

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Assessment Of Zinc (II) Removal From Aqueous Solutions Using Prepared Activated Carbon And Bentonite.

Abdulrahman G Alhamzani^{1*}, Mohamed I Attia¹, and Mohamed A Habib^{1,2}.

¹Chemistry Department, College of Science, Al-Imam Mohamed ibn Saud Islamic University (IMSIU), Riyadh, Kingdom of Saudi Arabia.

²Chemistry of Tanning Materials and Leather Technology Department, National Research Centre, P.O. 12622 Dokki, Giza, Egypt.

ABSTRACT

Recently, adsorbents from low-cost available materials is widely used as eco-friendly and economical approaches to safeguard the environment. It is a physical process of depositing substances on the solid with no any chemical reaction with the adsorbent. In this study, activated carbon was prepared from local biomass (e.g. date-palm tree fronds) and characterized. Saudi Bentonite is obtained from Jeddeh city and characterized. Both natural adsorbents were used to investigate the adsorption of zinc (II) from aqueous solutions. Isotherms models, such as Langmuir, Freudlich, and Brauner-Emmett-Teller, were undertaken and evaluated. Series of investigation such as rate constant of adsorption (K_{ad}), rate constant for intraparticle diffusion (K_p), pore diffusion coefficient (D), overall reaction rate(K), equilibrium constant (K_c), activation energy (E) and the thermodynamic functions ΔG° , ΔH° and ΔS° were examined. The effect of time, sorbent dose, initial concentration and the pH at different temperatures were experimentally studied. Results show that zinc adsorption onto the studied adsorbents is pH dependent. The kinetics of adsorption of zinc (II) on the studied adsorbents were investigated as first order diffusion controlled, endothermic, and spontaneous process. Bentonite are capable of removing zinc (II) from an aqueous solutions.

Keywords: Zinc (II), Activated Carbon, Bentonite, Adsorption, Kinetics

**Corresponding author*

INTRODUCTION

Heavy metals are one of the possible sources of chemical pollutants in water and environment. They have harmful impacts in both environment and societies including toxicity, hazards to human health, and aquatic life [1-2]. There is a relation between trace elements and environmental quality. It is based upon the need to safeguard human's health. Alkali-earth and specially alkali metals participate in some dynamic activities in human bodies, such as muscle function and nerve conduction. Many Metal ions are soluble in aqueous solutions, so they do not undergo biodegradation which may be subject for living systems and accumulate in the environment [3]. If trace elements increased in the physiological processes, they have become pollutants and toxic which will cause serious problems diseases symptoms [4]. In the other hand, heavy metals cause many kinds of diseases represented in headache, cancer, distort reproduction, and kidney failure which may lead to death. Their accumulation in the living body is a gradual process because of their non-biodegradability coupled with a long half-life [5]. Combination of certain metals with other metals increases the toxicity under specific environmental conditions. For example, cadmium toxicity was increased in the presence of copper or zinc. Zinc, copper, cadmium, nickel, and lead may toxic to aquatic life depending on other water quality conditions, such as pH, temperature, hardness, turbidity, and carbon dioxide content. Copper is toxic to fish but toxicity depends upon other parameters such as alkalinity, pH, hardness and organic compounds frequently present in water [6].

Common methods, including oxidation, reduction, ion exchange, chemical precipitation, complexation, reverse osmosis, membrane filtration, adsorption, etc [7-11], have been used for removal of heavy metals from aqueous solutions. However, these processes have significant disadvantages, such as incomplete removal of metal ions, high quantities of toxic sludge, required additional reagents and have high operation cost. Adsorption metals at the solid-liquid interface is an efficient physicochemical process because it can remove metals in a simple approach [12]. Natural materials such as Bentonite have been widely used for adsorption metals from aqueous solutions because of its capacity, effectiveness, abundance, and low-cost. Recent studies showed that bentonite has a higher surface area and cation exchange capacity [13-16]. These advantages of the natural clays make them suitable for water purification uses. In contrast, prepared activated carbon from abundant biomass has attracted attention of many researchers and research centers because its reliability in adsorption pollutants from water and waste water. Activated carbon has large surface area, high adsorption capacity, high degree of surface reactivity, and porous structure [17-18].

Activated carbon is commonly used in a wide range of adsorption to increase extent in the water treatment to eliminate substances affecting odor, taste and color in halogenized hydrocarbons and other organic pollutants. Its being low-cost biomass, it has been reported that is feasible for removing heavy metals from aqueous solution and aqueous effluents [19-22].

