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Zinc adsorption from aqueous solutions using disposal sheep manure waste (SMW)

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Abstract

Available and disposal low price adsorbent (i.e. sheep manure waste (SMW)) was used for adsorption studies of Zn^{2+} from aqueous solutions. The adsorption experiments were performed under various conditions such as different adsorbent particle size (0.064–1.0 mm), Zn^{2+} initial concentration (20–150 ppm), shaking time (1–300 min), pH (1–6), and adsorbent concentration (2–30 g/l).

About 10 g/l of SMW (0.064 mm in diameter) was found to be enough to remove 93.3% of 100 ppm Zn^{2+} from 50 ml aqueous solution after 1 h. The optimum pH value was found to be at 4.

The kinetic curves show very clearly the selectivity of the SMW for Zn^{2+}. The uptake obeys both the Freundlich and Langmuir isotherms. The applicability of Lagergren kinetic model has also been investigated.

Activated carbon was also prepared by heating a grinded SMW at (105–800°C) and the adsorption capacity is investigated. About 10 g/l of activated (heated to 600°C) SMW was enough to remove 98.8% of 100 ppm Zn^{2+} from 50 ml aqueous solution after 5 h.

Keywords: Sheep manure waste (SMW); Aqueous solution; Adsorption; Heavy metal

1. Introduction

It is well known that heavy metals such as lead, cadmium and zinc are very toxic elements and their discharge into receiving water causes detrimental effects on human health and environment. Elevated levels of zinc may come from a variety of sources, such as effluents from manufacturing of batteries, pharmaceuticals and agricultural chemicals. Other sources of metallic zinc traces in drinking water are water treatment processes and pickup of metallic ions during storage distribution. These toxic metals can cause accumulative poisoning, cancer, brain damage, etc., when they are found above the tolerance levels [1,2]. According to some surveys from the public health services of different countries, significant numbers of people have been exposed to the hazards of excess metals in the municipal water supplies [3]. Therefore, different methods have been used to remove heavy metals from aqueous solutions such as chemical precipitation, membrane processes, ion exchange resins, activated carbon adsorption, etc. [4].

Adsorption is a mass transfer operation, which involves contact of solids with either liquids or gases followed by mass transfer from the fluid phase to the solid phase. The high cost of activated carbon has inspired search for the development of activated carbon from cheaper and readily available materials. Some of the low-cost adsorbents already reported for the removal of heavy metals are waste tea leaves for the removal of Pb^{2+}, Cd^{2+}, and Zn^{2+} [5], agricultural by products such as almond shells, olive stones and peach stones for the removal of Zn^{2+}, Cd^{2+} and Cu^{2+} [6], denatured rhizopus arrhizus biomass for the removal of La^{3+} and Zn^{2+} [7], sediments of rivers for the removal of Cd^{2+}, Zn^{2+}, Cu^{2+}, and Pb^{2+} [8], rice husk [9] and peanut hull [10] for the removal of Hg^{2+}.

In this work, the adsorption of Zn^{2+} using sheep manure waste (SMW) was investigated. The effect of adsorbent particle size, adsorbent concentration, pH of solution, initial concentration of Zn^{2+}, shaking time and heating the adsorbent on the adsorption capacity were investigated.

2. Materials and methods

2.1. Adsorbent

The adsorbent used in this work was prepared from SMW collected from one specific farm in a village called Shatana

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Table 1
Characteristics of fresh and activated SMW

Parameter	Fresh SMW	Activated (heated) SMW (activation temperature = 600°C)
Apparent density (g/ml)	0.588	0.667
Ash content (%)	31.6	84.6
Iodine number (%)	948.2	1031.9
Moisture (%)	4.7	0.3
Crude protein (%)	15.4	1.26
NDF (%)	36.92	21.04
Average particle size (mm)	0.064	0.0225
pH	7.24	12.06
Pb^{2+} (ppm)	–	–
Cr^{2+} (ppm)	–	–
Cd^{2+} (ppm)	–	–
Fe^{2+} (ppm)	0.29	0.01
Zn^{2+} (ppm)	0.05	–
Mn^{2+} (ppm)	0.02	–
Cu^{2+} (ppm)	0.04	0.06
Ni^{2+} (ppm)	–	–

in the north of Jordan. This is because the capacity of the adsorbent depends on its chemical composition, which can have a very wide range of properties depending upon source and pretreatment. The SMW was washed, dried, ground and sieved to a particle size ranging from 0.064 to 1.0 mm. After that it was dried for 2 h at 105°C. Most of the experiments were carried out on the dried (or fresh) SMW without any further activation. Some were carried out on an activated (or heated) SMW by heating it gradually from room temperature to the activation temperatures (105–800°C) for 1 h and keeping it at the required activation temperature for 2 h.

