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KINITICS STUDIES ON THE ADSORPTION PROCESSES FOR THE REMOVAL OF Fe(III) IONS BY CATION EXCHANGE RESIN (DOWEX™ HCR-SIS) FROM WASTEWATER

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ABSTRACT

The adsorption of Fe(III) ions from wastewater solution was studied in abatch adsorption system. The study investigates the removal characteristics of Fe(III) ions from wastewater under various operating variabels such as: effect of pH, initial concentration, effect of adsorbent dosage, effect of time and temperature (25, 35 and 45 ^{o}C) and study the adsorption isotherm modeling using: langmuir, fruendlich, temkin and pyzhev isotherm, also the adsorption kinetics modeling intra-particle diffusion model and caculation the thermodynamic parameters (ΔS, ΔG, ΔH and E_a).

KEYWORDS: Adsorption, Fe(III) ions, cation exchange resin, kinetics.

INTRODUCTION

Furthermore, the adsorption of Fe(II) ions increased with increasing in solution pH. Increasing solution pH more than 3 causes precipitation rather than adsorption. The adsorption isotherm data were well fitted with the linearized Langmuir, Freundlich equations showed that adsorption process is chemisor-ptions.[1]

Fe(II) adsorption onto Saudi activated bentonite was well represented by the pseudo-second-order kinetic model. Saudi activated bentonite can be considered as a promising adsorbent for the removal of heavy metals from wastewater. It was found that adsorption of Fe(II) onto bentonite using batch techniques was effective to remove Fe(II) from wastewater. The adsorption process was affected by solution pH. Most Fe(II) removal was observed at pH of 3. The kinetics of adsorption developed also support the removal of low conce-ntrations of Fe(II) from waste water.[1]

F(II) is among the most common heavy metals in these wastewaters. Although, F(II) is essential for human, its presence above a certain level may cause harm to the human body. The maximum amount allowed of Fe(II) in drinking water is 0.3 mg/L. Excessive amount of Fe(II) in public water supplies causes turbidity, unpleasant taste and odor and vomiting. Consequently, the removal of Fe(II) is a very important issue in aquatic environments and water pollution control.[1]

Wastewaters from metal industries such as metal finishing and galvanized pipe manufacturing contains toxic substances, heavy metals, acids, alkalis, and other substances. High concentrations of metals in the effluents can ultimately reach the food chain and thus become a risk factor for human health.[2]

Iron occur in dissolved forms as single ions (Fe^{2+}) or in undissolved higher forms mainly as $Fe(OH)_3$. They can also be present in colloid form (bound to humic substances). The form of their occurrence depends on oxygen concentration, solubility of Fe compounds in water, pH value, redox potential, hydrolysis, the presence of complex-forming inorganic and organic substances, water temperature, and water composition (e.g. CO_2 content).[3]

Removal of Fe^{2+} from ground-water and surface water can be done by several methods:

- Oxidation by aeration,
- Removal of Fe^{2+} by oxidizing agents (O_2, Cl_2, O_3, KMnO4), • removal of Fe^{2+} by alkalinization (by adding the lime),
- Contact filtration for removal of Fe
- Removal of Fe^{2+} by ion exchange,
- Removal of Fe^{2+} using membrane pro-cesses,

- Removal of Fe^{2+} using biological filtr-ation,
- Removal of Fe^{2+} using in situ method.

Fe^{2+} oxidation rate as well as hydrolysis of emerging oxides of higher iron oxidation forms in groundwater depends on the pH value. Various graphic dependencies of these relationships with respect to oxidation time are listed in the literature. The pH value should be equal or greater than 7 in the removal of iron from groundwater.[3]

To remove soluble iron efficiently from ground waters, various modern processes could be implemented for their treatments. For instance, an important water-treatment technology that is often used by drinking water supply companies in developed countries to remove soluble iron from ground waters consists to inject O_2-rich water into an aquifer. However, industrial methods are extremely expensive for poor people in developing countries. This has led many researchers to develop low-cost effective and economic techniques that can be easily used in rural and remote regions.[4]

The presence of these heavy metals in industrial waste waters is of serious concern because they are highly toxic, non-biodegradable, carcinogen, and continuous deposition into receiving lakes, streams and other water sources within the vicinity causes bioaccumulation in the living organisms. These perhaps, could lead to several health problems like cancer, kidney failure, metabolic acidosis, oral ulcer, renal failure and many more.[5]

Adsorption is one of the most useful methods to remove heavy metals from industrial effluents. This method explores the availability of different kinds of adsorbents associated with convenient procedures for obtaining high efficiency. The capacity of the produced adsorbent for adsorbed heavy metals like Pb(II), Fe(II), from the effluent with emphasis on the effects of contact time, adsorbent dosage, pH and stirring rate was carried out. Several treatment methods have been suggested, developed and used to remove heavy metals from wastewaters. These methods include chemical precipitation, ion exchange, cementation,[6] coagulation and flocc-ulation[7] and membrane processes.[8]

EXPERIMENTAL

Cation Exchange Resin (DOWEX™ HCR-S/S)

DOWEX™ HCR-S/S is obtained from Dow Chemical Company. It is a strongly acidic gel type Cation Exchange Resin, Table (1) is a high capacity resin with excellent kinetics and good physical, chemical and thermal stability. DOWEX™ HCR-S/S composed from copolymer styrene divinyl benzene sulfonic acid and high economical product for use in high quality process water treatment. DOWEX™ HCR-S/S present in Sodium form but in our study we use it in Hydrogen form by treated with 1 M HCl for 24 hours then washed with distilled water till neutrality.

Table 1: Typical Chemical and Physical Properties.