The objective of this work is devoted to study the kinetics and thermodynamics models of zinc (II) adsorption from aqueous solution using prepared activated carbon (PAC) from date-palm tree (*Phoenix dactylifera*) and Saudi clay bentonite. Adsorption isotherms, rate mechanism, adsorption dynamics, and thermodynamic parameters were investigated in this study. As well as, the suitability of Langmuir, Freundlich, and Brunauer-Emmett-Teller, were undertaken and evaluated. Kinetic constants, pH, temperature, and thermodynamic functions were studied and evaluated.

METHODOLOGY

MATERIALS AND METHODS

Adsorbents Materials:

Preparation of Activated carbon

Prepared activated carbon (PAC) used in this work was prepared from fronds of date palm tree waste. It was obtained from a local farm in Riyadh city, Saudi Arabia. Fronds were washed with distilled water to remove impurities and dust, dried in an open air at room temperature for one day, and then grinded using stainless steel grinder several times until desirable particle size.

Carbonization process:

The grinded materials were dried in an oven at 100 °C for 2 hours. The dried materials were burned at 400° C for 2 hours in a furnace. The obtained sample were cooled at room temperature, then soaked with concentrated ortho-phosphoric acid for 2 hours in a ratio of 2:1 (H₃PO₄ solution /sample, W/W). Then, the material was washed with excess of water to remove the acid till the pH become 7.0. The washed material was dried at room temperature for 90 minutes, and dried in an oven at 200 °C for 90 min. Thermal activation was carried out at 650° C for 20 min.

Adsorption studies investigation:

Investigation of adsorption studies were carried out against bentonite. The Bentonite clay was obtained from Jeddah city, west coast of Kingdom of Saudi Arabia. The adsorbents (i. e. Prepared Activated Carbon and Bentonite) were dried in an oven at 100°C for one hour. Uniform materials of the adsorbents were obtained through sieving (a sieve 30 mesh/inch; 0.1 – 0.315 mm) to remove large solids.

All the chemicals that used in this work were of analytical grade and were obtained from BDH, and E. Merck. A stock aqua zinc (II) solution (1000 mg Zn/L) was prepared using zinc sulphate heptahydrate (ZnSO₄.7H₂O).

Analytical Procedures:

The adsorbents used in this study were chemically analyzed. Chemical compositions of PAC and Bentonite [13] are listed in Table (1). The determination of divalent zinc in solution was carried out by 902 GBC double beam atomic absorption spectrometer (Australia), with air-acetylene burner-head provided with integrated readings in absorbance or concentration. The optimum instrumental conditions for determination were: lamp current 6mA, observation height (slit width) 0.2 cm and wave length 240.7nm.

Experimental procedures

The experiments were designed to determine (1) Adsorption isotherms; (2) the rate mechanism and adsorption dynamics, and (3) thermodynamic parameters. The adsorption kinetics of Zn (II) on PAC and bentonite were evaluated through the use of controlled experiments in a batch system. A working solution of Zn (II) was prepared by diluting a sufficient volume of the stock solution to achieve the desired concentration.

For each adsorption data point, the dry adsorbents were accurately weighed and placed into the glass vials. The glass vials were then filled with the zinc solution (with the specified concentration), sealed immediately and allowed to equilibrate in a gyrating shaker equipped with a constant temperature bath 20°C (GFL 1083, THERMOLAB).

The following parameters were investigated:

Effect of Contact Time (Equilibrium Time)

The equilibrium time was investigated at different temperatures 30°C, 40°C, 50°C, and 60°C for each adsorbent type.

Effect of Initial Concentration

Effect of initial concentration was investigated at different temperatures 30°C, 40°C, 50°C, and 60°C for each adsorbent type. The loaded vials were left in water bath to the equilibrium time found in the above experiment, then the solution in each vial was filtered and zinc concentration was determined in the filtrate.

Effect of Mass of the Added Adsorbents

To collect the data required for fitting the different adsorption isotherms, a series of (0.05-0.2) g from each adsorbent were placed in a series of glass vials. To each vial 25 mL of zinc (II) solutions (25 ppm Zn) was

added. The temperature of the shaker water bath (150 rpm) was maintained at 20°C. After shaking for a time equal to the equilibrium time, the solution was filtered and zinc concentration was determined in the filtrate. These all steps were repeated at different temperatures 30°C, 40°C, 50°C, and 60°C for each adsorbent type.

Effect of pH of Solution

0.1 g from each adsorbent were placed in a series of stocked glass vials To each vial 25 mL of zinc (II) solution (25 ppm Zn) with variable pH (2-8) was added. The shaker water bath (150 rpm), temperature was maintained at 20°C. The loaded vials were left in water bath to the equilibrium time, then the solution in each vial was filtered and zinc concentrations were determined in the filtrate. These all steps were repeated at different temperatures of 30°C, 40°C, 50°C, and 60°C for each adsorbent type.

