are the most serious contributors of water pollution as they are persistent nature in water, highly toxic and non-degradable Unlike other pollutants, but have a tendency to bio accumulate and bio magnify through the food chain, producing potential human health risks and ecological. The pollution by heavy metals is a global issue, although severity and levels of pollution differs from place to place. At least 20 metals are classified as toxic with half of them emitted into the environment that poses great risks to human health [2]. many industries such as electroplating, dyes and dye intermediates, textiles, tanneries, oil refineries, electroplating, mining, smelters, and so forth, released heavy metals into water stream at higher concentrations beyond the limit of the prescribed value [3]. Heavy metals exhibit their toxicity even in low concentrations of about 1.0–10.0 mg/L [4]. Iron and copper are

particularly metals among at least 20 elements designated as hazardous released into the environment [2]. Copper were discharged from the copper mining activities, smelting, electroplating industries, and brass manufacture make copper-pollution more severe [5]. Copper Cu (II) ion plays an important role in the development of enzyme synthesis, tissues and bones for humans [6]. However, the excessive Cu(II) may cause serious health problems in brain, kidney and anemia[7]. Therefore Cu (II) ion concentration is restricted in water samples by the World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) and the maximum allowed concentration in drinking water is 1.3 mg/L and 2.0 mg/L respectively. The sources of iron in water bodies mainly pollution from mining, iron and steel industry, and metal erosion. Eye disorders such as retinitis, conjunctivitis , choroiditis, cancer and heart diseases are also some of the common health issues faced due to high concentration of iron in the water [8]. Apart from health related problems, several others issues of high iron content in water have been

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reported. The metal imparts an odor, metallic taste and red color to the water at elevated concentrations. It can also be at the origin of corrosion in drains sewers, due to the development of microorganisms and the ferrobacteries which leads to deterioration of water quality and reduction of pipe flow cross-section[9].The maximum amount allowed of Fe(II) in drinking water is 0.3 mg/l as WHO. It is clear from the above that the removal of copper and iron is a very important issue in the aquatic environment and the control of water pollution. A numbers of technologies are available to treat of heavy metals polluted wastewater. Traditional techniques are chemical precipitation, ion exchange, ultrafiltration, reverse osmosis, nanofiltration, coagulation, flocculation, flotation. However, these have some limitations such as low removal efficiency, high operational cost and sludge production. Comparatively, the adsorption method is more advantageous for low energy consumption, ease of operation and high removal efficiency [10]. Activated carbon is common used as adsorbents for the removal of different heavy Metals. However due to their high production costs, researchers shifted their focus to the use of biomass and waste such as peanut shell, garden grass , green algae , ground coffee, sunflower leaves , egg shells, almond shell , orange peel , for the removal of metals from aqueous solutions [11]. Sewage sludge is an one of example of solid waste and, simultaneously, is a major by-product of wastewater treatment plant operation [12]. Due to increasing quantities and carbonaceous nature of Sewage sludge conversion it to adsorbents might be a promising way, not merely to ecofriendly solve for the problems of secondary pollution that result from Improper disposal of sludge, but also to allow its reuse in water and wastewater treatment applications [13] In this study, we will examine the response of the adsorbents prepared from sewage sludge to remove copper and iron from manufactured aqueous solutions. To fulfil the study's goal, the investigation was carried out under a set of adsorption factors, including pH, agitation speed, contact duration, adsorbent dosage, and starting metal ion concentration, with respect to the effectiveness of metal removal. Isothermal models will also be tested on the removal process.

2. Materials and Experimental

2.1. Materials

2.1.1. Adsorbate preparation

Standard solutions of Fe and Cu with a concentration of (1000 mg/l) was made for copper using Copper(II) chloride dihydrate salt, whose chemical formula, colour, molecular weight, and CAS number are $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, green, 170.48

g/mole, and 10125-13-0 respectively, as shown in figure (1). for iron using ferric chloride salt, whose chemical formula, colour, molecular weight, and CAS number are FeCl_3 , brown, 162.20 g/mole, and 7705-08-0 respectively, as shown in figure (2).The preparation process was achieved via using (2.702 g of Cu salt) and (2.941 g of Fe salt) were dissolved in (1 L) of distilled water in laboratory temperature in volumetric flask and shake manually for 1 minute to ensure obtains perfect dissolving. The prepared solution used to prepare (50 mg/l) of Cu (II) and Fe(II) as stock solutions, it is the concentration used for all experiments, except for that completed to examine the influence of the initial concentration of a metal. The specific concentration of metals solutions and stock solutions was found out using atomic absorption spectrophotometer (EPA method 213.2) (AAS nova 400, German 2007) in science and technology ministry, environment and water researches directorate, water analysis Laboratory - Baghdad -Iraq.



