Adsorption of Zn (II) on *Acacia Tortilis* Leaves Treated with Sulfuric Acid: kinetic studies

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***Abstract*--**In the present work, the potential use of Acacia tortilis leaves to remove Zn(II) from water media was evaluated. In case to activate the surface of Acacia tortilis leaves, some acids such as sulfuric, phosphoric and hydrochloric of 0.1 meq/ml were tried. High adsorption capacity was obtained when sulfuric acid was used. Kinetic data was measured in batch condition. The effect of some parameters such as: initial pH, adsorbent dosage and contact time on the adsorption of Zn(II) has been studied. Zn(II) adsorption was initial pH, adsorbent dosage and time contact dependent. It has been found that the adsorption capacity of Zn(II) on Acacia tortilis leaves increased as initial pH increased and rich equilibrium at pH 4. On the other hand, the adsorption capacity of Zn(II) decreased as adsorbent dosage increased. The maximum adsorption capacity of Zn(II) was found to occur after two hours. Three kinetic models including fist order, pseudo second order and intra particle diffusion were selected to follow the adsorption process. The process follows a pseudo second order. The following parameters used in this research are constant: contact temperature, $25^{o}C\pm1$; stirring speed, 400 rpm ; Zn(II) concentration, 400 mg/l and adsorbent size, less than 90 µm.

***Keywords*--**Acacia Tortilis, First Order, Pseudo Second Order, Intra Particle Diffusion

I. Introduction

ZN(II) may be found in wastewater discharges from acid mine drainage, galvanizing plants, natural ores and from municipal wastewater treatment plant discharges. Zn(II) travels through the food chain via bioaccumulation. Hence, there is significant interest regarding Zn(II) removal from wastewater streams [1]. The World Health Organization (WHO) recommends a maximum acceptable concentration of Zn(II) of 3 mg/l in drinking water [2]. Hence, the presence of Zn(II) in water environment is one of the most serious worldwide environmental problems [3]. Conventional methods for removing Zn(II) include electrodialysis, precipitation, solvent extraction, membrane separation and ion exchange have been reported in literature [2]. Since all these methods have various disadvantages, specifically, high operating cost, incomplete removal, or the high energy consumption. It is therefore a low cost techniques is necessary.

A sorption processes using agricultural materials can be used for waste water treatment because they are cheap, simple and free sludge [4].

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In this regard, a wide variety of dead biomass such as sawdust, peanut shell and tree fern are being considered as adsorbents of heavy metals for treatment of industrial and domestic wastewaters as well as natural waters, including drinking water [5].

In this work, the sorption of Zn(II) from water media by activated *Acacia tortilis* leaves with sulfuric acid was investigated. Influence of several parameters such as: initial pH, adsorbent dosage and contact time on the adsorption of Zn(II) has been studied. Three simplified kinetic models including fist order, pseudo second order and intra particle diffusion were selected to follow the adsorption process.

II. Experimental Methods

2.1 Reagents, Instruments And Solutions

The following chemicals were used for the kinetic studies for adsorption of Zn(II) onto the surface of Acacia tortilis leaves. Zinc acetate, hexa methylene tetra amine (EDTA), xylenol orange were reagent grade chemicals and they obtained from Merck, Germany. Sulfuric acid, phosphoric acid, hydrochloric acid, acetic acid and ammonium hydroxide were also reagent grade chemicals and they procured from BDH, England.

The oven of Naber model was obtained from Germany. The sensitive balance was obtained from Mettler, China. The pH meter of 3505 model was procured from Jenway, England. The shaker water bath was obtained from Clifon, Italy.

Zinc stock solution of 1000 mg/l was prepared by dissolving the required amount of zinc acetate in double distilled water. Working solutions were prepared by dilution of stock solution.

