

Elimination of Cu (II) Cations from Water Media Using Clean Adsorbent as Application of Green Chemistry: *Acacia Tortilis* Seeds

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Abstract—*Acacia tortilis* seeds were treated with natural lemon juice and used as clean adsorbent for removal of Cu (II) cations from water environment. Adsorption experiments were preformed by studying some parameters include initial pH, contact temperature, contact time and initial Cu (II) concentration, on adsorption of Cu (II) cations onto *Acacia tortilis* seeds. The optimum conditions were obtained 3, 50 °C, 90 minutes, 600 mg/l as initial pH, contact temperature, contact time and initial Cu (II) concentration, respectively. Adsorption kinetic models include Lagergren first-order, pseudo-second-order and intra-particle diffusion were applied in order to investigate the adsorption mechanism. Two different isotherm models include Langmuir and Freundlich were used to investigate the adsorption process. Thermodynamic parameters, such as ΔG° , ΔH° and ΔS° , were calculated.

Index Terms—*Acacia tortilis*, adsorption, Lagergren first-order, pseudo second order.

I. INTRODUCTION

Copper is known to be one of the heavy metals most toxic to living organisms and it is one of the more widespread heavy metal contaminants of the environment. The mainly sources of copper in industry include plating baths, metal cleaning, pulp, paper board mills, wood pulp production, fertilizer industry, paints and pigment [1]. The common methods for removal of heavy metals from water environment include oxidation, reduction, precipitation, ion exchange, membrane filtration and adsorption. Among all these methods, adsorption is highly recommended due the effectively and economically of this method [2]. Agriculture waste materials such as apple wastes, wood, banana pith, orange peel, tree fern, tree bark, peanut shells, and rice bran have been widely used as adsorbents for reducing Cu (II) cations from aqueous solutions [2],[3].

The aim of the present work is to study the ability of treated *Acacia tortilis* seeds with natural lemon juice as clean adsorbent for the removal of Cu (II) cations from aqueous solutions. To reach this aim, several parameters controlling the adsorption capacity of Cu (II) cations onto the surface of *Acacia tortilis* seeds were study.

II. EXPERIMENTAL

A. Materials

In this study, *Acacia tortilis* seeds as adsorbent, and zinc acetate (BDH, England) as adsorbate were used. A new preparation method for adsorbent was tried as follows: 5 ml of natural lemon juice (from fruit lemon tree) and 10 ml of distilled water was added to a glass bottle with stopper containing one gram of *Acacia tortilis* seeds. The contents of the bottle were shaken in water bath shaker for one hour at 60 °C. The mixture was filtered and dried in oven at 95 °C.

B. Methods

The solubility percent of the *acacia tortilis* seeds in water was measured as indicated in literature [4].

Surface area and pore volume of *acacia tortilis* seeds before and after adsorption of Cu (II) cations were determined using Nitrogen adsorption apparatus (Nova 2200 Quntachrome Corporation, USA)

Synthetic stock solutions of Cu (II) cations were prepare by dissolving required quantity of analar grade salt of zinc acetate in distilled water. The stock solutions were further diluted with distilled water to desired concentrations for obtaining the test solutions. Determination of initial concentration (C_o) and equilibrium concentrations (C_e) of Cu (II) cation solutions were carried out by titration with known concentration of EDTA using Xylenol orange dye (Merck, Germany) as indicator [5].

Adsorption operations were carried out by batch method [6]. The amount of Cu (II) cations per gram of *acacia tortilis* seeds at equilibrium (q_e) was calculated by the following expression [7]:

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

where C_o and C_e (mg/l) are the concentration of Cu (II) cation solutions before and after adsorption, respectively. V (l) is the volume of Cu (II) cations solution and W is the weight of *acacia tortilis* seeds (g).

The pH of Cu (II) ions solutions was controlled by addition of hydrochloric acid or sodium hydroxide and determined by pH meter (JENWAY 3205, USA).

