

## Comparative Study for Removal of $Zn^{+2}$ Ions from Aqueous Solutions by Adsorption and Forward Osmosis

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### Abstract

The aim of this paper was to investigate the removal efficiencies of  $Zn^{+2}$  ions from wastewater by adsorption (using tobacco leaves) and forward osmosis (using cellulose triacetate (CTA) membrane). Various experimental parameters were investigated in adsorption experiment such as: effect of pH (3 - 7), contact time (0 - 220) min, solute concentration (10 - 100) mg/l, and adsorbent dose (0.2 - 5)g. Whereas for forward osmosis the operating parameters studied were: draw solution concentration (10 - 150) g/l, pH of feed solution (4 - 7), feed solution concentration (10 - 100) mg/l. The result showed that the removal efficiency by using adsorption was 70% and the removal efficiency by using forward osmosis was 96.2 %.

**Key words:** Tobacco leaves; Adsorption; Forward osmosis; Heavy metal wastewater; Membranes separation.

### Introduction

Heavy metals are considered an important sources of environmental pollution. Generally heavy metals are those whose density exceeds  $5 \text{ g/cm}^3$  [1]. Removal of heavy metals from wastewater is very important because it is toxic to human bodies and tend to bioaccumulate which may lead to anemia, and damage to lung, brain, and kidney [2]. Zinc is one of the toxic metals that causes depression, lethargy, nausea, vomiting, and neurological signs. The important sources of zinc metal pollution are the combustion of petroleum and its products, and incineration of solid waste [3].

To reduce the heavy metals content of industrial effluents waste water, many different techniques have

been utilized such as chemical precipitation, electrolytic methods, filtration, and ion-exchange, membrane processes. All these methods have their advantages and limitations in application such as incomplete heavy metals removal, require high energy, toxic sludge production and expensive equipment. So more effective methods have been utilized to remove metal pollution like adsorption and membrane process [4].

To show effective adsorption of heavy metals, many studies using agricultural products and by-products such as walnut shells, peanut skins, wool, tea leaves, coffee powder, sugar beet pulp, hazelnut shell [5], granular activated carbons [6], rice husk [7],

and maize husk [8]. The advantages of adsorption are relatively low cost material, simple design, and easy operation [9].

Membrane technology has been increasingly used for removing of heavy metals from waste water and improving water recovery rate because of its main advantage like high removal efficiency and low cost. Huge improvements have been made in recent years, and the use of membrane technology has increased in potable water treatment [10]. The most widely used membrane processes for water treatment include micro-filtration (MF), ultra-filtration (UF), nano-filtration (NF), reverse osmosis (RO), and forward osmosis process which is an active process that can effectively remove heavy metals from waste water [11, 12].

The principle of forward osmosis (FO) depends on osmotic pressure gradient generated by high concentration of draw solution (DS) and low concentration of feed solution (FS) to allow water diffuse through semi permeable membrane from FS to DS. The FO process offers the advantages of low operation pressure, high recovery, and low cost and disadvantages of require special membrane, and the membrane need periodically clean [13].

The aim of the present study is to investigate the removal of Zn<sup>+2</sup> ions from wastewater by adsorption and forward osmosis (FO) methods using tobacco leaves as an adsorbent for adsorption and cellulose triacetate (CTA) membrane for forward osmosis and compare the removal efficiency between them. In addition, investigate the parameters that influence the separation efficiency, such as contact time, pH, dose of adsorbent, initial metal concentrations, and concentration of draw solution. Also

present work aims to determine isotherm model and kinetic models for adsorption system.

## Experimental Work

### Materials

Heavy metal solution zinc chloride (ZnCl<sub>2</sub>) has a molecular weight of 136.29 g/mole was used for preparing synthetic solution. To prepare a desired concentration of Zn<sup>+2</sup> ions, a known quantity of zinc chloride is dissolved in deionized water (DI), of 3-8 μS/cm conductivity. Solution pH was adjusted (3-7) by adding 0.1 M HCl or 0.1 M NaOH as required. Mass of heavy metal salt added to water by assuming complete dissolution according to equation below:

$$W = V \times C_i \times \frac{M.Wt}{At.Wt} \quad \dots(1)$$

where: W: weight of heavy metal salt (ZnCl<sub>2</sub>) (mg), V: volume of solution (l), C<sub>i</sub>: Initial concentration of metal ions (Zn<sup>+2</sup>) in solution (mg/l), M.wt: molecular weight of metal salt (ZnCl<sub>2</sub>) (g/mole), At.wt: Atomic weight of metal ions (Zn<sup>+2</sup>) (g/mole).

### Adsorbent

The tobacco leaves are used as adsorbent. The tobacco leaves were washed several times with distilled water to remove all excess and then dried for 24 hr at temperature 60 °C. The dried tobacco leaves was ground and then sieved to get the particle size of 0.77 mm. The properties of adsorbent are shown in Table 1.