2.2 Adsorption Preparation

The *Acacia tortilis* leaves was collected from sebha area at south of Libya, washed with double distil water, dried at room temperature for one day and dried in oven at 95oC for one hour. In order to activate the surface of adsorbent, three selected acids such as sulfuric, phosphoric and hydrochloric acid were tried. One gram of dried *Acacia tortilis* leaves was added to 20 ml of each acid (0.1 meq/ml) in a 50 ml stoppered glass bottles. The mixture in each bottle was mixed using shaker water bath at 60 ^{o}C, filtered, dried in oven at 95 ^{o}C then stored in a plastic containers for farther use. The optimum conditions to adsorb Zn(II) onto *Acacia tortilis* leaves treated with mentioned acids as follows: initial pH, 4; adsorbent dosage, 0.02 g; Zn(II) concentration, 400 mg/l; stirring speed, 400 rpm and contact time, 2 hours.

2.3 Batch Adsorption Studies

Generally, the effects of initial pH, adsorbent dosage and contact time on adsorption of Zn(II) were performed in conical flasks by stirring a certain amount of activated *Acacia tortilis* leaves with 100 ml of Zn(II) solutions. The pH of solutions was varied from 2 to 6 and contact time was varied from 15 to 150 minute. The concentration of Zn(II) solution were determined by titration with ethylene diamin tetra acetic acid using xylenol orange as indicator. The constant parameters used in this research as follows: contact temperature, 25oC±1; stirring speed, 400 rpm ; Zn(II) concentration, 400 mg/l and adsorbent size, less than 90 µm.

2.4 Zn(II) removal

The amount of Zn(II) adsorbed, q_e (mg/g) was determined by using the following expression [1]:

$$q_e = \frac{(C_o - C_{eq})V}{W} \quad (1)$$

Where C_o and C_{eq} are Zn(II) concentration (mg/l) before and after adsorption, respectively, V is the volume of Zn(II) solution (l), W is the weight of *Acacia tortilis* leaves (g).

III. Results and Discussion

3.1 Activation of Acacia Tortilis leaves

Table 1 shows the adsorption capacity of Zn(II) by the use of sulfuric, phosphoric and hydrochloric acid. It can be observed that, high adsorption capacity of Zn(II) was obtained when sulfuric acid was used.

TABLE I
THE OBTAINED ADSORPTION CAPACITIES USING DIFFERENT ACIDS

Type of acid	q_e(mg/g)
Sulfuric	309.56
Phosphoric	214.75
Hydrochloric	82.25

3.2 Effect of pH

The effect of pH on adsorption capacity of Zn(II) by Acacia tortilis leaves was evaluated within the pH range of 2-6 (Figure 1). It was found that the adsorption capacity increased from 30.25 mg/g to 235.22 mg/g with increase in pH from 2 to 4. Hence, the pH of 4 was found as optimum pH for adsorption of Zn(II) onto Acacia tortilis leaves. These phenomena can be explained as following: at low pH the hydrogen ion concentration is too high therefore it is difficult for ion-exchange to take place. On the other hand, increasing of pH produced a low hydrogen ion concentration hence it is so easy for ion-exchange between the active sites of Acacia tortilis particles and Zn(II) to take place. It is also observed from Figure 1 that, the adsorption capacity is decreased after pH 4. This is due to the precipitation of Zn(II) as hydroxides [7].

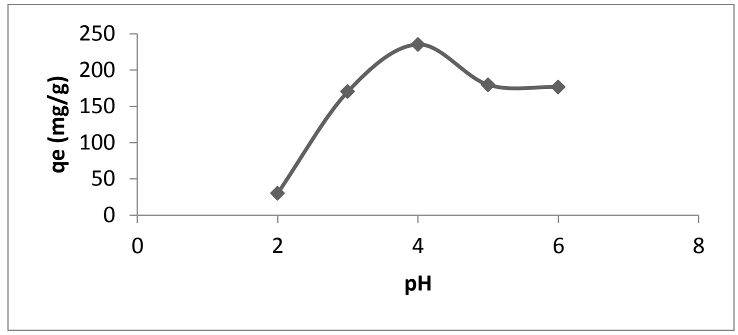

Fig. 1: Effect of pH on adsorption capacity of Zn(II)

3.3 Effect of Adsorbent Dosage

As shown in Figure 2, the adsorption capacity of Zn(II) decreased from 235.32 to 32.73 with increase in adsorbent dosage from 0.2 g/l to 1 g/l. This phenomena is mainly due to the overcrowding of adsorbent particles and also due to the competition among zinc ions onto *Acacia tortilis* surface [8].