Application of adsorption Models:

The adsorption data points obtained at different conditions as described above were utilized to fit some adsorption isotherms and describing the kinetics of adsorption.

Adsorption Isotherms

Langmuir isotherm

$$\frac{1}{(x/m)} = \frac{(1/b)+1}{abc} \dots\dots\dots (1)$$

Plotting the relation between **1/(x/m)** against **1/C**, finding the Langmuir. Constants **a** and **b** from the slope and the intercept respectively, where,

- x = amount of material adsorbed (mg)
- m = weight of adsorbent (mg)
- c = concentration of material remaining in solution after attainment of adsorption
- a,b = are constants corresponds to the surface concentration and mono layer coverage and represents the maximum value of x/m that can be achieved as c is increased. The constant b is related to the energy of adsorption and increases as the strength of the adsorption bond increases.

Freundlich’s Isotherm:

$$\log(x/m) = \log k + (1/n) (\log c) \dots\dots\dots (2)$$

Plotting the relation between **log x/m** against **log c**, finding the Freundlich constants **k** and **n**, where,

- x = amount of solute adsorbed (mg)
- m = weight of adsorbent (mg)
- c = concentration of solute remaining in solution after adsorption is completed (mg/L). k,n = are constants and the units of k are determined by the units of x/m and c. The constant k in the Freundlich equation is related primarily to the capacity of the adsorbent for the adsorption.

BET isotherm :

$$C/(C_s - C) x / m = 1/A X_m + C / C_s . A-1/A X_m ..(3)$$

Plotting the relation between **C/(C_s-C) x / m** against **C / C_s** , finding the BET constant **A**, where :

- x = amount of solute adsorbed (mg),
- m = weigh of adsorbent (mg),
- X_m = amount of solute adsorbed in forming a complete monolayer (mg/mg),

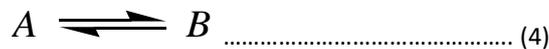
C_s = saturation concentration of solute (mg/L),
 C = concentration of solute in solution at equilibrium (mg/L) and
 A = a constant to describe the energy of interaction between the solute and the adsorbent surface.

Adsorption dynamics:

Determination of overall reaction rate constant K:

The kinetics of sorption by the solute uptake rate which determines the residence time required for completion of the sorption reaction was described [23]. The sorption kinetics ultimately controls the process efficiency. In this research following the same approach as described [23], it was considered that the sorption of organic compounds from a liquid phase to a solid phase is a reversible process with equilibrium being established between the two phases. In the same way the sorption of the metallic ions from a liquid phase to a solid phase can be considered, also, a reversible process with equilibrium being established between the two phases.

The kinetic model used in this research to describe the reaction rates was based on the assumption that the adsorption of the metallic ions onto the used adsorbents (PAC and bentonite) is a diffusion controlled first order reversible process. It can be expressed as:



The rate equation for the reaction can be written as:

$$\frac{dC_B}{dt} = \frac{dC_A}{dt} = K_1 (C_{A0} - X_A C_{A0}) - K_2 (C_{B0} + X_A C_{A0}) \dots\dots\dots (5)$$

where,

- C_{A0} : initial concentration of solute in solution at time, $t=0$
- C_{B0} : initial concentration of solute on sorbent at time, $t=0$
- C_A : concentration of solute in solution at any time during the reaction
- C_B : concentration of solute on sorbent at any time during the reaction
- K_1 : first order adsorption rate constant
- K_2 : first order desorption rate constant

At the equilibrium condition:

$$\frac{dC_B}{dt} = - \frac{dC_A}{dt} = 0 \dots\dots\dots (6)$$

and hence:

$$X_{ae} = \frac{\{K_c - C_{B0}/C_{A0}\}}{(1 + K_c)} \dots\dots\dots (7)$$

where,

- X_{ae} = fraction of solute adsorbed at equilibrium
- K_c = equilibrium constant defined as

$$K_c = K_1 / K_2 = C_{B0} + (C_{A0} \cdot X_{Ac}) / C_{A0} - (C_{A0} \cdot X_{Ac}) \dots\dots\dots(8)$$

In terms of equilibrium conversion the differential form of the rate equation is:

$$dX_A/dt = K_1(X_{Ae}-X_A) - K_2(X_A-X_{Ae}) = (K_1+K_2) (X_{Ae}-X_A) (9)$$

Integration of equation (9)

$$-\ln(1 - X_A / X_{ae}) = (K_1 + K_1 / K_c) t$$

$$\ln(1 - X_A / X_{ae}) = -K t \dots\dots\dots(10)$$

where, $K = \text{overall rate constant} = (K_1 + K_1 / K_c) = (K_1 + K_2) \dots\dots\dots(11)$

The overall rate constant (K) is calculated from the plot of: $\ln(1 - X_A / X_{ae})$ versus reaction time K_1 and K_2 can be calculated by using equations (8) and (11)

Particle diffusion control process:

The intracrystalline diffusivity is determined by application of Bhattacharya and Venkobachar equation (1984) in the form:

$$t_{1/2} = 0.03 r_0^2 / D \dots\dots\dots(16)$$

where, $t_{1/2}$: time for the adsorption of half amount of metal
 r_0 : radius of the adsorbent, calculated by an electronic microscope for bentonite and r_0 for both PAC and carbon soot as determined elsewhere (El-Sarawy A.A., 1994).
 D: pore diffusion coefficient.