Fig 1. Sample of commercial Copper chloride dihydrate salt.



Fig 2. Sample of commercial of ferric chloride salt.

2.1.2. Adsorbent preparation

2.1.2.1.. Source of adsorbent

In this study, the important part of sludge was the solid fraction. The required sludge was obtained from the Rustamiya wastewater treatment plant, third

expansion project - Baghdad, where samples were collected from drying basins at a depth of 5 cm, where the sludge is muddy and little moisture.

2.1.2.2. Preparation of adsorbent

The steps in the preparation of sewage sludge are as follows:

- Drying of sewage sludge collected under sun rays for 14 days at $(20 \pm 2^\circ\text{C})$ as shown in figure (3).
- Grinding the dried sludge by using a mill as shown in figure (4).
- Sieving the milled sludge with two (England-BS410) sieves of 1.18/0.6 mm respectively as shown in figure (5). The prepared sewage sludge as shown in figure (6) storing in sealed plastic container to prevent reabsorption of moisture.



Fig 3. Bed of collected sewage sludge under sun.



Fig. 4. Mill Machine



Fig 5. Sieves 1.18mm and 0.6mm



Fig 6. Prepared Sewage sludge (adsorbent).

Table 1 shows the physical, chemical tests of sewage sludge prepared.

Table 1. Physical and chemical features of sewage sludge collected

Physical property	value	Chemical property	Value
Actual ρ , kg cm^{-3}	1741.6	PH	7.5
Apparent ρ , kg cm^{-3}	609.9	Ash content %	12
Particle porosity	0.65	CECmeq/100g	51.15
Average particle diameter, mm	0.89		

These tests were conducted in laboratories of the Ministry of Industry and Minerals (Ibn Sina State Company).

2.2. Experimental:

The batch approach was used to measure the adsorption of Cu (II) and Fe(II) by prepared sewage sludge as an adsorbent. In batch adsorption tests, 100 ml of each metal stock solution which initial concentration of 50 mg/l was added to a 250 ml covered glass bottle containing 2 g of the prepared sludge. The number of bottles used for the two metals according to the values chosen for each of the variables studied. At first, the bottles were then put on a rotary shaker at 200 rpm for 3 hours to ensure proper mixing. At the end of the agitation period, the solutions are filtered using filtration paper (Whatman 150 mm filter paper). A sample of (20 ml) was withdrawn from each container for analysis to determine the concentration of metals using (ASS). Various parameters, including pH, agitation speed, adsorbent dose, contact time, and initial concentration, were tested. The removal percentage (R_E , %) and metal ion amount adsorbate onto unit weight of adsorbent (q_e) using the following equations (1) and (2), respectively [14]:

$$RE = \frac{C_i - C_o}{C_i} \times 100 \quad (1)$$

$$qe = \frac{V}{m} \times (C_{in} - C_f) \quad (2)$$

Where: **R**: is the percent removal of metals (II) ions (-), **q**: is the capacity of adsorption by sewage sludge (**mg/g**), **C_{in}** and **C_f**: initial and final concentrations of metals ions respectively (**mg/l**), **m**: mass of sewage sludge used for adsorption (**g**) and **V**: volume of solution (**l**).