Table 1: Properties of tobacco leaves

Properties	Adsorbent (Tobacco leaves)
pH for (1% sol.)	6.5
Moisture content (%)	0.52
Sp.Gr. for (1% sol.)	1.0026
Density @ 15.6 °C for (1% sol.)	1.0016
Viscosity @ 21°C for (1% sol.)	1.018

### Draw Solution

Magnesium chloride MgCl<sub>2</sub> was dissolved in deionized water of 3-8 µs/cm conductivity, for preparing draw solutions with concentration of 10, 30, 50, 70, 90 and 150 g/l, and then the solutions were mixed by using a stirrer at an agitation speed of 1000 rpm for 15 min. Magnesium chloride MgCl<sub>2</sub> was used in preparation of draw solutions due to its low molecular weight, dissociated ions number (i = 3), low viscosity, high solubility, high osmotic pressure, non toxic, and easily separated and recycled. Table (2) shows the chemical specification of the salt (MgCl<sub>2</sub>).

Table 2: Chemical specifications of draw solutions

Magnesium Chloride (MgCl <sub>2</sub> )	Assay	98% min.
MW = 95	Max. limits of impurities (%)	
	Sulfate	0.002
	Copper	0.002
	Lead	0.005
	Iron	0.0005
	Zinc	0.0005

### Apparatus

The concentration of the zinc ion was measured by Atomic Absorption Spectrometry (AAS) (Buck 210/211, U.S.A., Perkin Elmer, Sr.Nr:1159A). pH-meter (Model 2906, Jenway Ltd, UK) was used for measuring the pH of metal solution. To measure the concentration of the draw solutions, digital laboratory conductivity meter was used (Type : WTW ino Lab cond 720 with range (0 - 2 ×10<sup>6</sup> µS/cm).

Mechanical stirrer (Model: RZR 2021, speed range of 40 - 2,000 rpm) was used to mixing feed and draw solutions. Shaker (HV-2 ORBTAL, Germany) was used for shaking the solutions. A digital balance with 4 decimal points (Sartorius BP 3015 max. 303 g, d= 0 -1 mg) was used to measure the weight of feed and draw solutions in experiments.

### Forward Osmosis System

For forward osmosis process experiments, the cellulose triacetate (CTA) membrane (X-Pack™ supplied by Hydration Technology Inc., Albany, OR) was used as flat sheet module. The thickness of cellulose triacetate membrane is less than 50 µm and lacks a thick support layer consist of a woven fabric mesh embedded within a continuous polymer layer. The specific characteristics of the CTA membrane module are rejection of salt (95-99 %), and maximum operating temperature 50 °C. Experiments were done using a laboratory-scale forward osmosis system consisting of two cylinders, each one with a capacity of 5 liters were used as vessel of feed and draw solution, two high pressure pumps (flow rate ≥ 0.6 l/ min, 24 VDC, TYP 2500, DENG YUAK) were used to pump feed and draw solutions from vessels to osmosis element. Two calibrated flow meters: first one was used to measure the feed solution volumetric flow rate and the second one was used to measure the draw solution volumetric flow rate each of ranged (30 - 300 l/h). To indicate the feed solution pressure, a pressure gauge (range of 0 - 2 bar gauge) was used. The forward osmosis cell composed of two semi-cells which were made of Teflon. The osmosis cell consisted two channels has dimensions of 12.3 cm length and 12.3 cm width,

providing an effective membrane area of 151.2 cm<sup>2</sup>.

## Experimental Procedure

### Adsorption Process

Stock solution of ZnCl<sub>2</sub> was prepared by dissolving a known quantity of ZnCl<sub>2</sub> in distilled water and then the solution diluted to the required initial concentration range from (10 to 100 mg/L). A sample of 100 ml of known concentration was added to each flask (250 ml) with a required amount of adsorbent and was shaken at a speed of 200 rpm at 25 °C for a specified period of contact time, then the metal solution and adsorbent was filtered through a 0.45 μm membrane filter. The metal solution pH was adjusted to the desired pH value. The effect of pH for Zn<sup>+2</sup> ions removal was studied in pH range of 3 - 7. Effect of initial metal concentrations were conducted using 10, 30, 50, 80 and 100 mg/l metal solutions at temperature 25 °C and optimum pH value. Amount of tobacco leaves resin (0.2 - 5)g were conducted at temperature 25 °C and optimum pH value. To investigate the contact time effect on the adsorption process 1 g of adsorbent dosage was added to 100 ml of 50 mg/l metal solution. The system was subjected to shaking speed of 200 rpm, and the samples were collected from (0 to 220) min to determine the remaining concentration of metal. The final equilibrium concentrations were measured by means of AAS. For the remaining metal concentration the filtrate was analyzed. At time *t*, the amount of Zn<sup>+2</sup> adsorbed in mg/g was calculated by using Equation 2.