Determination of the rate constant for intraparticle diffusion k_p :

Plotting the relation between the adsorbed amounts against the square root of time, the slope will be equal to the k_p [24-25].

Determination of rate constant for adsorption k_{ad} :

Application of Lagergren’s equation [26], in the form:

$$\log(Q_e - Q) = \log Q_e - (k_{ad} / 2.303)t \dots\dots(17)$$

where,

- Q_e : amount of metal adsorbed at equilibrium
- Q : amount of metal adsorbed at time t
- k_{ad} : rate constant for adsorption vary according to the temperature.

Then, plotting the relation between $\log(Q_e - Q)$ against (t) , a linear relation is obtained, the slope of which will be equal to $(-k_{ad}/2.303)$

Estimation of thermodynamic parameters E , ΔG° , ΔH° , & ΔS° :

Determination of activation energy (E):

The experimental activation energy was determined using different values of overall rate constant (K) against their corresponding temperatures values in Kelvin from Arrhenius’ equation

$$K = A e^{-E/RT}$$

- Where, A: is a temperature-independent factor called “frequency factor”
- K: is a specific rate constant
- E: is the activation energy, representing the minimum energy that the reacting system must have for the reaction to proceed.

The equation can be written in logarithmic form (Poos, V.J.P. et.al., 1978):

$$\ln(K) = \ln(A) - (E/R)(1/T) \dots\dots(18)$$

The values of (E) can be calculated by plotting the relation between **Ln(K)** against the **reciprocal of the Kelvin temperature**, the slope will be equal to **(-E/R)**.

Thermodynamic parameters ΔG, ΔH, & ΔS:

Following the same approach [23], the thermodynamic parameters such as ΔG, ΔH, & ΔS:

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots(19)$$

where, ΔG: change in free energy, cal/mol
 ΔH: change in enthalpy, cal/mol
 ΔS: change in entropy, cal/mol
 T: absolute temperature,(K)

$$\ln(K_c) = (\Delta S/R) - (\Delta H/R)(1/T) \dots\dots(20)$$

R: gas constant=1.986 cal/mol K
 K_c: equilibrium constant

then, plotting the relation between **ln(K_c)** and **(1/T)** finding the **ΔS** and **ΔH** from the slope and the intercept, hence **ΔG** can be calculated, where,

$$K_c = (C_{B0} + C_{A0} \cdot X_{AC}) / (C_{A0} - C_{A0} \cdot X_{AC}) \dots\dots(21)$$

C_{AO}: initial concentration of solute at time, t
 C_{BO}: initial concentration of solute on sorbent at time, t
 X_{AC}: fraction of solute adsorbed on sorbent at equilibrium

RESULTS

Activated carbon investigation

Surface morphology of the prepared active carbon is shown in figure 1. The images of the Scanning Electron Microscopy [SEM] describe the morphology of the surface, they show good porosity and grooves formation inside the surface of the sample. Regular distribution of the grooves confirms that the prepared activated carbon sample has a great adsorption capacity and it is possible to use as a high absorption nonconventional surface. Therefore, the prepared activated carbon of a great surface area and uniform porous structure has been successfully attended.

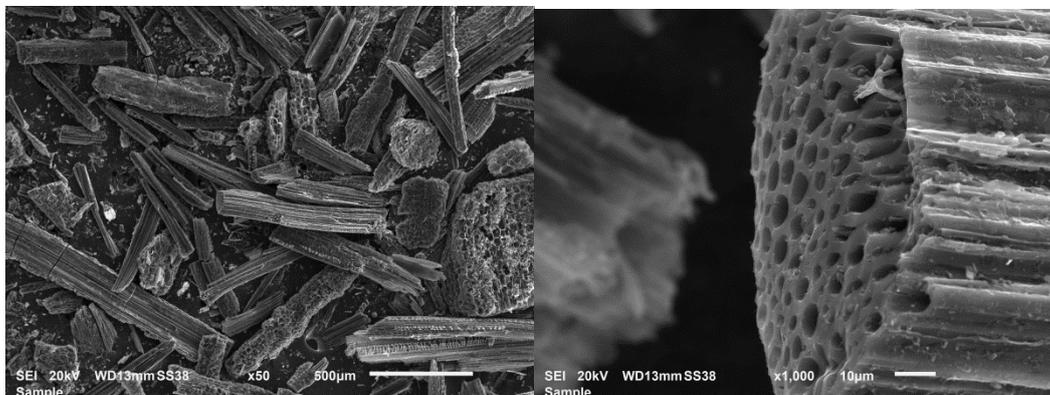


Figure1: SEM images of prepared activated carbon.