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III. RESULTS AND DISSECTION

A. Characterization of *Acacia tortilis* Seeds

The solubility of *Acacia tortilis* seeds treated with natural lemon juice in water was found as 4.4 % (Table I). The low value of solubility means that, *Acacia tortilis* seeds treated with natural lemon juice can be applied as adsorbent material in aqueous solutions. It can be noticed from Table I that, the decrease of the surface area and volume pore of *Acacia tortilis* seeds after adsorption is probably due to the occupied of active sites with Cu (II) cations.

TABLE I: CHARACTERIZATION OF ACACIA TORTILIS SEEDS

Adsorbent state	Solubility in water (%)	Surface area (m ² /g)	Pore volume (ml/g)
Native	6.8	370	0.265
Treated with NLJ	4.4	640	0.405
With Cu (II) cations		570	0.343

B. Effect of Initial pH

Table II presented the influence of initial pH value on the adsorption capacity of Cu (II) cations. The applied optimum conditions as follows: particle diameter of sample, < 500 µm; contact temperature, 30 °C; contact time, 30 minutes; initial concentration, 101 mg/l; adsorbent dose, 0.1 g/l and contact speed, 400 rpm.

As shown in Table II, the optimum initial pH of Cu (II) cations solutions was observed at 3. The increase of adsorption capacity as initial pH decreased might be due to the weakening of electrostatic force of attraction between the oppositely charged Cu (II) and *Acacia tortilis* seeds. The decrease of adsorption capacity after optimum initial pH may be due to the precipitation of Cu (II) cations as hydroxides [8].

TABLE II: EFFECT OF INITIAL pH ON ADSORPTION CAPACITY

Initial pH	q _e (mg/g)
2	99
3	128
4	59
5	61

C. Effect of Contact Temperature

The contact temperature behavior between Cu (II) cations and *Acacia tortilis* seeds was study within the range of temperatures 20-50 °C and displayed in Table III. The adsorption capacity increased as the contact temperature increased indicating the endothermic behavior of the adsorption system.

TABLE III: EFFECT OF CONTACT TEMPERATURE ON ADSORPTION CAPACITY

Contact temperature (°C)	q _e (mg/g)
20	435
30	451
40	523
50	578

D. Effect of Adsorbent Dose

The effect of the adsorbent dose on adsorption capacity of Cu (II) cations onto *Acacia tortilis* seeds was studied by changing the concentration of the adsorbent from 0.1 to 0.9 g/l. The applied optimum conditions as follows: particle

diameter of sample, < 500 µm; contact temperature, 30 °C; contact time, 30 minutes; initial concentration, 101 mg/l; initial pH, 3 and contact speed, 400 rpm. The obtained results are displayed in Table IV. It is very clear from Table IV that the adsorption capacity of Cu (II) cations decreased as the adsorbent dose increased, this phenomena is probably due to the high number of unsaturated active sites on the surface of *Acacia tortilis* seeds [9].

TABLE III: EFFECT OF ADSORBENT DOSE ON ADSORPTION CAPACITY

Adsorbent dose (g/l)	q _e (mg/g)
0.1	555
0.3	205
0.5	119
0.7	93
0.9	72

E. Effect of Sodium Chloride

To investigate the adsorption capacity of Cu (II) cations onto *Acacia tortilis* seeds in the presence of other cations, sodium chloride is added to the Cu (II) cations solution. Table IV presented the effect of sodium chloride on adsorption capacity at particle diameter of sample, < 500 µm; contact temperature, 30 °C; contact time, 30 minutes; initial concentration, 101 mg/l; initial pH, 3; adsorbent dose, 0.1 g/l and contact speed, 400 rpm. It was observed from Table IV that, the adsorption capacity decrease with increase in sodium chloride concentration from 0 to 1.2 M. The increase of amount of sodium chloride can help to swamp the surface of *Acacia tortilis* seeds, which decreases Cu (II) cations access to the *Acacia tortilis* seeds for adsorption.