$$q_e = \frac{(C_o - C_e) \times V}{m} \quad \dots(2)$$

where: C<sub>o</sub> and C<sub>e</sub> are initial and equilibrium concentrations of Zn<sup>+2</sup> ions in the water (mg/l), respectively, V is

the volume of the Zn<sup>+2</sup> solutions in L, *m* is the weight of tobacco leaves in g. The percentage of removed Zn<sup>+2</sup> ions (*R* %) in solution was calculated using Equation 3

$$R(\%) = \frac{(C_o - C_e)}{C_e} \times 100 \quad \dots(3)$$

### Forward Osmosis Process

Heavy metal waste water (feed solution) and draw solution were placed in cylindrical vessels. The volume of both draw solution (DS) and feed solution (FS) were 2.5 liters and they were run in a closed loop. The outlet valve of the feed vessels was opened to let the whole pipes of the system filled with solutions. The feed solution and draw solution flow tangentially to membrane in a co-current flow. This operation provides constant Δπ along the membrane module to make the process more efficient. The streams of feed and draw solution outlet were recycled back to the main vessels. All experiments were done with applying a pressure of 0.25 bar gauge in the feed side across the membrane sheets. The temperature of feed and draw solutions were 25°C, and the volumetric flow rate of both solutions were controlled using calibrated flow meters. The time of experiment was 3 hours. For checking, every 0.5 hour, the increasing in volume of the draw solution (DS) was measured and compared with the reduction in the volume of feed solution (FS). Water flux was calculated by dividing the water transported through the membrane by the effective area of CTA membrane and the time. Measuring of metal concentration in FS outlet was carried out by using AAS and measuring of MgCl<sub>2</sub> concentration in DS outlet was done by using conductivity meter. Figure 1 illustrates the schematic diagram of forward osmosis apparatus.

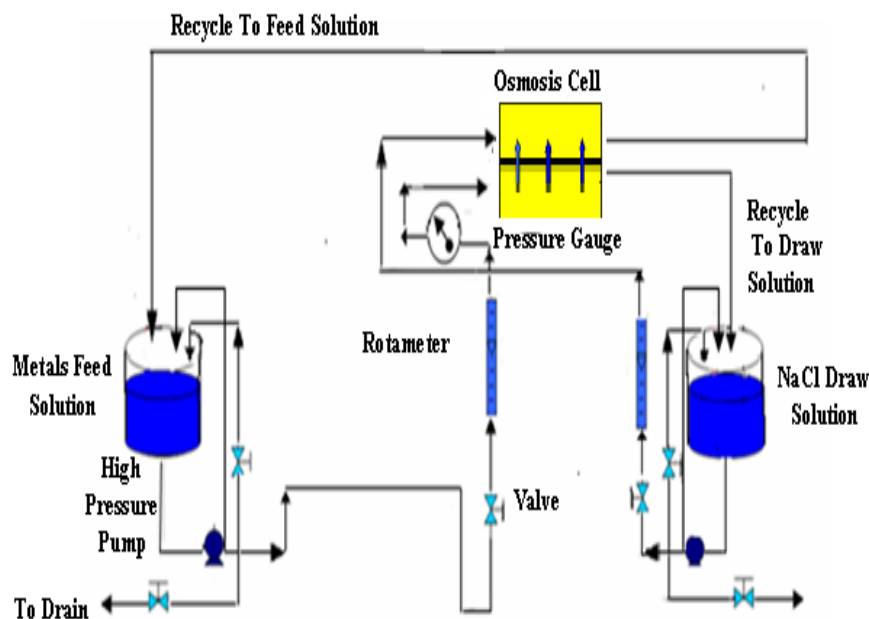


Fig. 1: The schematic diagram of forward osmosis process

## Results and Discussion

### Adsorption Process

#### Effect of Contact Time

The  $Zn^{+2}$  ions removal efficiency from waste water was studied as function of contact time. It was found that the  $Zn^{+2}$  ions adsorption capacity was higher at the beginning and after that, the adsorption rate became very slow. The degree of adsorption differs because of existence of greater number of adsorbent sites available for the adsorption of metal ions at beginning. The adsorption rate slowed down when the remaining vacant surface sites decreased because of the formation of repulsive forces between the metal ions on the solid surface and in the liquid phase, the same behaviour was observed by [14]. Depending on these results 140 min was considered as the optimum time for the rest of the experiments. Figure 2 shows the contact time effect on  $Zn^{+2}$  ions removal.

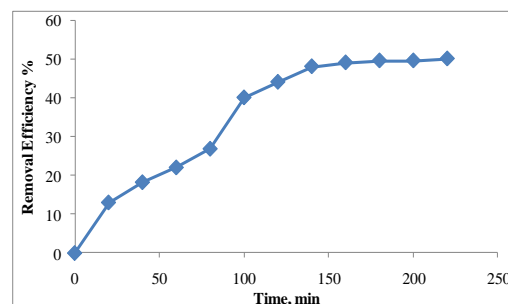


Fig. 2: Contact time effect on  $Zn^{+2}$  ions removal efficiency using tobacco laves. (pH=5; dosage=1g/100 ml; T=25°C; Ci=50 mg/L; speed=200 rpm)

#### Effect of pH Metal Solution

The pH is a significant factor affecting the  $Zn^{+2}$  ions removal from waste water. At low pH minimum adsorption was observed. This is because of the presence of higher concentration and higher mobility of  $H^+$  ions. At high  $H^+$  concentration the surface of the adsorbent becomes more positively charged so that the attraction between adsorbents and metal cations is reduced. But when pH increases, the negatively charged surface area becomes more so greater removal of metal is facilitated and then at very high pH also the percentage of metal removal decreases because that causes precipitation of metal ions on the



adsorbent surface by nucleation [15]. pH 5 is the optimum pH used for the Zn<sup>+2</sup> ions removal for all experiments. Figure 3 illustrates the pH effect on Zn<sup>+2</sup> ions removal efficiencies.