Chemical Analysis of the used adsorbents:

The used adsorbents were chemically analyzed for different oxides and metal concentrations. Also, the pH of adsorbents solutions was determined. As shown in Table (1), It is obvious, from these results that the adsorbent solutions are neutral (pH = 8). The concentration of zinc found was considered in the calculations.

Table (1): Characteristics and Chemical Composition of Used Adsorbents

Analyte %	Bentonite	PAC
SiO ₂	58.00	2.14
CaO	2.00	0.51
MgO	1.85	0.60
Na ₂ O	2.00	1.65
K ₂ O	1.00	0.90
Al ₂ O ₃	20.00	0.14
SO ²⁻ ₄	7.65	0.00
Cl ⁻	0.15	0.00
P ₂ O ₅	0.20	0.00
Fe	1.98	0.60
Co (ppm)	00.00	0.00
Zn (ppm)	00.04	0.01
Mn (ppm)	94.01	21.29
pH	7.9	7.80
Loss of weight at:		
100°C	8.3	2.10
1000°C	16.53	94.96

Evaluation of the sorption process:

Two important physical-chemical aspects for the evaluation of the sorption process as a unit operation are the equilibrium of sorption and the kinetics. Sorption equilibrium is established when the concentration of metal in a bulk solution is in dynamic equilibrium with that of the interface.

Sorption equilibrium:

Critical equilibrium time and effect of initial zinc concentration on metal adsorption:

The remaining concentration of zinc in solution decreases with time up to 50, 60 and 70 min. for PAC and bentonite respectively, this shows that equilibrium is attained at 50, 60 and 70 min. for them respectively, Fig.(1). The least equilibrium time for different metal ions is achieved when utilizing PAC as adsorbent. Bentonite demonstrates the longest equilibrium time. However, the results indicate that, the effect of the initial metal-ion concentration on the remaining concentration of metal ions, in liquid phase at the determined equilibrium time indicates a linear trend between the amount of the adsorbed ion and the initial concentration. These results commensurate first order reactions.

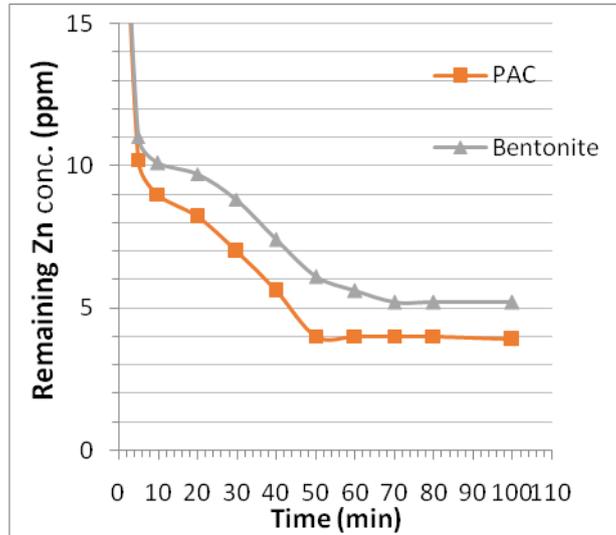


Fig (1): Variation of remaining Zn concentration with time at 20°C

Effect of the solution pH on zinc adsorption:

The effect of pH change on zinc adsorption at 20°C is illustrated in Fig.(2), The data demonstrate that, Zn(II) removal by the used adsorbents increases with increasing in pH till the equals pH 6.0. A similar behavior has been reported by many authors [33-37], for the uptake of metal ions on various adsorbents. The influence of pH on Zn (II) removal can be explained on the basis of an electrostatic interaction model [38]. As the pH decreases, the surface of the adsorbents exhibits increasing positive characteristics. Since the species to be adsorbed, Zn^{2+} , is also positive, the adsorption is not favored. In addition, H^+ ions present at higher concentration in the reaction mixture compete with Zn^{2+} ions for the adsorption sites resulting in the reduced uptake of Zn (II). On the contrary, as pH increases the adsorbent surface becomes more and more negatively charged and therefore the adsorption of positively charged Zn^{2+} and $Zn(OH)^+$ species are more favorable.