4. Results and discussion

4.1 The effect of conditions on adsorption

4.1.1 Influence of acidic function (pH)

The acidic function (pH) has been identified as the most significant variable affecting not just site dissociation but also the chemistry of heavy metal solutions: furthermore, pH strongly influences hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, and precipitation; moreover, pH strongly influences heavy metal speciation and adsorption availability [15]. The effect of pH was examined at various PH values of the samples (1-6). The effect of pH was studied at these values because at pH more than 6 the metal ions tend to precipitate and accumulate by a combined sorption micro-precipitation mechanism.[16].The previously indicated pH values are determined by correcting the prepared solutions with 0.1 M (HCl, NaOH) for acidic and basic pH, as needed, using a portable digital PH metre (Hanna, HI98103, Romania). Other experimental variables include agitation speed, adsorbent dose, contact time, and starting concentration were held constant (200 rpm, 2g, 3 hours, 50mg/l) respectively. The experimental solution's temperature was within the range of room temperature (30-35 C). Figure (7) illustrates the relation between the solution's acidic function and the removal %. Cu (II) and Fe (II) adsorption was lower at very low pH (1-3), which is attributable to the fact that the adsorbent surface protonate and the adsorbent surface become positively charged, limiting metal ion access to the adsorbent surface due to repulsive interactions. Metal uptake increased as pH 4, with the maximum removal effectiveness of 80.90 and 76.05 percent for Fe and Cu respectively. At this pH, functional groups on the adsorbent surface deprotonate and the adsorbent surface becomes negatively charged (i.e., the number of OH⁻ groups increases), therefore metal ions can be attracted to the adsorbent in this region of pH [17]. Furthermore, increasing the pH leads a decrease of binding sites, reducing removal efficiency[18]. The optimum PH was set at 4 in subsequent trials. This result agreement with [19].

4.1.2. Influence of agitation speed

Effect of agitation speed was studied by varying the speeds (100,150,200,250,300) rpm. Other experimental variables include: PH, adsorbent dose,

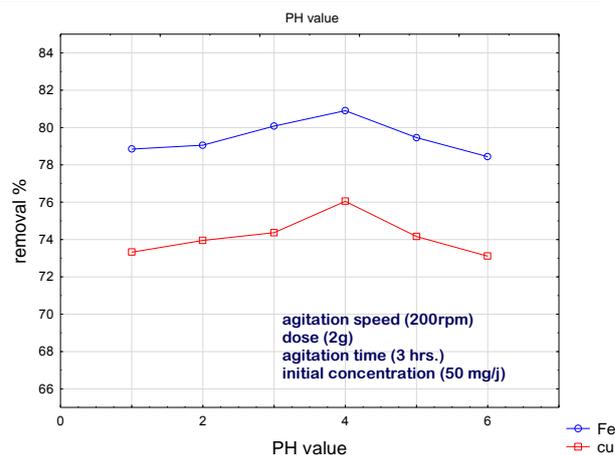


Fig 7. Influence of PH in %adsorption of metals.

contact time and initial concentration were kept fixed on (4, 2g, 3 hrs, 50 mg/l) respectively. The temperature of the experimental solution was within the range of room temperature (30-35 C). The efficiency value of metals increase from 62.42 to 95.27.12 % for Fe and from 58.66 to 91.12% for Cu as shown in figure (8). It is apparent that increasing the mixing speed increases the removal efficiency, also we note that the efficiency of removal between 250-300 rpm is equal, this no change means the solution was reach to equilibrium state. Duo to increasing the speed above 250 rpm no gives change in the percentage of removal therefore the optimum agitation speed was set at 250 rpm in subsequent experiments. The rise in efficiency is attributed to a rise in turbulence and, as a result, a reduction in the external mass transfer resistance thickness around the adsorbent particles as speed increases [20]. This results agreement with [21].

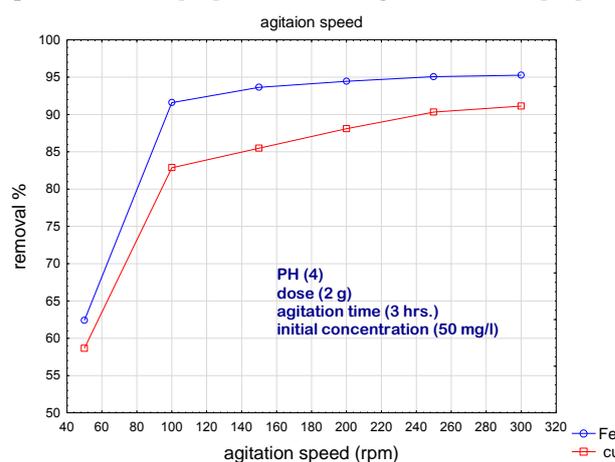


Fig 8. Influence of agitation speed in %adsorption of metals.