TABLE IV: EFFECT OF SODIUM CHLORIDE ON ADSORPTION CAPACITY

Concentration of sodium chloride (M)	q _e (mg/g)
0	73
0.17	66
0.51	58
0.85	53
1.19	51

F. Effect of Contact Time

Fig. 1 shows the effect of contact time on the adsorption capacity of Cu (II) cations from aqueous solutions at different initial concentrations by *Acacia tortilis* seeds. The following conditions of adsorption process were applied: adsorbent dose, 0.1 g/l; particles diameter of sample, < 500 µm; initial pH, 3; contact temperature, 30 °C and contact speed, 400 rpm. As observed from Fig. 1 that, the adsorption capacity increased with the increase of contact time and reached equilibrium after 90 minute. It is also clear from Fig. 1 that, the adsorption capacity increased as the initial concentration of Cu (II) cations increased.

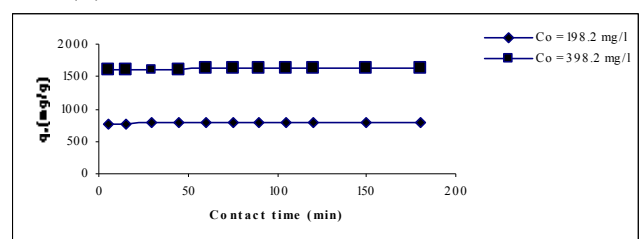


Fig. 1. Effect of contact time on adsorption capacity.

G. Kinetic Study

Adsorption kinetic studies are describe the adsorbate uptake rate which in turn controls the residence time of adsorbate at the solid–liquid interface. In order to investigate the mechanism of adsorption, three kinds of kinetic models: first order, pseudo second order and intra particle diffusion models were used in the present work to test the experimental data.

The first order equation is described by Lagergren as follows [10]:

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

where q_t is the amount of adsorbed Cu (II) cations at time t (mg/g) and k_1 is the first order rate constant (min^{-1}).

The values of K_1 and the calculated adsorption capacity ($q_{e \text{ calcu}}$) were obtained respectively from the slope and intercept of the plot of $\log(q_e - q_t)$ versus t (Fig. 2). Table V presents the first order parameters of Cu (II) cations onto *Acacia tortilis* seeds.

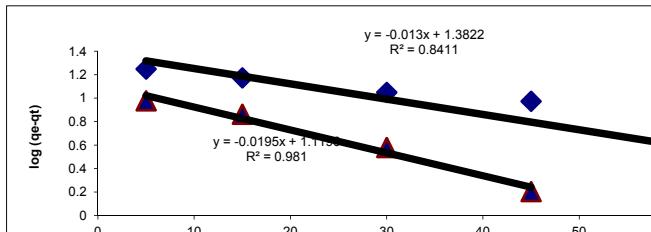


Fig. 2. First order kinetic plot for the adsorption of Cu (II) cations by *Acacia tortilis* seeds.

TABLE V: FIRST ORDER PARAMETERS

C_0 (mg/l)	$q_e \text{ exp}$	$q_e \text{ calcu}$	K_1 (l/min)	R^2
198.2	787	24.1	0.0299	0.8411
398.2	1619	13.17	0.0449	0.9810

A pseudo second order equation was expressed by the following form [11]:

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

The plot of t/q_t versus t (Fig. 3) could provide a linear relationship, from which q_e and K_2 (pseudo second order constant) can be calculated.

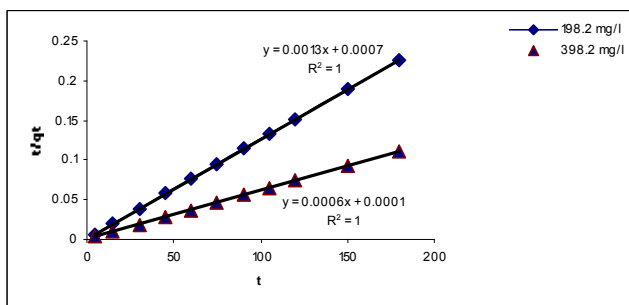


Fig. 3. Pseudo second order kinetic plot for the adsorption of Cu (II) cations by *Acacia tortilis* seeds.