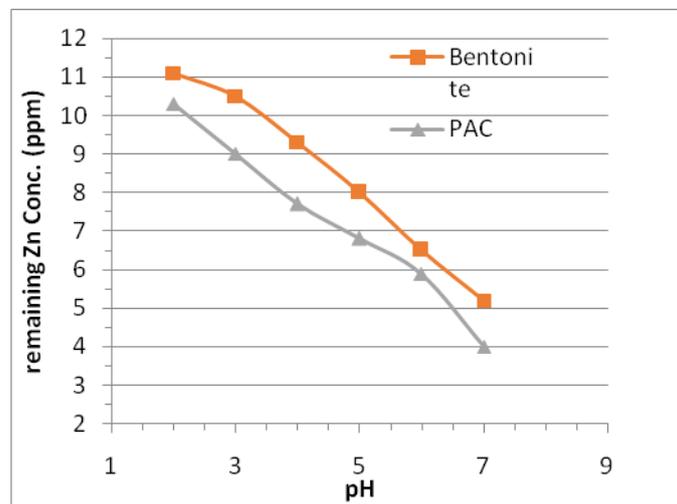


Fig (2): Variation of remaining Co concentration with pH 20°C

Application of adsorption models:

Adsorption Isotherms:

For studying the adsorption isotherms, the effect of adsorbent dose on the adsorption process (keeping the metal concentration, pH, and time of agitation constant) were studied indicating that by increasing in the adsorbent doses, the remaining zinc concentration is decreasing.

Isothermal data have been used to calculate the ultimate sorption capacity of the adsorbents by substituting the required equilibrium concentrations in the Langmuir, Freundlich and Brunauer, Emmett & Teller (BET) equations. Table (2) summarizes the Langmuir, Freundlich and BET parameters of zinc adsorption at different temperatures. With increasing the temperatures, the Langmuir constant, a (which is an indicative of maximum adsorption capacity) was found to decrease whilst the Langmuir constant, b (which is a measure of adsorption energy), decrease in low trend. On the other hand, Freundlich constant, K (which is a measure of adsorption capacity) showed an increasing trend with increasing the temperature. At the same time, the Freundlich constant, n , (a measure of adsorption intensity), show a slight decrease with increasing the temperature. In case of Brunauer-Emmett-Teller (BET) constant, A , (describing the energy of interaction between the solute and adsorbent surface) showed a decreasing trend with increasing the temperatures indicating that in all cases there is a decreasing trend in the interaction between the zinc ions and the adsorbents by increasing the temperature.

Sorption kinetics:

Determination of overall reaction rate K:

The kinetics of zinc adsorption by two adsorbents were investigated during this phase of the experiment. Kinetic experiments were conducted at various temperatures ranging between 20°C and 60°C.

The results of the overall rate constant (K) calculated from the negative value of the slope of the relation between $\ln(1-X_a/X_{ac})$ versus time (t) and the results are summarized in Table(2). These results may be correlated with the thermodynamic functions ΔH given in Table (2) which indicate that the process is endothermic one, indicating that the adsorption rate increases with the increasing of temperature.

Determination of Intra-crystalline Diffusivity D_c and Intraparticle diffusion coefficient: Determination of pore diffusion coefficient D :

The pore diffusion coefficient D and intra-crystalline diffusivity D_c , were determined and collected in Table (2). D were found to be 1.6×10^{-8} and $4.6 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for zinc adsorption on bentonite and PAC, respectively, D_c values were found to be approximate values. From the values of K_p and D , it may be indicated that the process is governed by diffusion but pore diffusion is not the only rate limiting step [27].

Determination of rate constant for intraparticle diffusion k_p :

In a batch reactor with rapid stirring, there is also a possibility that the transport of adsorbate ions from a solution into the pores of the adsorbent is the rate controlling step [28-29]. This possibility was tested in terms of a graphical relationship between the amount of zinc adsorbed and the square root of time. It may be explained as: in the initial curved portions are attributed to boundary layer diffusion effects [28], while the final linear portions are due to intraparticle diffusion effects [29].

The rate constant for intraparticle diffusion K_p , at different temperatures was determined from the slopes of the linear portions of the respective plots and are given in Table (2).

Determination of rate constant for adsorption k_{ad} :

The rate constant for adsorption of the zinc on different adsorbents were determined using Lagergren's equation. The values of K_{ad} at different temperatures were calculated from the slopes of the respective lines plots and listed in Table (2). It may be concluded from the values of K_{ad} that the reaction taking place is of first order.