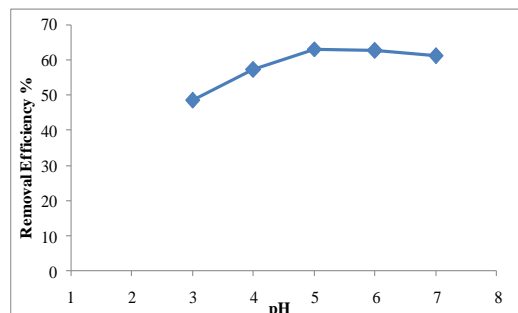


Fig. 3: pH effect on Zn<sup>+2</sup> ions removal efficiency using tobacco leaves. (t= 140 min; dosage=1g/100 ml; T=25 °C; Ci=50 mg/L; speed=200 rpm)

#### Effect of Tobacco Leaves Dose

The tobacco leaves dose effect on the removal of Zn<sup>+2</sup> ions was studied using dosages of tobacco leaves. The tobacco leaves adsorbent dose effect on Zn<sup>+2</sup> ions removal efficiencies is shown in Figure 4. When the tobacco leaves adsorbent dose increased up to 1 g/100 ml, the Zn<sup>+2</sup> ions retention will increase. This value was used as the optimum amount for other trials. It was found that when the amount of adsorbent increased, adsorption of Zn<sup>+2</sup> ions will increase because of the limited availability of the adsorbing species number for relatively large number of active surface sites on the adsorbent at higher adsorbent dosage. After this dose of adsorbent, the removal efficiency remains unchanged as shown in Figure 4. This may be attributed to overlapping of adsorption sites due to overcrowding of tobacco leaves (adsorbent) particles [16]. This appears after a certain adsorbent dose, the maximum adsorption sets in and so the amount of ions (Zn<sup>+2</sup>) were bound to the adsorbent and the free ions (Zn<sup>+2</sup>)

remain constant even with further addition of the adsorbent dose.

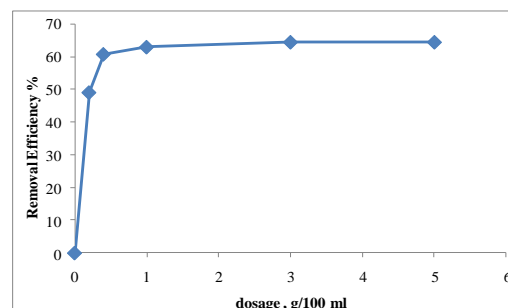


Fig. 4: Adsorbent amount effect on Zn<sup>+2</sup> ions removal efficiency using tobacco leaves. (t=140 min; pH=5; T=25 °C; Ci=50 mg/L; speed=200 rpm)

#### Effect of Initial Zn<sup>+2</sup> Ions Concentration

The increasing in initial Zn<sup>+2</sup> ions concentration decreases the adsorption percentage removal efficiency. This behaviour is due to that the adsorbent may contain limited exchangeable sites for the certain Zn<sup>+2</sup> ions concentration range, but when the concentration increase the exchangeable sites in adsorbent will not be enough to accumulate this concentration so the removal percentage will decrease. At lower Zn<sup>+2</sup> ions concentration, the percentage uptake increases due to larger active surface adsorbent area available for adsorption [17]. Figure 5 illustrates the effect of initial concentration of Zn<sup>+2</sup> ions on removal efficiency.

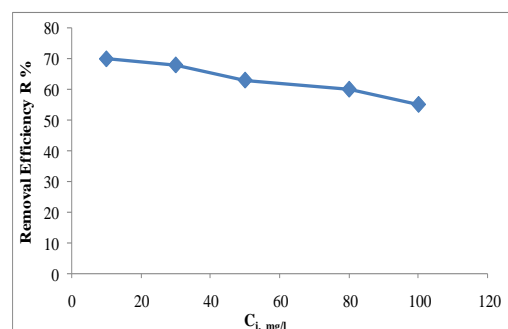


Fig. 5: Initial concentration effect on Zn<sup>+2</sup> ions removal efficiency using tobacco leaves. (pH=5; dosage=1g/100 ml; T=25°C; t= 140 min; speed=200 rpm)

**Adsorption Isotherms Models**

Adsorption isotherms models are very significant tools for the analysis of adsorption process. The adsorbent unit mass at constant temperature is decided the relationship between the equilibrium concentration and amount of adsorbate adsorbed [18]. Langmuir and Freundlich isotherm model are widely used to investigate the process of adsorption.