Table VI present the pseudo second order parameters of Cu(II) cations onto *Acacia tortilis* seeds at different initial concentrations of Cu (II) cations.

TABLE VI: PSEUDO SECOND ORDER PARAMETERS.

C_0 (mg/l)	$q_e \text{ exp}$	$q_e \text{ calcu.}$	K_2 (g/ mg. min)	R^2
198.2	787	769	0.0024	1
398.2	1619	1667	0.0036	1

A comparison between Table VI and Table V showed that, R^2 equal 1 and the values of $q_e \text{ calcu.}$ are agree with experimental adsorption capacity ($q_e \text{ exp.}$) in case of pseudo second order parameters. This finding suggests that, the adsorption of Cu (II) cations onto *Acacia tortilis* seeds follows the pseudo second order model.

To confirm the mechanism of the adsorption process, intra particle diffusion model was applied. The intra-particle diffusion model [12] is characterized by a linear relationship between q_t and the square root of the time and classified as a rate determine limiting step. This relation expressed according to the following expression:

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

where k_p is the intra particle diffusion coefficient and C gives an idea about the thickness of the boundary layer.

The linear portion describes the gradual adsorption stage, where intra-particle diffusion is the rate limiting step. The values of the rate constant of intra particle diffusion (K_p) were calculated from the slop of the straight lines (Fig. 4) and presented in Table VII. As observed in Table VII, the boundary layer thickness is increased with increase the initial concentration of Cu (II) cations. Also all the straight lines were not passed through the origin points which proved that, the intra particle diffusion model probably not be the only rate-controlling step of the adsorption process [12].

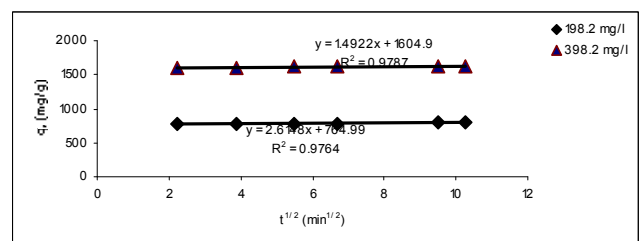


Fig. 4. Intra particle diffusion kinetics of Cu (II) cations on to *Acacia tortilis* seeds.

TABLE VII: RATE PARAMETERS OF INTRA PARTICLE DIFFUSION OF CU (II) CATIONS ON TO *ACACIA TORTILIS* SEEDS

C_0 (mg/l)	K_p (mg/g. min ^{1/2})	C	R^2
198.2	2.615	764.9	0.9764
398.2	1.492	1604.9	0.9787

H. Adsorption Isotherm Study

Adsorption isotherms are very important for the design of adsorption. They represent how the cations are partitioned between the adsorbent and liquid phases at equilibrium as a function of cation concentration.

Langmuir and Freundlich isotherms are the most widely isotherms employed for fitting the experimental data. To get

the experimental data, initial concentrations of Cu (II) cations were varied (50-700 mg/l) whereas the weight of Acacia tortilis seeds was kept constant (0.1 g/l). Two hours of equilibrium time for adsorption experiments were used to ensure equilibrium conditions at different contact temperatures varied from 293 to 323 K.

Langmuir adsorption isotherm is given by the following expression [13]:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} b} C_e \quad (5)$$

where q_{\max} (mg/g) and b (l/mg) are the Langmuir constants related to the maximum adsorption capacity and energy of adsorption, respectively. When C_e/q_e is plotted against C_e , a straight line with the slope of $1/q_{\max}$ and intercept of $1/q_{\max} b$ are obtained (figure not shown). The Langmuir constant, K_L will be used later for calculating the Gibbs free energy of the adsorption process. K_L was determined, as in

$$K_L = q_{\max} \times b \quad (6)$$

The parameters q_{\max} , b , K_L and R^2 of Cu (II) cations adsorption at different contact temperatures are listed in Table VIII. It is observed from Table VIII that, the obtained data were unfitted with langmuir isotherm due to the too much difference between the $q_{e \text{ exp}}$ and $q_{e \text{ calcu}}$ and also due to the lower values of R^2 .