4.1.3. Influence of Adsorbent dose

Because of its impact on the amount of metal ions removed per unit mass of adsorbent, adsorbent dosage is a significant parameter in the adsorption of metal ions from aqueous solution [22]. Effect of adsorbent dose was studied by varying dose of the adsorbent (0.1-2) g/100 ml. Other experimental parameters for example PH, agitation speed, contact time and initial concentration were kept fixed on (4, 250 rpm, 3 hrs, 50 mg/l) respectively. The temperature of the experimental solution was within the range of room temperature (30-35 C). Figure (9) shown the percentage of adsorption of metals (II) was increased from 44.24 to 95.71 for Fe and 33.05 from to 90.55 for Fe. This finding can be attributed to the fact that when the adsorbent dosage increases, more and greater surface area becomes available, exposing more active sites for metal ion binding. After a value of 1.5 g, increasing the doses has no effect on the removal rate due to reaching a occupying all available sites on the surface of the adsorbent material, this is equilibrium state. This result is agreement with [23]. This result agreement with [24]. The best sludge dosage was fixed in subsequent experiments to be 1.5g.

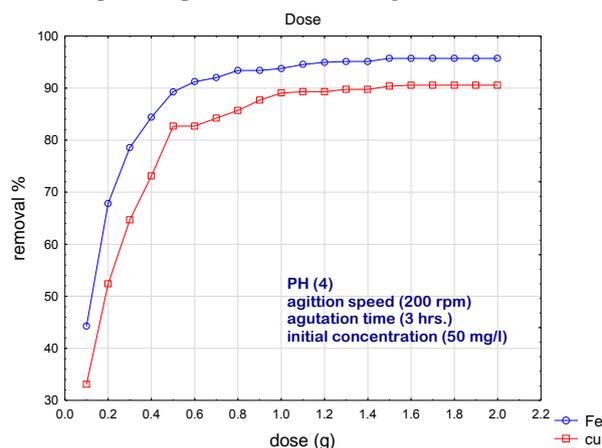


Fig 9. Influence of adsorbent dose in %adsorption of metals.

3.1.4 Influence of agitation time

The time-dependent function of metals adsorption was tested by changing the time from 15 to 240 minutes, Where 10 for each metal were prepared and placed in the shaker. In the first hour, four samples were taken every 15 min sample, in the second, third and fourth hours, samples were taken at a rate of every 30 min. Other experimental variables include: PH, adsorbent dose, agitation speed and initial concentration were kept fixed on (4, 1.5g, 250 rpm, 50 mg/l) respectively. The temperature of the experimental solution was within the range of room temperature (30-35 C). Figure (10) shows the adsorption movement of Cu and Fe consisting of two stages: a fast initial stage and a slower second stage. The first stage showed rapid adsorption during the first 120 min where the removal efficiency reaches to 65% for Cu and for Fe, after this time the rate of removal increased with increasing contact time, but slowly where the removal efficiency

to 82 % at 240 min. In the beginning, a significant number of active places on the adsorbent are available, the metal ions occupied selectively the active sites on the adsorbents. As the sites become exhausted, the uptake rate depends on the rate adsorbate transportation from the outside to inside the adsorbent particles [25].this result agreement with [26]. To save time, and because the removal difference between 180 and 210 minutes is simple, It is possible to choose 180 minute (3 hrs.) As a best agitation time in the next experiments.

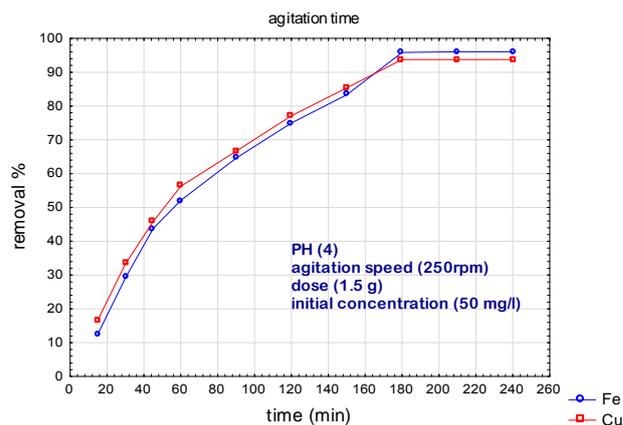


Fig 10. Influence of agitation time in %adsorption of metals.