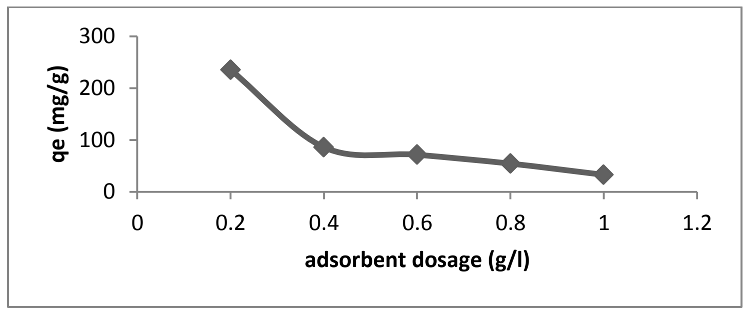

Fig. 2: Effect Of Adsorbent Dosage On Adsorption Capacity Of Zn(Ii)

3.4 Effect of Contact Time

Figure 3 shows the effect of contact time on the adsorption of Zn(II). The experimental data indicated that the adsorption capacity of Zn(II) was found to increase with increasing contact time reached maximum value of 187.25 mg/g after 2 hours and then no further significant increase was observed.

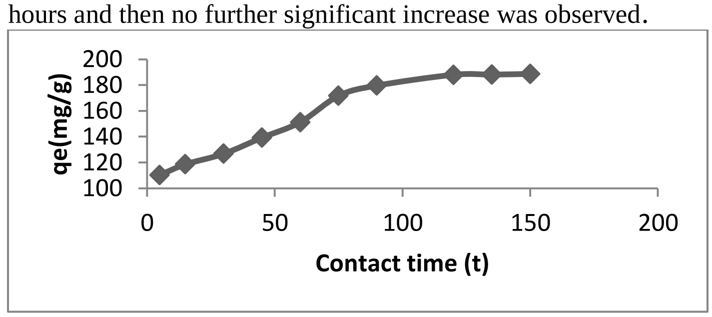

Fig. 3: Effect Of Contact Time On Adsorption Capacity Of Zn(II)

3.5 Kinetic Models

The adsorption kinetics of Zn(II) were tested using first-order, pseudo second-order and intra particle diffusion equations.

The first-order equation is shown below [9]:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \qquad (2)$$

Where q_t refer the amount of Zn(II) adsorbed per unit weight of adsorbent (mg/g) at time t (min). K_1(l/min) is the rate constant of the first-order sorption. A plot of $\log(q_e\text{-}q_t)$ versus t gives the result shown in Fig. 4. The values of K_1, experimental adsorption capacity ($q_e$exp.) and calculated adsorption capacity ($q_e$cal.) are presented in Table 2

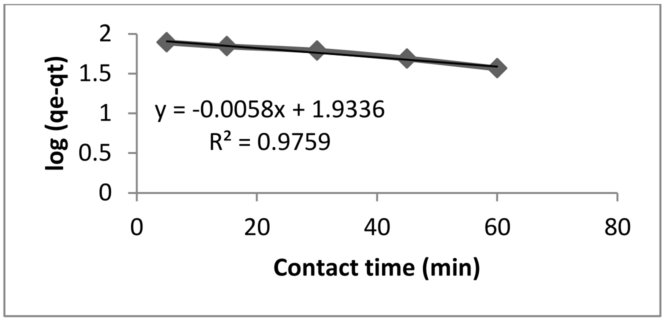

Fig. 4: First Order Kinetic Plot For Adsorption Of Zn(II)

TABLE II
FIRST ORDER PARAMETERS FOR ADSORPTION OF ZN(II)

q_e exp.	q_e cal.	K_1 (l/min)	R^2
187.25	85.82	0.0134	0.9759

The pseudo second-order equation can be written as [9]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^{\;2}} + \frac{1}{q_e} t \qquad (3)$$