**Langmuir Isotherm Model**

Langmuir isotherm model shows that the adsorption occurs on the homogenous surfaces by adsorption of monolayer without interaction between adsorbed molecules [19]. The model describes by the Equation 4:

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \dots(4)$$

where  $K_L$  is the Langmuir constant related to the adsorption capacity (l/mg),  $q_e$  is the amount of  $Zn^{+2}$  ions adsorbed on the surface of biomass at the equilibrium (mg/g),  $C_e$  is the equilibrium of  $Zn^{+2}$  ions concentration in the solution (mg/l), and  $q_m$  is the maximum capacity of adsorption for  $Zn^{+2}$  ions adsorbed on the surface of biomass (mg/g). From Figure 6 the adsorption parameters ( $q_m, K_L$ ) can be determined from the intercept and slope plotting  $C_e/q_e$  vs.  $C_e$ , Equation 5 and Table 3 illustrate these parameters.

$$\frac{c_e}{q_e} = \frac{1}{q_m K_L} + \frac{c_e}{q_m} \dots(5)$$

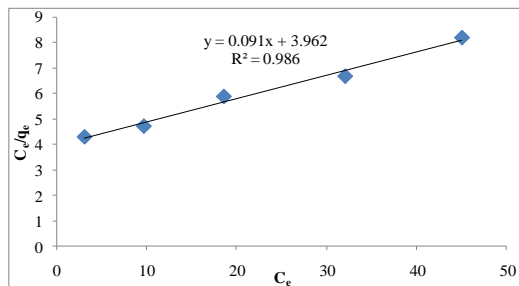


Fig. 6: Langmuir isotherm for adsorption of  $Zn^{+2}$  ions on tobacco leaves. (pH=5; T=25 °C; dosage=1g/100 ml; t=140 min; speed=200 rpm)

**Freundlich Isotherm Model**

Freundlich equation is the model of multilayer adsorption and the adsorption on the heterogeneous surface [20]. The equation of Freundlich is:

$$q_e = K_f C_e^{1/n} \dots(6)$$

A linear form of Freundlich, Equation 6 is:

$$\text{Log} q_e = (1/n) \text{log} C_e + \text{log} K_f \dots(7)$$

where  $C_e$  and  $q_e$  are as mentioned before,  $K_f$  is Freundlich constant which shows the relative adsorption capacity of the adsorbent (mg/g), and  $n$  is Freundlich constant and refers to the adsorption intensity. If  $1/n$  approaches 1, the equation becomes linear. If  $1/n$  value is within 0.1 and 1, it shows a suitable adsorbate adsorption on the given adsorbent. The values  $K_f$  and  $n$  can be determined from the intercept and slope plotting of experimental data of  $\text{log} q_e$  versus  $\text{log} C_e$  respectively as shown in Figure 7 and Table 3. The correlation coefficient ( $R^2$ ) values got from Langmuir isotherm is 0.986 and from Freundlich isotherm is 0.99 for  $Zn^{+2}$  ions adsorption on to tobacco leaves so Freundlich isotherm represents a better adsorption than Langmuir isotherm.

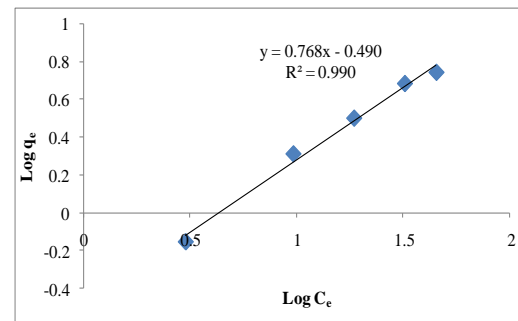


Fig. 7: Freundlich isotherm for adsorption of  $Zn^{+2}$  ions on tobacco leaves. (pH=5; T=25 °C; dosage=1g/100 ml; t=140 min; speed=200 rpm)

Table 3: Langmuir and Freundlich isotherm parameters for Zn<sup>+2</sup> ions adsorption onto tobacco leaves

Langmuir	q <sub>m</sub> (mg/g)	K <sub>L</sub> (l/mg)	R <sup>2</sup>
		10.989	0.0229
Freundlich	K <sub>f</sub> (mg/g)	1/n	R <sup>2</sup>
	3.090	0.768	0.990

### Adsorption Kinetics Models

Adsorption kinetics study the solute uptake rate which in turn determines the resident time reaction [21]. To be able to predict the mechanism which involved in the adsorption process different kinetic models have been used by several researchers. These contain pseudo-first-order model, pseudo-second-order model are widely used [19, 22].