Estimation of thermodynamic parameters E , ΔG° , ΔH° , & ΔS° :

Determination of activation energy E :

The values of E can be calculated from the relation between LnK against the reciprocal of the Kelvin temperature. The activation energy summarized in Table (2) for different adsorbents indicates that these values are small. Low activation energy

Determination of thermodynamic parameters:

The kinetic model that was used in this research to describe the reaction rate was based on the assumption that the adsorption of zinc onto the used adsorbents is a diffusion controlled and first-order process. The thermodynamic parameters such as free energy change ΔG° , enthalpy change ΔH° , and entropy change ΔS° , were determined from the logarithmic values of the equilibrium constant K_c versus the inverse temperature in Kelvin ($1/T$), revealed the values of the ΔH° , and ΔS° , from the slope and the intercept respectively and hence ΔG° can be calculated, summarized in Table (2). The positive values of differential heat of adsorption ΔH° , suggests that the adsorption of zinc onto the different used adsorbents is an endothermic process. The negative values of the free energy change ΔG° , suggest the spontaneous nature of the adsorption process. However, the negative ΔG° value increased with an increase in temperature, indicating that the spontaneous nature of adsorption is inversely proportional to the temperature [30].

Table (2): Adsorption parameters of zinc by powdered activated carbon (PAC) and bentonite

Parameter	PAC					Bentonite				
	T=20°C	T=30°C	T=40°C	T=50°C	T=60°C	T=20°C	T=30°C	T=40°C	T=50°C	T=60°C
L a	-0.122	-0.130	-0.102	-0.198	-0.244	-0.103	-0.118	-0.127	-0.157	-0.169
b	-4.6×10^{-3}	-5.2×10^{-3}	-9.5×10^{-3}	-3.1×10^{-3}	-1.9×10^{-3}	-4.3×10^{-3}	-3.9×10^{-3}	-4.3×10^{-3}	-	-
F n	0.457	0.498	0.418	0.353	0.472	0.474	0.408	0.380	0.248	0.400
k	0.214	0.363	0.282	0.214	5.890	0.162	0.115	0.115	0.015	2.29
BET A	-1.66	-1.77	-1.96	-2.90	-3.55	-1.34	-1.59	-2.11	-2.47	-2.57
Kad	0.036	0.037	0.042	0.034	0.0300	0.329	0.325	0.378	0.269	0.279
K	0.036	0.037	0.041	0.043	0.046	0.046	0.047	0.0489	0.0499	0.052
Kc	5.25	6.67	5.76	6.81	7.33	6.14	5.76	4.95	4.95	3.81
Kp	1.268	1.254	1.247	1.208	1.167	1.242	1.196	1.188	1.148	1.135
ΔG	-0.704	-0.784	-0.864	-0.944	-1.024	-0.77	-0.87	-0.97	-1.07	-1.17
ΔH	1.64					2.16				
ΔS	0.008					0.01				
E	1.24					0.589				
D	4.6×10^{-10}					1.6×10^{-8}				
ro	6.24×10^{-4}					4.35×10^{-3}				

L a: Langmuir constant (mg/g), **b**: Langmuir constant (l/mg); **F n**: Freundlich constant, **k**: Freundlich constant (mg/g); **B A**: Brunaur-Emmet-Teller constant; **Kad**: Lagergren' rate constant (min^{-1}); **K**: Overall reaction rate(min^{-1}); **Kc**: Equilibrium constant (min^{-1}); **Kp**: Rate constant of intraparticle diffusion (min^{-1}); **ΔG**: Free energy change (kcal/mol); **ΔH**: Enthalpy change (kcal/mol); **ΔS**: Entropy change (kcal/mol); **E**: Activation energy(kcal/mol); **D**: Pore diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$); **ro**: Radius of adsorbent (cm)

CONCLUSION

Bentonite (a natural ore, which are cheap and abundant) may be used as a substitute for PAC for the removal of zinc ions from aqueous solutions and may be an alternative for the more costly adsorbents, giving promising results. Bentonite compared against PAC for the capability of removal of zinc ions from an aqueous solution, the equilibrium time for their adsorption was of the order bentonite > prepared activated carbon.

The kinetics of adsorption of the studied metal onto the utilized adsorbents were investigated as first order and diffusion controlled process, and on the other hand from the linear relationship between the initial

and remaining metal concentration, and linear relationship between the Log ($Q_e - Q$) and Time indicated that the process is first order.

Thermodynamic functions ΔH , ΔG and ΔS were evaluated and indicated that the processes of adsorption of zinc is endothermic and spontaneous.

Zinc adsorption on the used adsorbents bentonite and PAC was pH dependent. The most suitable pH for its removal was found to be 6, after the corresponding pH precipitation may occur.

The removal of hydrolyzed form of the studied heavy metal cation Zn at high pH was preferred than the heavy metal cation and this may be referred to the increase in cation exchange capacity which may result from increasing the hydrolysis of the exchanging cations, since the hydroxy complexes e.g. $ZnOH^+$, is sorbed on most solids in preference to the uncomplexed cations Zn^{2+} .