The characteristics of both fresh (dried at 105°C) and activated (heated to 600°C) SMW are shown in Table 1. The apparent density, and iodine number were determined according to the ASTM methods. The ash contents were obtained by burning the sample in air at 973 K. The pH values were measured in a suspension of 1 g of the sample in 20 cm^3 of CO_2-free distilled water, after a contact time of 48 h at 298 K. The neutral detergent fiber (NDF), which includes insoluble protein, cellulose, lignin and bound nitrogen, the moisture contents, and crude proteins were determined according to the AOAC methods [11].

2.2. Experimental procedure

Adsorption studies on both fresh and activated SMW were carried out using stock wastewater solutions of 1000 ppm Zn^{2+} prepared from hydrated zinc sulfate ($ZnSO_4 \cdot 7H_2O$). This solution was diluted as required to obtain standard solutions containing 20–150 ppm Zn^{2+}. All experiments were carried out using reagent bottles of 100 ml capacity containing 50 ml solutions at different concentrations adjusted to a desired pH using phosphoric acid or sodium hydroxide solutions with 0.1–1 g of SMW. The bottles were shaken for a predetermined periods at room temperature (25 ± 1°C) in a reciprocating shaker. The solids were separated using a centrifuge and the supernatant solutions were analyzed for Zn^{2+} by an atomic absorption spectrophotometer. Metal solutions without adsorbent were analyzed before and after filtration. Neither precipitate nor metal ions adsorbed to the wall of the flasks were observed with the tested metals under the experimental conditions. All the experiments were duplicated to confirm the reproducibility of the experimental effects.

3. Results and discussion

3.1. Effect of particle size

The effect of different adsorbent particle sizes (0.064, 0.212, 0.5, 0.71, and 1 mm) on percentage removal of Zn^{2+} is investigated.

Fig. 1 reveals that the adsorptions of Zn^{2+} on SMW decreases from 96 to 82% with the increased particle sizes

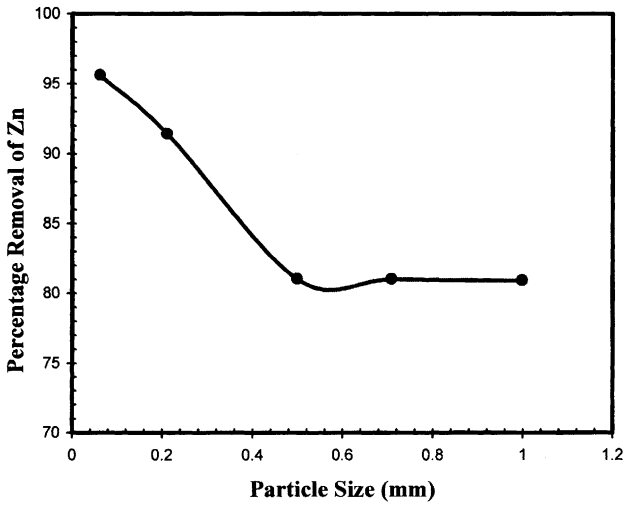

Fig. 1. Effect of particle sizes on percentage removal of Zn^{2+}. Shaking time: 5 h; pH 4; SMW concentration: 10 g/l and Zn^{2+} concentration: 20 ppm.