Where K_2 (g/mg.min) is the rate constant of the pseudo second order sorption. The equilibrium adsorption capacity and the pseudo second order rate constant were determined experimentally from the slop and intercept of plot t/qt versus t (Fig. 5). The calculated correlations (R^2) are closer to unity for pseudo-second order kinetic model; Therefore the adsorption kinetics are favorably by the pseudo-second order rather then the first order for Zn(II) adsorption. The K_2 and q_e values for the pseudo-second order kinetic, calculated from Fig. 5 are listed in Table 3. By comparing the $q_e$exp. and $q_e$cal. of the two kinetic models, the pseudo second order kinetic model seems to be best fitted for the experiment because the values of $q_e$exp. and $q_e$cal are close together.

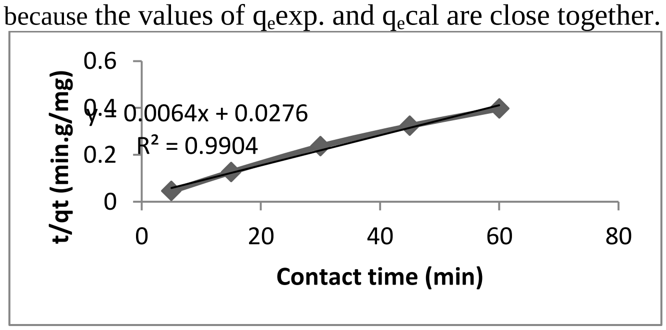

Fig. 5: Pseduo second order kinetic plot for adsorption of Zn(II)

TABLE III
PSEDUO SECOND ORDER PARAMETERS FOR ADSORPTION OF ZN(II)

q_e exp.	q_e cal.	K_2 (g/mg.min))	R^2
187.25	156.26	0.0015	0.9904

The intra particle diffusion is the most common technique used for confirming the adsorption mechanism in the adsorption process [10]. This model of Weber and Morris is shown as:

$$q_t = K_p t^{1/2} + C \qquad (4)$$

Where K_p is the intra particle diffusion rate constant, mg/g.min. and C is the boundary layer thickness. The linear plots of q_t versus $t^{1/2}$ as shown in Fig. 6 is probably due to the intra particle diffusion. This plots is not passed through the origin points indicating that, the pore diffusion may not be only the rate-determine step in the removal of Zn(II) [11]. The slop and intercept of the linear portion represents K_p and boundary layer thickness, respectively. The values of K_p and R^2 are listed in Table 4. These results suggest that the mechanism of Zn(II) onto the surface of *Acacia tortilis* leaves was carried out by two steps: adsorption and intra particle diffusion.

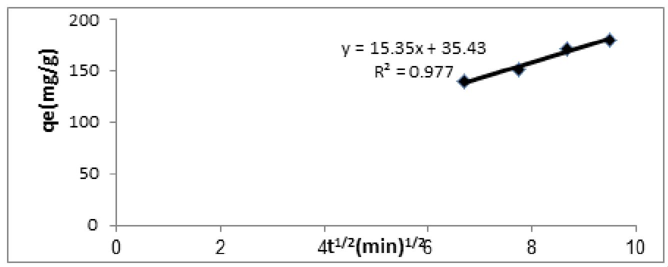

Fig. 6: Intra particle diffusion kinetic plot for adsorption of Zn(II)

TABLE IV
INTRA PARTICLE DIFFUSION PARAMETERS FOR ADSORPTION OF ZN(II)

Kp (mg/g.min)	C	R^2
15.35	35.43	0.997

IV. CONCLUSION

From the experimental results, it was concluded that the maximum adsorption capacity of Zn(II) ions from aqueous solution occurred when sulfuric acid was used as activator rather than hydrochloric and phosphoric acids. The maximum adsorption capacity was obtained at pH 4 after 2 hours. The adsorption capacity of Zn(II) was pH, adsorbent dosage and contact time dependent. Batch experiments have shown that the adsorption process can be better described by pseudo second order kinetic model and can be controlled by adsorption and intra particle diffusion.

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