4.1.5 Influence of Initial metal ion concentration

Within a range of (50, 100, 150,200) mg/l, the influence of initial concentration on the treatment process efficacy of aqueous contaminated with Fe and Cu was investigated with Other experimental variables include: PH, adsorbent dose, contact time and agitation speed were kept fixed on (4, 1.5g, 4 hrs., 250 rpm) respectively. The temperature of the experimental solution was within the range of room temperature (30-35 C). The efficiency values declines from 98.19 to 77.41 % for Fe and from 98.22 to 76.34 % for Cu as the initial concentration increased from 50 to 150 mg/L as shown in figure (11). This is because the particles of adsorbent sample lacks binding sites for metal ion adsorption at higher concentrations. The following could be used to explain the influence of initial metal concentration: Metal ion adsorption involves more energy binding sites when the metal ion/adsorbent ratio is low. The greater energy active sites are saturated as the metal ion/adsorbent ratio increases (i.e., at greater initial concentration), and adsorption commences on minor energy binding sites, bring about a drop in adsorption efficiency [27]. this result agreement with [28].The best initial concentration was chosen as 50 mg/l in all experiments.

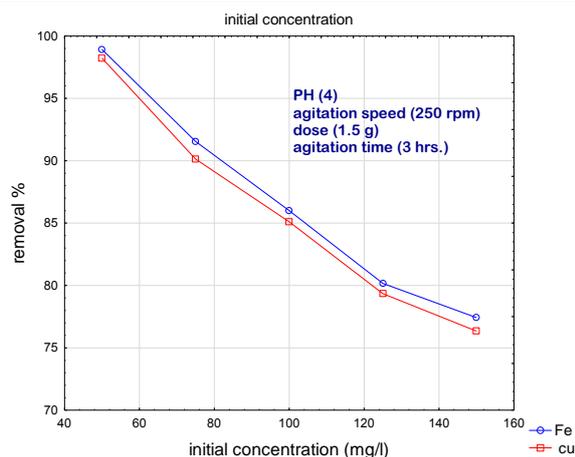


Fig 11. Influence of Initial concentration in % adsorption of metals.

4.2. Equilibrium Isotherm Study

Adsorption isotherms describe the concentration dependence of extent of adsorption at constant temperature. These isotherms also describe the nature of binding forces between adsorbate and adsorbent such as physical or chemical forces [29]. In the present study, three equilibrium models are analysed to investigate the suitable adsorption isotherm.

4.2.1 The Langmuir model

The Langmuir model (Langmuir, 1918) represents one of the first theoretical treatments of nonlinear sorption and suggests that the adsorption process occurs on a monolayer surface, that the adsorption sites are identical and have a limited number, that the maximum adsorption occurs by saturating the primary layer with solute ions, and it also assumes that the adsorption layer is only one part thick and that the energy distribution on the adsorption surface is uniform. Equation 3 represents the mathematical relationship of the Langmuir isotherm model [30]. The indispensable characteristic of this model is the ability to determine the type of adsorption whether it is preferred or not by finding the separation factor R_L , which can be calculated from the following Equation 4.

$$q_e = \frac{q_{max} \cdot K_L C_e}{1 + K_L C_e} \dots (3)$$

$$R_L = \frac{1}{1 + K_L C_i} \dots (4)$$

Where: q_e : adsorption capacity at the equilibrium (mg/g), C_e : adsorbed concentration at the equilibrium (mg/l) C_i : initial concentration of adsorbate (mg/l), K_L : Langmuir constant, expressed the binding sites (l/mg) and q_{max} : maximum adsorption capacity (mg/g).

The value of separation factor gives a good indication about the type of adsorption, therefore if the value of $R_L > 1$, then the adsorption is unfavorable while the adsorption is linear if the value of $R_L = 1$. The adsorption is favourable type if $1 > R_L > 0$ and when $R_L = 0$ the adsorption is become irreversible.