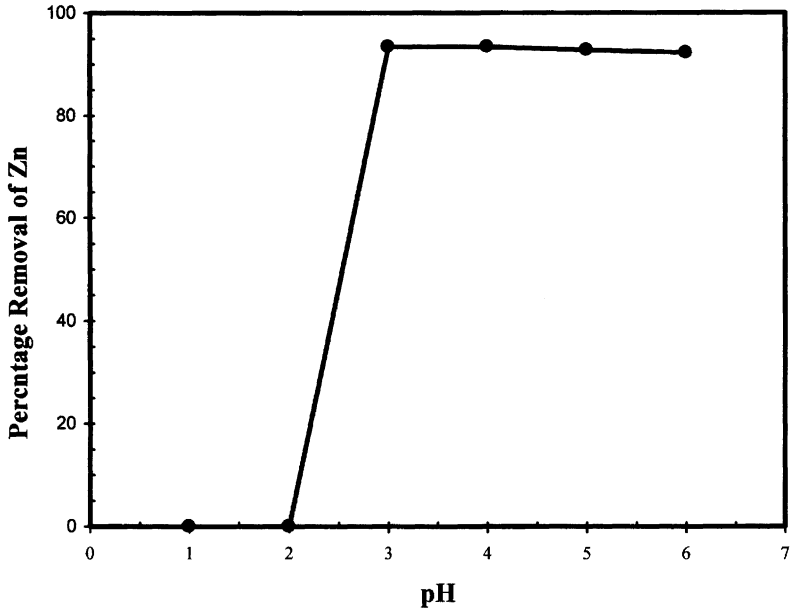

Fig. 2. Effect of pH on percentage removal of Zn^{2+}. Particle size: 0.064 mm; SMW concentration: 10 g/l; shaking time: 5 h and Zn^{2+} concentration: 20 ppm.

from 0.064 to 1 mm. It is evident from the plot that the percentage removal of Zn^{2+} was constant at particle size of 0.5 mm and larger. This means that there is a possibility of the presence of some internal blocking of pores due to the large size of the Zn^{2+} ions and therefore they can only penetrate a certain distance inside the particle without reaching the available internal sites. The smallest size obtained was 0.064 mm due to the available grinder constrictions. It is well known that decreasing the average particle size of the adsorbent increases the surface area, which in turn increases the adsorption capacity. This is evident in Fig. 1 for particle sizes between 0.1 and 0.5 mm.

3.2. Effect of pH

Fig. 2 illustrates the effect of pH on percentage removal of Zn^{2+} for zinc concentration of 20 ppm, waste concentration 10 g/l, particle size of 0.064 mm and shaking time of 5 h. It is evident that at pH values below 2.0, the percentage removal of Zn^{2+} is negligible because of the electrostatic force of repulsion between adsorbent SMW and adsorbate Zn^{2+}. At this very low pH, there is a possibility of Zn^{2+} precipitation on the carbon surface by nucleation. Between pH 2 and 3, the percentage removal increases sharply then stays constant for pH values larger than 3.0. This might be due to the fact that metal ions start replacing hydrogen ions from the carbon surface.

3.3. Effect of adsorbent concentration

Fig. 3 shows the percentage removal of Zn^{2+} at a concentration of 100 ppm as a function of SMW concentration for a particle size of 0.064 mm. It is evident that the percentage removal of Zn^{2+} increases from 27.12 to 95.25% with increasing the SMW concentration from 2.0 to 30.0 g/l. The best economical adsorbent concentration was chosen to be 10 g/l.

3.4. Effect of heating

The variation of percentage removal of Zn^{2+} with heating temperature of SMW (i.e. physical activation) is shown in Fig. 4. It can be seen that as the SMW is heated from 105 to 800°C, the percentage removal of Zn^{2+} is increased from 93 to 99.8%, respectively. This may be attributed to the fact that

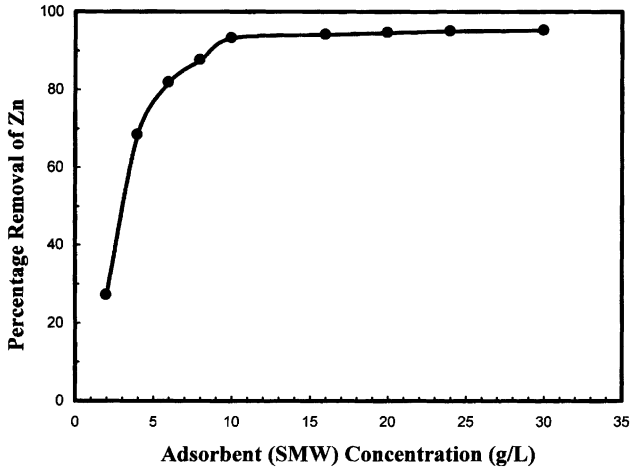

Fig. 3. Effect of adsorbent SMW concentration on percentage removal of Zn^{2+}. Shaking time: 5 h; particle size: 0.064 mm; pH 4 and Zn^{2+} concentration: 100 ppm.