#### Pseudo First-Order Kinetic Model

The liquid-solid phase adsorption kinetic process is explained by simple linear equation for pseudo - first order reaction kinetic [23]. It can be shown as follows [24]:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad \dots(8)$$

where q<sub>e</sub> is the amount of Zn<sup>+2</sup> ions adsorbed on adsorbent dose surface at equilibrium (mg/g) and q<sub>t</sub> is the amount of Zn<sup>+2</sup> ions adsorbed on adsorbent dose surface at time t (min), respectively. K<sub>1</sub> is the constant of pseudo-first-order adsorption rate (min<sup>-1</sup>). By integrating Equation 8 with the boundary conditions q<sub>t</sub>=0 at t=0 and q<sub>t</sub> = q<sub>t</sub> at t=t, then Equation 8 becomes:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} \times t \quad \dots(9)$$

By plotting log (q<sub>e</sub>-q<sub>t</sub>) against t, the values of pseudo-first-order rate constant (K<sub>1</sub>, q<sub>e</sub>) are determined from the slope and intercept as shown in Figure 8.

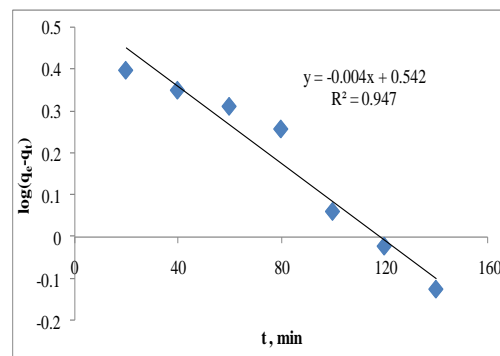


Fig. 8: Pseudo first order test for the Zn<sup>+2</sup> ions adsorption on tobacco leaves (pH=5; dosage=1g/100 ml; speed= 200 rpm; T= 25°C, C<sub>i</sub>= 50 mg/l)

#### Pseudo-Second-Order Kinetic Model

Pseudo - second order reaction kinetic showed the adsorption kinetic process of divalent metal ions onto natural adsorbents [25]. The Pseudo-second order kinetic rate is shown in Equation 10 [26].

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad \dots(10)$$

where K<sub>2</sub> is the constant of pseudo-second-order adsorption rate, (g/mg min).

Then after integration and applying boundary conditions q<sub>t</sub>=0 at t=0 and q<sub>t</sub> = q<sub>t</sub> at t=t; the Equation 10 becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_2 t \quad \dots(11)$$

Equation 11 is rearranged to obtain Equation 12 in linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad \dots(12)$$

The values (K<sub>2</sub>, q<sub>e</sub>) can be obtained from the slope and intercept by plotting t/q<sub>t</sub> against t as shown in Figure 9.



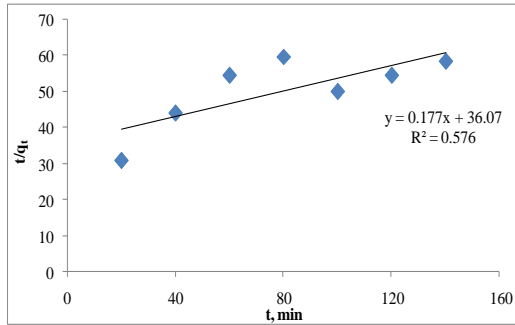


Fig. 9: Pseudo second order test for the Zn<sup>+2</sup> ions adsorption on tobacco leaves (pH=5; dosage=1g/100 ml; speed= 200 rpm; T= 25°C, C<sub>i</sub>= 50 mg/l)

The correlation coefficient values (R<sup>2</sup>) show a good fit of pseudo-first -order model with the experimental data compared to pseudo-second -order model. Between the  $q_{e,exp}$  and  $q_{e,cal}$  there is only a little difference as shown in Table 4. Therefore, the first-order model can be applied for Zn<sup>+2</sup> ions adsorption process.

Table 4: Comparison of adsorption rate constants, experimental and calculated  $q_e$  values for the pseudo-first- and -second-order reaction kinetics for removal of Zn<sup>+2</sup>ions by tobacco leaves

Pseudo-first - order	$q_{e,exp}$ (mg g <sup>-1</sup> )	$K_1 \times 10^{-3}$ (min <sup>-1</sup> )	$q_{e,cal}$ (mg g <sup>-1</sup> )	$R^2$
		3.15	9.212	3.483
Pseudo-second - order	$q_{e,exp}$ (mg g <sup>-1</sup> )	$K_2 \times 10^{-3}$ (min <sup>-1</sup> )	$q_{e,cal}$ (mg g <sup>-1</sup> )	$R^2$
	3.15	2.792	5.649	0.576

**Forward Osmosis Process**

**Effect of Draw Solution Concentration**

Increasing the draw solution concentration (C<sub>d</sub>) caused increasing the water flux due to an increase in driving force and water transport through the membrane. These observations are well agreed with the results of [27]. In the FO process as the feed solution is placed at the active layer of the membrane and draw solution is placed at the support layer of the membrane, with time the water

flux decreased and reached the steady state after 3 h due to decreasing in driving force for water transport through the membrane and increasing in dilution of the draw solution, These results are well agreed with the results of [28], the results as shown in Figure 10.