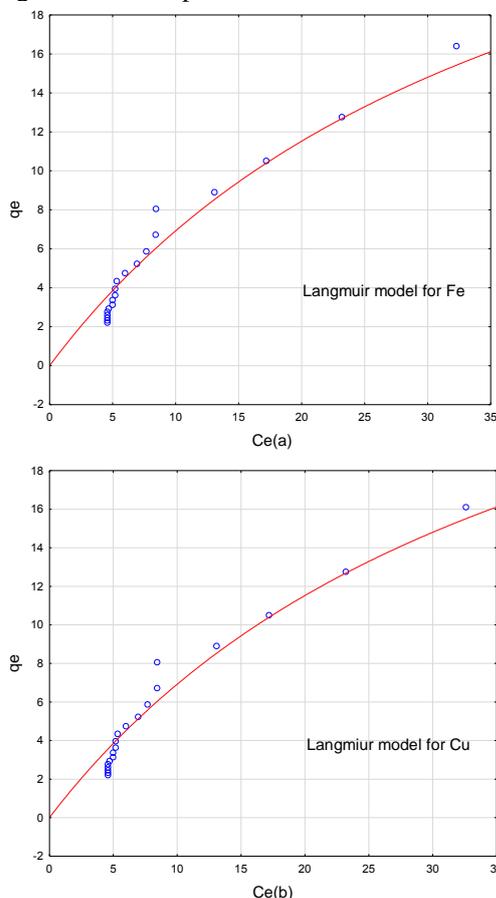


Fig 12. Langmuir isotherm model (A) for Fe (b) for Cu.

4.2.2 The Freundlich model

The Freundlich isotherm (Freundlich, 1906) is an oldest nonlinear adsorption model. This model assumes that the adsorbent surface consists of several heterogeneous layers, and that the adsorption sites are unsaturated and located at varying levels of energy, so the underlying energy changes are not uniform [30]. The isotherm equation for Freundlich can be represented as shown in Equation 5.

$$q_e = K_F C_e^{\frac{1}{n}} \dots (5)$$

Where: K_F : Freundlich constant represent the measured capacity of adsorption [(mg/g).(l/mg)^{1/n}], n : intensity of adsorption (-).

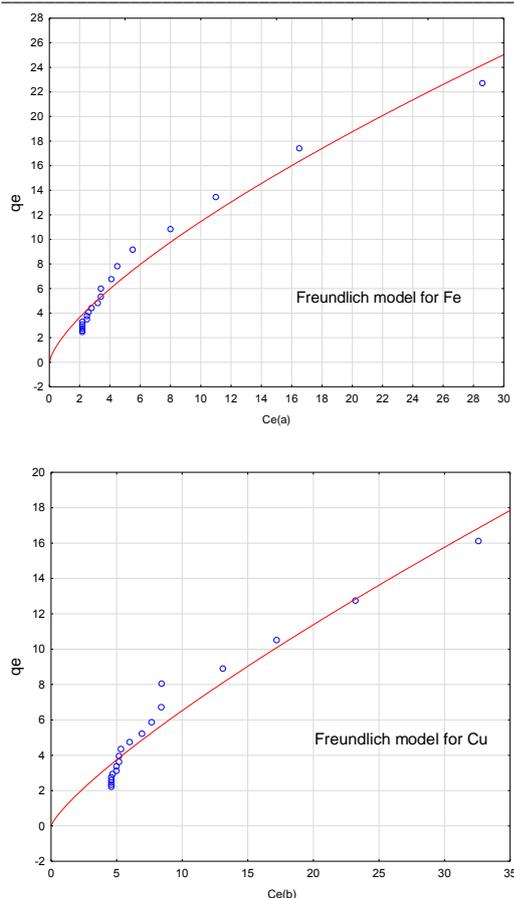


Fig 13. Freundlich isotherm model (A) for Fe (b) for Cu.

4.2.3 The Temkin model

Temkin isotherm model (Temkin & Pyzhev, 1940) evaluates that the adsorption heat of all molecules decreases linearly with the increase in coverage of the adsorbent surface [31]. The general formula for isotherm can be described by Equation 6, while the linear form of Temkin isotherm model is shown in Equation 8.

$$q_e = \frac{RT}{b} \ln K_T C_e \dots (6)$$

$$B = \frac{RT}{b} \dots (7)$$

Where: q_e : adsorption capacity at the equilibrium (mg/g), R: Universal gas constant (8.3144 J/mol.K), C_e : adsorbed concentration at the equilibrium (mg/l), T: Absolute temperature (K), K_T : Temkin isotherm equilibrium binding constant (L/g), b: Temkin isotherm constant related to adsorption heat (J/mol), B: Constant.