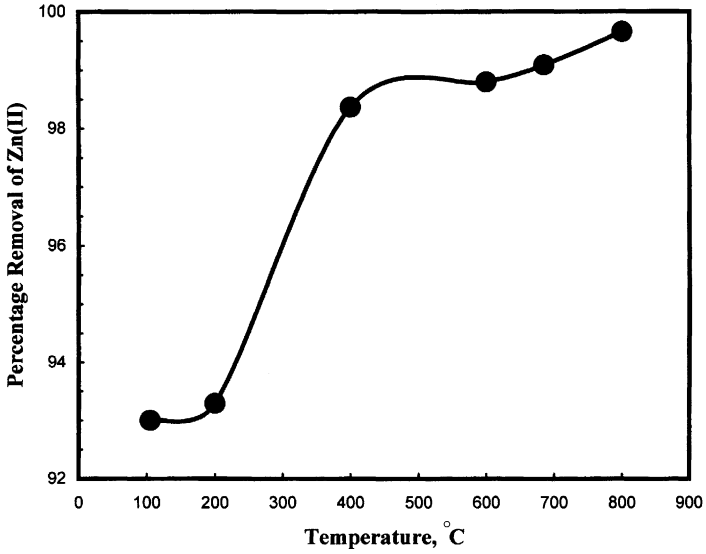

Fig. 4. Effect of heating the adsorbent SMW on percentage removal of Zn^{2+}. Particle size: 0.064 mm; pH 4; SMW concentration: 10 g/l and shaking time: 5 h.

heating of the SMW makes it more active by increasing the number of active sites on the SMW surface. Reducing the water, crude protein, cellulose, lignin and other impurities from the SMW created these active sites. In addition to that heating, the fresh SMW that has an average particle size of 64.4 μm resulted in an activated SMW with an average particle size of 22.4 μm as shown in Table 2. This means that heating the SMW increases the surface area of the adsorbent, which increases the adsorption capacity. Another important factor is the higher pH value of the activated (heated) SMW, which indicates that this adsorbent shows a negative charge potential, and will have a higher tendency to adsorb cations such as Zn^{2+}.

3.5. Effect of shaking time and initial concentration

Fig. 5 presents the effect of shaking time on the percentage removal of Zn^{2+} by the prepared fresh carbon from SMW. The percentage removal increases with time and attains equilibrium at 60 min for initial concentrations of 20, 50, 80, 100 and 150 ppm. At any constant shaking time, the percentage removal of Zn^{2+} decreases as the initial concentration of Zn^{2+} increases. The effect of initial concentration of Zn^{2+} on the equilibrium time is almost negligible. There was no evidence of any solid breakup during contact; therefore, there is no possible effect on adsorbent structure during shaking.

Table 2
Particle size distributions for fresh and activated SMW

Fresh SMW		Activated (heated) SMW (activation temperature = 600°C)	
Screen size (μm)	Remaining (%)	Screen size (μm)	Remaining (%)
1	98.9	1	98.2
1.5	98.6	1.5	97.7
2	97.6	2	96.3
3	96.6	3	94.8
4	95.5	4	93.1
6	94.0	6	89.0
8	92.2	8	84.5
12	89.2	12	74.4
16	85.0	16	63.5
24	79.8	24	46.9
32	74.0	32	33.5
48	61.8	48	14.8
64	50.2	64	5.8
96	25.1	96	0.8
128	2.6	128	0.2
192	0.0	192	0.0