TABLE VIII: LANGMUIR ISOTHERM CONSTANTS OF OF Cu (II) CATIONS ON TO ACACIA TORTILIS SEEDS AT DIFFERENT CONTACT TEMPERATURES.

T (K)	Linear equation	$q_e \text{ exp}$ (mg/g)	$q_e \text{ calcu}$ (mg/g)	b (l/mg)	K_L (l/g)	R^2
	$Y = aX + b$					
293	$a = 0.0009$ $b = 0.1994$	717	1111	0.0045	4.99	0.883
303	$a = 0.0008$ $b = 0.1768$	802	1250	0.0045	5.63	0.8116
313	$a = 0.0007$ $b = 0.1500$	901	1428	0.0045	6.71	0.6865
323	$a = 0.0006$ $b = 0.1462$	1001	1666	0.0045	6.83	0.586

The Freundlich expression was applied in the present study, as in [14]

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

where K_F and n are the Freundlich constants and they are determined from the plots of $\log q_e$ versus $\log C_e$ (figure not shown). The values of K_F and n as well as R^2 are displayed in Table IX. It is apparent from this table that, the values of n lie in the range of 0-10 indicating that, the adsorption of Cu (II) cations onto Acacia tortilis seeds is favorable [11]. The R^2 values in case of Freundlich adsorption isotherm are higher when compared with Langmuir adsorption isotherm, this means that the adsorption process at different temperatures is more favorable in case of Freundlich adsorption isotherm than Langmuir adsorption isotherm.

TABLE IX: FREUNDLICH ISOTHERM PARAMETERS OF Cu (II) CATIONS ONTO ACACIA TORTILIS SEEDS AT DIFFERENT CONTACT TEMPERATURES

T (K)	Linear equation $y = ax + b$	K_F	n	R^2
273	$a = 0.5532$ $b = 1.4226$	26.46	1.81	0.9787
303	$a = 0.5204$ $b = 1.5479$	35.31	1.92	0.9451
313	$a = 0.4843$ $b = 1.6979$	49.88	2.06	0.8734
323	$a = 0.4859$ $b = 1.7290$	53.58	2.06	0.8629

I. Adsorption Thermodynamic Study

Thermodynamic parameters such as standard free energy change (ΔG°); standard enthalpy change (ΔH°) and standard entropy change (ΔS°) can be calculated as [15]:

$$\Delta G^\circ = -RT \ln K_L \quad (8)$$

$$\text{Link} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

where R is universal gas constant (8.314 J/mol K).

The values of ΔH° and ΔS° were calculated respectively from the slope and intercept of the plots of $\ln K$ versus $1/T$ as (2) and figure not shown. The thermodynamic parameters for the adsorption process are shown in Table X. It is seen from this table that, the negative values of ΔG° proved that, the adsorption process is spontaneous in nature and the spontaneity increases as the temperature increases. The positive value of ΔH° indicates the endothermic nature of adsorption. The positive value of ΔS° showed the increase randomness at the solid-liquid interface during the adsorption process.

TABLE X: THERMODYNAMIC OF ADSORPTION OF Cu (II) CATIONS ON TO ACACIA TORTILIS SEEDS AT DIFFERENT CONTACT TEMPERATURES.

ΔG° (KJ/mole)				ΔH° (KJ/mole)	ΔS° (KJ/mole)
293 K	303 K	313 K	323 K		
-3.93	-4.35	-4.94	-5.15	9.13	0.045

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The experience in the field of removal of heavy metals and dyes from aqueous media using agriculture materials. The address of current job is Chemistry Department, Faculty of Science, Sebha university, Libya. Several papers were published. At the current time, some researches include the use of agriculture adsorbents treated with natural activators for heavy metals removal from aqueous solutions, reuse of some agriculture adsorbents for heavy metals removal from aqueous solutions and removal of heavy metals from hard aqueous media by agriculture adsorbents.