From the correlation coefficient for the different isotherm models, it is indicated that, in case of zinc it was found that zinc adsorption is more fitted with Langmuir isotherm model on PAC at 30°C.

ACKNOWLEDGMENTS

The authors would like to thank and appreciate the Deanship of Academic Research at Al-Imam Mohammad Ibn Saud Islamic University (IMSIU), Riyadh, Kingdom of Saudi Arabia, for funding this research through research project Number 361221, 1438 H.

REFERENCES

- [1] Woodford C. "Water pollution: an Introduction". June 4, 2017, (<https://www.explainthatstuff.com/waterpollution.html#gesampfn>) [Accessed Aug 28, 2018]
- [2] Manahan, S. E. Environmental Chemistry. 7th Ed, (2000), Lewis Publishers, USA, ISBN: 1-56670-492-8.
- [3] Laws E.A., Aquatic Pollution an Introductory Text, third ed., John Wiley and Sons, New York, 2000, pp. 23-25
- [4] Scott, M.L., Trace elements in animal nutrition, Chap. 22, pp. 555 - 591, in "Micronutrient In Agriculture", J. Mortvedt et.al., Soil Sci. Soc. of American Inc., Madison, Wisconsin, USA, 1982.
- [5] Salihi, I. U, Kutty, S. M., Isa, M. H., and Aminu, N. J. Water, Sanitation & Hygiene for Development; 2016, 6 (3): 377-388.
- [6] Hodges, L., Environmental Pollution, 2nd Ed. Holt, Reinhart and Windston, USA, 1977 p. 10.
- [7] Mohan, K. P., Singh, Water Res. 2002; 36 : 2304-2318.
- [8] Akar, T., Tunali, S., and Kiran, I. Biochem. Eng. J. 2005; 25: 227-235.
- [9] Sari, A., et al, J. Hazard. Mater. B 2007; 149: 283-291.
- [10] Patterson, J. W. Industrial Waste Water Treatment Technology, Science, New York, 1997.
- [11] Alshammari, A. G. Research Journal of Envir. Toxicology, 2015; 9(1): 17-33, 2015.
- [12] Bellir, K., Lehocine, M. B., and Meniai, A. Desalination and Water Treatment, (2013); 1-14
- [13] Kaya, A. and Oren, A. H. J. Hazardous Materials, 2005;, B125: 183-189.
- [14] K.G. Bhattacharyya, S.S. Gupta. Adv. Colloid Interface Sci., 2008; 140(2): 114-131.
- [15] Bellir, K. et al, Desalination and Water Treatment, 2013; 1-14
- [16] Alshammari, A. G. Trends in Applied Sciences Research, (2014); 9(10): 557.
- [17] Almeida, C. A. et al. Journal of Colloid and Interface Science, (2009), 332, 46.
- [18] Fernandes, A. N.; Almeida, C. A. P.; Debacher, N. A.; Sierra, M. M. S. Journal of Molecular Structure 2010; 982: 62.
- [19] K. Kadirvelu, K., Faur-Brasquet, C. and Cloirec, P. Le. Langmuir, 2000; 16 (22): 8404-8409.
- [20] Kadirvelu, K., Thamaraiselvi, K., and Namasivayam. Bioresource Tech. 2001; 76 (1): 63-65.
- [21] Kobya, M. et al. Bioresource Technology, 2005; 96 (13): 1518-1521.
- [22] Imamoglu, M. and Tekir, Oktay. Desalination, 2008; 228(1-3): 108-113.
- [23] Banerjee, K.; Paul, N. and Su Ling, C. Water Res. 1997; 31,(2): 249.
- [24] Weber, W.J. Jr and Morris, J.C. J. Sanit. Engng Div. Am. Soc. Civ. Engrs. 1963; 89, SA 2, 31.
- [25] Poots V.J.P.; McKay G. and Healy, J.J. Wat; Pollut. Control Fed. 1978; 50: 926.
- [26] Lagergren, S. 1898. Bil K. Svenska Ventenskapskad. Handl 24 as cited by Trivedi et. al. (1973) Eur. Polym. J. 9, 525.



- [27] Michelson, L.O., Gideon, P.G., Pace, E.G. and Kotal, L.H. Removal of soluble mercury from wastewater by complexing techniques, U.S.D.I. Office of Water Research and Technology, 1975; Bull. No. 74.
- [28] Crank, J. The mathematics of diffusion, Clarendon Press, London, (1965).
- [29] Mckay, G., Otherburn, M.S., and Sweeney, A.G. Wat. Res 1980; 14: 15.
- [30] Masterton, W.L., and Hurley, C.N. Chemistry principles & Reactions, Ch. 20 Saunders College Publishing Co 1989.