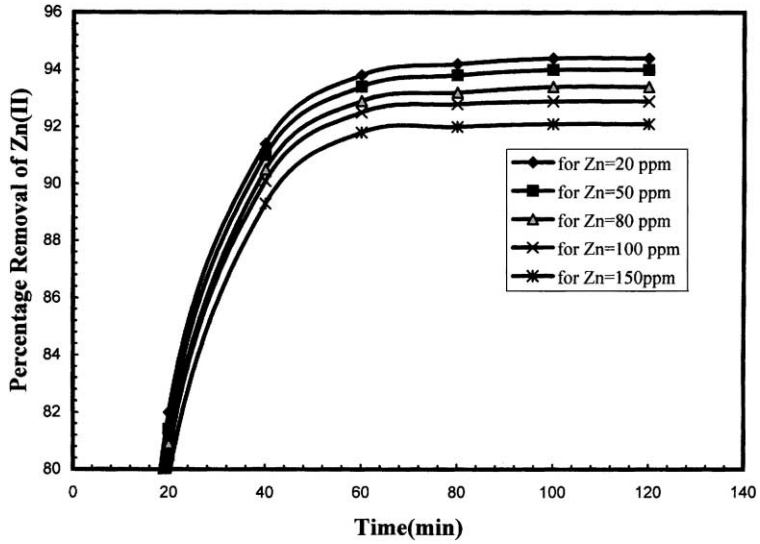

Fig. 5. Effect of shaking time on percentage removal of Zn^{2+} for different initial Zn^{2+} concentrations 20, 50, 80, 100, and 150 ppm. Particle size: 0.064 mm and pH 4.

3.6. Adsorption isotherms

Using Langmuir equation

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (1)$$

where C_e is the equilibrium concentration (mg/l), q_e the amount adsorbed at equilibrium (mg/g), Q_o the Langmuir constant related to adsorption capacity and b the Langmuir constant related to adsorption energy. Values of C_e and q_e are presented in Table 3. Fig. 6 shows that the adsorption isotherms fit well with Langmuir isotherm model. Langmuir constants were determined from Fig. 6 and found to be $Q_o = 40.32$ mg Zn^{2+}/g SMW and $b = 0.42$ l/mg Zn^{2+}.

The dimensionless constant separation factor or equilibrium parameter, R_L [12] is given by

$$R_L = \frac{1}{1 + bC_0} \quad (2)$$

where b is the Langmuir constant and C_0 the initial concentration of Zn^{2+} was also used. The values of R_L were found to be 0.106, 0.0454, 0.0289, 0.0232, and 0.0156 for initial concentrations 20, 50, 80, 100 and 150 ppm, respectively. This indicates favorable adsorption of Zn^{2+} on SMW

Table 3
Values of equilibrium concentration, C_e and amount adsorbed at equilibrium, q_e

C_e (mg/l)	q_e (mg/g)
1.12	1.89
3.00	4.70
5.28	7.47
7.10	9.29
11.85	13.82

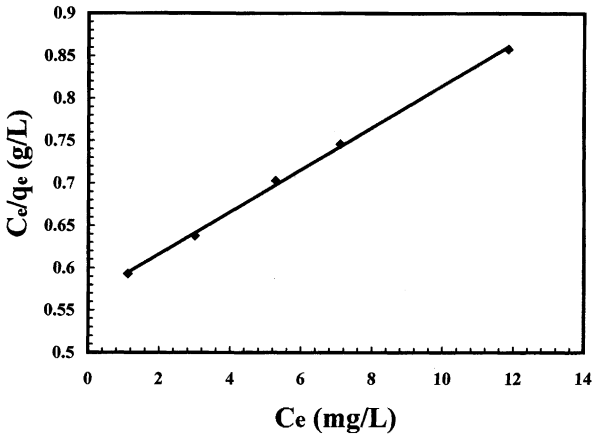

Fig. 6. Langmuir plot for the adsorption of Zn^{2+} on SMW.

because all R_L values between 0 and 1. The correlation coefficient for the linear regression was found to be 0.9986.

To explain the observed phenomena more clearly, the Freundlich isotherm model was also used

$$\log\left(\frac{x}{m}\right) = \log k_f + \left(\frac{1}{n}\right)\log C_e \quad (3)$$

where x is the amount adsorbed (mg/l), m the weight of the adsorbent (g/l), k_f a measure of adsorption capacity, n a measure of adsorption intensity and C_e the equilibrium concentration (mg/l). Fig. 7 shows that adsorption of Zn^{2+} on SMW obeys Freundlich isotherm model and the constant k_f and n were determined as 1.727 and 1.18063, respectively. The values of n were between 1 and 10, which means favorable adsorption of Zn^{2+} on SMW. The correlation coefficient for the linear regression was found to be 0.9999.