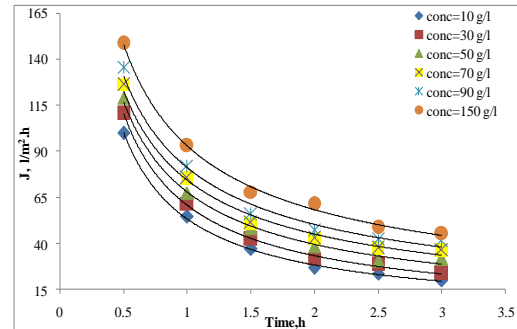


Fig. 10: Water flux with time at different MgCl<sub>2</sub> concentration (Cd) (Zn<sup>+2</sup> concentration = 50 mg/l, Temp. of FS & DS = 25 °C, pH of feed = 5, Q<sub>d</sub> = 40 l/h, Q<sub>f</sub> = 40 l/h, and p = 0.25 bar)

**Effect of Zinc Concentration in Feed Solution**

Figure 11 shows the effect of different feed solution concentration (C<sub>f</sub>) (Zn<sup>+2</sup>) on water flux with time. The amount of the permeate water flux decreased when the Zn<sup>+2</sup> ions concentration increased with the time due to increase in the osmotic pressure of feed solution and leads to reducing the overall driving force (high osmotic pressure of DS – low osmotic pressure FS) for water transport through the membrane. This conclusion corresponds with the results of, [29].

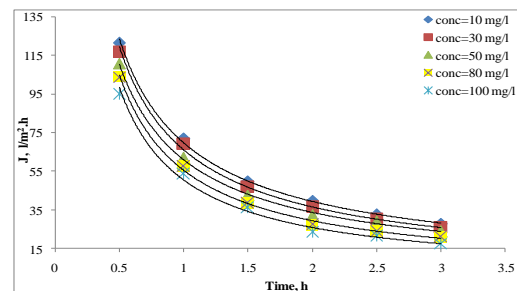


Fig. 11: Water flux with time at different Zn<sup>+2</sup> concentration in feed solution (MgCl<sub>2</sub> concentration = 30 g/l, Temp. of FS & DS =25 °C, pH of feed =5, Q<sub>d</sub> = 40 l/h, Q<sub>f</sub> =40 l/h, and p = 0.25 bar)

### Effect of Zinc Feed Solution pH

In forward osmosis process, pH effect on the permeate flux with time as shown in Figure 12. Lowering the pH of feed solution leads to increase the solubility of dissolved salt and decrease the rate of zinc salt scaling on the membrane surface, this lead to decrease the feed solution osmotic pressure and increase the water flux [30]. But increasing the feed solution pH leads to accelerate the zinc salt deposition on the membrane surface and causes concentrative external concentration polarization (ECP) on the membrane, this leads to decrease the water flux with time. This behaviour in agreement with [31].

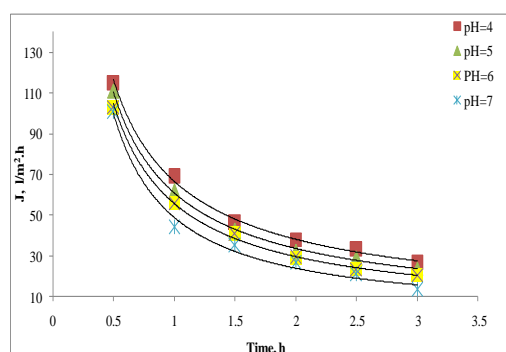
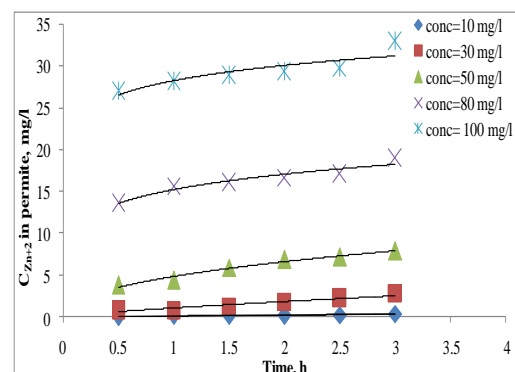


Fig. 12: Water flux with time at different pH of Zn<sup>+2</sup> feed solution (MgCl<sub>2</sub> concentration = 30 g/l (Zn<sup>+2</sup> concentration = 50 mg/l, Temp. of FS & DS = 25 °C , Q<sub>d</sub> = 40 l/h, Q<sub>f</sub> = 40 l/h, and p = 0.25 bar)

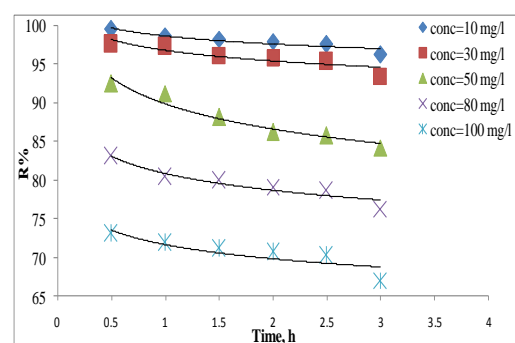
### Concentration of Feed Solute in Permeate and Membrane Rejection Percentage (R %)

Figure 13 illustrates concentration of zinc salt in permeate increased and rejection percentage (R %) of zinc salt decreased with increasing in operating time. Increasing in concentration of zinc metal decreases rejection percentage with the time due to formation of zinc layer on the surface of membrane retarding the back diffusion of the zinc salt from the membrane surface back to the bulk solution. Consequently, a

larger concentration of zinc metal is created and it is prepared for its diffusion across the CTA membrane and this observation agree with, [32].