Figures (12-14) show the isotherm of Langmuir, Freundlich and Temkin respectively, while Table 2 shows the values of the constants of these isotherm models. It is clear that the adsorption of the heavy metals ions using sewage sludge as adsorbent is better subjected to the Langmuir isotherm than other models.

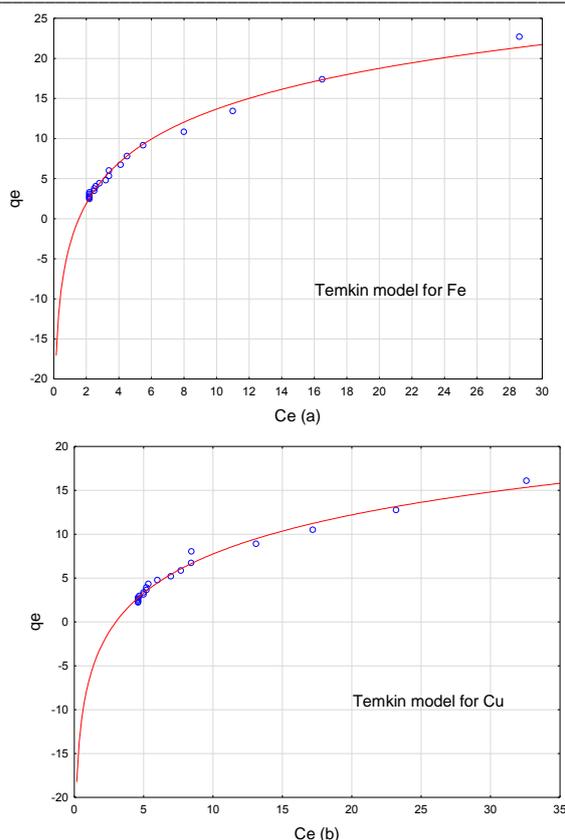


Fig 14. Temkin isotherm model (A) for Fe (b) for Cu.

Table 2. Constant values of Langmuir, Freundlich and Temkin isotherms for absorption of Fe and Cu.

	Langmuir	Freundlich	Temkin
Fe	q_{max}	34.3	K_F 2.22
	K_L	0.025	$1/n$ 0.712
	R^2	0.933	R^2 0.925
			b 0.16
			R^2 0.925
Cu	q_{max}	34.37	K_F 1.025
	K_L	0.025	$1/n$ 0.803
	R^2	0.927	R^2 0.927
			b 0.467
			R^2 0.927

due to the high correlation coefficient $R^2 = (0.9339, 0.927)$ for Fe and Cu perceptively. This means that the adsorption occurs on a monolayer surface with a limited number of identical sites, and that the adsorption process is preferred according to the value of the separation factor $R_L = 0.44$ for two metals. While, the Freundlich and Temkin isotherm models was the least closely related to the obtained results, as its coefficient of correlation $R^2 = (0.925, 0.927)$ to Fe and Cu perceptively for the two models.

5. Conclusion

Prepared sewage sludge showed effective performance on Fe (II) and Cu (II) adsorption. The pH has the most influence on the adsorption of these metals ions from aqueous solutions. The percentage elimination of metals ions by prepared adsorbent was increased with increasing agitation speed, dose of adsorbent, and agitation time up to the state of equilibrium while it was increased by increasing PH reaches to 4 then started decreasing but this removal percentage decreased with increasing of ion metal concentration. The maximum removal efficiency was 98.91 for iron and 98.22 for copper % at optimum factors pH=4, agitation time =250 rpm, adsorbent dose=1.5, agitation time=3 hours, and initial concentration=50 (mg/l). Also, Langmuir had the best isotherm model, between freundlich and Temkin models, because it gave the highest correlation coefficient. It is clear from this study, which produced adsorbents from recycling sewage sludge, found an effective and sustainable mutual solution to a dual problem represented by sewage sludge disposal and heavy metals removal.

6. Acknowledgments

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7. Conflict of interest

The authors declare that this article does not cause a conflict of interest.

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