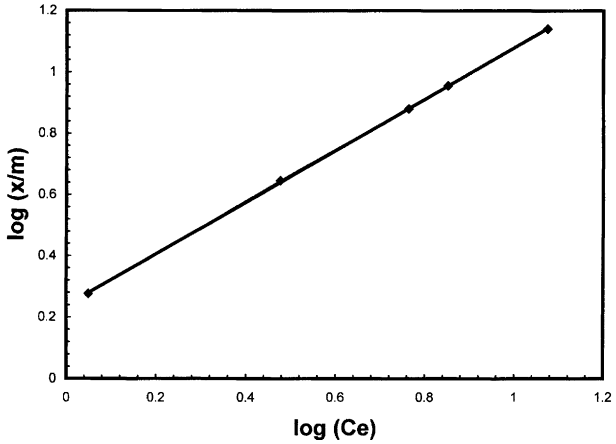

Fig. 7. Freundlich plot for the adsorption of Zn^{2+} on SMW.

3.7. Adsorption kinetics

The kinetics of Zn^{2+} adsorption on SMW follow the first-order rate expression given by Lagergren [13]

$$\log(q_e - q) = \log q_e - \left(\frac{k_{ad}}{2.303}\right) \times t \quad (4)$$

where q is the amount of Zn^{2+} adsorbed at time t (mg/g), q_e the amount adsorbed at equilibrium time (mg/g), and k_{ad} the rate constant of adsorption. Linear plots of $\log(q_e - q)$ versus t show the applicability of the above equation for SMW as shown in Fig. 8. The k_{ad} values from the slopes of the plots for SMW are 0.06761, 0.06761, 0.06842, 0.07491, and 0.07654 min^{-1} for the initial Zn^{2+} concentration of 20, 50, 80, 100 and 150 ppm, respectively. The rate constant for intraparticle transport, k_d, was calculated using the equation of Weber and Morris [14]

$$k_d = \frac{q}{t^{1/2}} \quad (5)$$

where q is the amount of Zn^{2+} adsorbed at time t (mg/g). The k_d values calculated from the plots of q versus $t^{1/2}$ (Fig. 9) were found to be 0.035, 0.088, 0.139, 0.172, and 0.257 mg/g $min^{1/2}$ for the initial Zn^{2+} concentration values of 20, 50, 80, 100 and 150 ppm, respectively. The plots of q versus $t^{1/2}$ show linear variation for a certain initial fraction

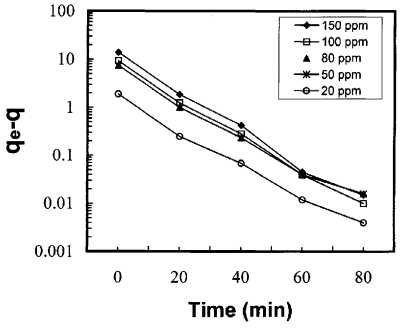

Fig. 8. Lagergren plots for the adsorption of Zn^{2+} on SMW.

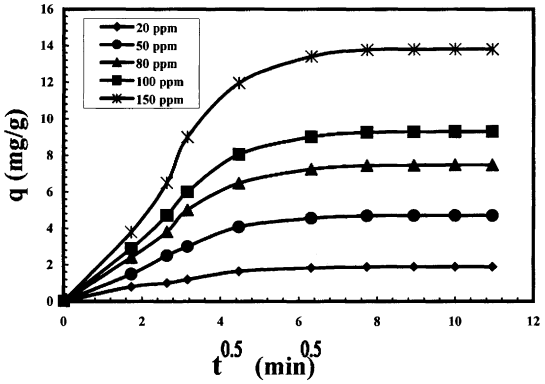

Fig. 9. Plots for intraparticle diffusion for the adsorption of Zn^{2+} on SMW.

of adsorption. This implies that in the initial stage of adsorption, Zn^{2+} removal is governed by diffusional transport.

4. Conclusion

This work showed clearly that the SMW is an excellent adsorbent for Zn^{2+} from aqueous solutions. About 10 g/l of SMW was enough to remove about 93.3% of the initial Zn^{2+} concentration (100 ppm and pH 4) within shaking time of 1 h. The experimental data fit very well with Langmuir, Freundlich and Lagergren models. The contact time necessary for maximum adsorption was not significantly influenced by the initial concentration of Zn^{2+}. Heating the SMW to 600°C reduces the average particle size from 64.4 to 22.4 μm, which means an increase in the surface area and adsorption capacity.

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