(a)



(b)

Fig. 13: Effect of time on (a) product Zn<sup>+2</sup> ions concentration (b) rejection percentage (R %) at different Zn<sup>+2</sup> concentration in feed solution. Experimental condition : MgCl<sub>2</sub> concentration = 30 g/l, Temp. of FS & DS = 25 °C, pH of feed =5, Q<sub>d</sub> = 40 l/h, Q<sub>f</sub> =40 l/h, and p = 0.25 bar

### Comparison Between Adsorption and Forward Osmosis Process

Table 5 shows that forward osmosis process is an excellent process for removal of Zn<sup>+2</sup> ions from wastewater with removal efficiency percentage 96.2 % compared with the adsorption process with removal efficiency percentage 70 %. Figure 14 shows the comparison of the rejection percentage (R%) between adsorption and forward osmosis.

Table 5: Comparison the rejection percentage (R%) between adsorption and forward osmosis at different inlet concentration of zinc solution

Initial zinc conc.	Adsorption (R %)	forward osmosis (R %) (after 3hr)
10	70	96.22
30	68	90.423
50	63	84.202
80	60	76.282
100	55	67.009

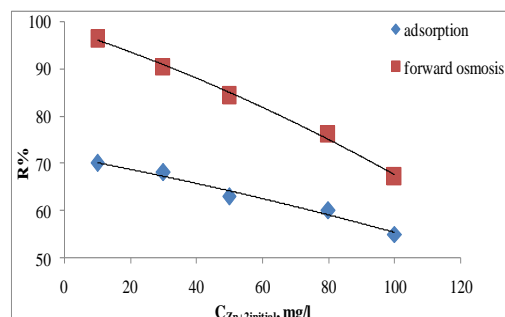


Fig. 14: comparison the rejection percentage (R %) between adsorption and forward osmosis (forward osmosis process, MgCl<sub>2</sub> concentration = 30 g/l, Temp. of FS & DS = 25 °C, pH of feed =5, Q<sub>d</sub> = 40 l/h, Q<sub>f</sub> =40 l/h, and p = 0.25 bar, adsorption process, pH=5; dosage= 1g; T=25°C; t= 140 min; speed=200 rpm)

### Conclusions

- 1- The adsorption studies showed that the adsorbent (tobacco leaves) is effective for the Zn<sup>+2</sup> ions removal from aqueous solutions.
- 2- It was found that maximum adsorption occur at optimum contact time 140 min, optimum pH 5, and optimum dose of adsorbent about 1g/100 ml.
- 3- removal percentage of Zn<sup>+2</sup> ions was decreased with increasing the concentration.
- 4- Freundlich isotherm model give best fit to experimental data in comparison with Langmuir isotherm model, and in addition that Zn<sup>+2</sup> ions adsorption followed pseudo-first -order kinetics.
- 5- The water flux produced from the forward osmosis cell increased when the concentration of draw solution increased and decreased when the concentration of feed

solution increased and pH of zinc solution increased.

- 6- The water flux produced from the forward osmosis decreased with the time and reached the steady state after 3 h.
- 7- It was found the removal efficiency for Zn<sup>+2</sup> ions by forward osmosis is 96.2 % better than the removal efficiency by adsorption 70%.

### Nomenclature

- A.wt Atomic weight (g/mole)
- C<sub>o</sub> Initial Concentration (mg/l)
- C<sub>D</sub> Concentration of draw side (g/l)
- C<sub>e</sub> Equilibrium of Zn<sup>+2</sup> ions concentration in the solution (mg/l)
- C<sub>F</sub> Concentration of feed side (mg/l)
- C<sub>P</sub> Product concentration (mg/l)
- J Water flux (l/m<sup>2</sup>.h)
- K<sub>1</sub> Constant of pseudo - first-order adsorption rate (min<sup>-1</sup>)
- K<sub>2</sub> Constant of pseudo-second -order adsorption rate (g/mg. min)
- K<sub>f</sub> Freundlich constant (-)
- K<sub>L</sub> Langmuir constant related to the adsorption capacity (l/mg)
- M.wt Molecular weight (g/mole)
- M Amount of resin (g)
- n Freundlich constant (-)
- q<sub>e</sub> Amount of adsorbate adsorbed on the surface of biomass at the equilibrium (mg/g)
- q<sub>m</sub> Maximum capacity of adsorption for Zn<sup>+2</sup> ions adsorbed on the surface of biomass (mg/g)
- q<sub>t</sub> Amount of Zn<sup>+2</sup> ions adsorbed on adsorbent dose surface at time t (min)
- R Rejection Percentage (%)
- t Time (hr)
- T Temperature (°C)
- V Volume of solution (l)
- W Weight of metal solute (mg)

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