Physical form		White to amber translucent spherical beads
Matrix		Styrene-DVB gel
Functional group		Sulfonic acid
Ionic form as shipped		Na^+ form
Total exchange capacity, min.	eq/L kgr/ft³ as $CaCO_3$	1.9 41.5
Bead size distribution range 300–1,200 µm, min. <300 µm, max.	 % %	 90 1
Moisture retention capacity	%	48–52
Whole uncracked beads	%	90–100
Color throw, as packaged, max.	APHA	20
Acidity range	pH	7.0–10.5
Total swelling ($Ca^{++} \rightarrow Na^+$)	%	5
Particle density	g/mL	1.3
Shipping weight**	g/L lbs/ft³	800 50

Studies of adsorption processes for metal Ferric ions.

Effect of pH on adsorption of iron ions

The effect of pH metal ions adsorption batch experiments were conducted in a set of 15-mL centrifuge tubes using 10 mL of metal ion solution having an initial concentration 900 $mg \cdot L^{-1}$ with the amount of ion exchange 0.04g (4g/l) The initial pH of metal ions solution was adjusted to values in the range of 0.7–6.0 by the addition of 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH solutions. Meanwhile, the raw metal ions solution without pH adjustment was used as a control treatment. The suspensions were agitated in a temperature-controlled shaker operated at 25 °C with stirring 1200

rpm for a prescribed time. Then, the metal ions removal efficiency and adsorption amount were calculated.

Effect of metal ions concentration on adsorption of Ferric ions

The effect of metal ions conce-ntration adsorption was carried out by batch experiments in a set of 15-mL centrifuge tubes using 10 mL of metal ion solution having an initial conce-ntration 100 - 900 $mg \cdot L^{-1}$ with the amount of ion exchange 0.04g (4g/l). Meanwhile, the raw metal ions solution was used as a control treatment. The suspensions were agitated in a temperature-controlled shaker operated at 25 °C with stirring 1200 rpm for a prescribed time. Then, the metal ions removal efficiency and adsorption amount were calculated.

Effect of ion exchange dose on adsorption of Ferric ions

The effect of ion exchange concentration adsorption was carried out by batch experiments in a set of 15-mL centrifuge tubes using 10 mL of metal ion solution having an initial concentration 900 $mg \cdot L^{-1}$ for iron and lead respectively with the amount of ion exchange ranges from 0.02g to 0.1g (2-10 g/l). Meanwhile, the raw metal ions solution was used as a control treatment. The suspensions were agitated in a temperature-controlled shaker operated at 25 °C with stirring 1200 rpm for a prescribed time. Then, the metal ions removal efficiency and adsorption amount were calculated.

Effect of Time and Temperature on adsorption of Ferric ions

Batch equilibrium isotherm and kinetics studies, were carried out in the same manner. In each type of studies we prepared metal ion solutions containing metal ions (200, 500) ppm for iron and lead respectively and transferred them into (100 ml) wide-mouth propylene test bottles with screw closure caps using a Finn pipette. Each bottle contained a known volume (25 ml) of the metal ion solution. A known amount (0.1 g) of the ion exchange resin (DOWEX™ HCR-S/S). Was added into each bottle. The temperatures ranges from 298K^{o} to 318K^{o}. Afterwards, the bottled were shaken manually with time rages from 10 to 840 minutes. At certain intervals of contact time, the solution sample were withdrawn and filtered and the final concentration of metal ions was determined in the filtrate.

All samples after adsorption (metal concentrations in filtrate) were measured with Atomic Absorption Spectro-photometer (Unicam model Solaar 929).

Kinetics studies of the adsorption processes for metal ions

To describe the kinetic process, kinetic data were analyzed based on Lagergren pseudo first-order model,[9] and pseudo second order reaction rate model.[10] The mathematical representations of these models are given in Eqs. (1) and (2) as the following:

Pseudo first-order adsorption kinetic model

$$\log(q_e - q_t) = \log q_e - k_1 t \quad \text{----------(1)}$$

Where (q_t) is the amount of metal ion adsorbed at time (t).The adsorption rate constant (k_1) (min^{-1}) were calculated from the slope of linear plot of log (q_e-q_t) versus time (t).

Pseudo second-order adsorption kinetic model

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{----------(2)}$$

Kinetic model were plotted between (t/q_t) against (t).

The rate constant of intraparticle diffusion (k_{id}) at different temperatures were determined using the following equation:

$$q_t = k_{id} t^{1/2} \quad \text{----------(3)}$$

Where (q_t) is the amount adsorbed at time t, ($t^{1/2}$) is the square root of time.

Thermodynamic of the adsorption processes for metal ions

Thermodynamic parameters for the adsorption processes, including Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were used to decide whether the adsorption process is spontaneous (ΔG) was calculated from the following equation:

$$\Delta G = -RT \ln K_D \quad \text{----------(4)}$$

Where (R) is the universal gas constant (8.314 $J\ mol^{-1}K^{-1}$), (T) is the absolute temperature (K), (K_D) is the distribution coefficient of the adsorbate.

The (K_D) value was calculated using following equation:

$$K_D = \frac{q_e}{C_e} \quad \text{----------(5)}$$

Where (q_e) and (C_e) are the equilibrium concentration of metal ions on adsorbent ($mg\ l^{-1}$) and in the solution ($mg\ l^{-1}$), respectively.

Relation between (ΔG), (ΔH) and (ΔS) can be expressed by the following equation;

$$\Delta G = \Delta H - T\Delta S \quad \text{----------(6)}$$

This equation can be written as;

$$\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad \text{----------(7)}$$

The plot of ($\ln K_D$) Vs. (1/T) with (T in K) is linear with the slope and intercept values of (ΔH and ΔS) respectively.

Mechanisms of the adsorption process for metal ions

It is always important to predict the rate-limiting step in an adsorption process to understand the mechanism associated with the phenomena. For a solid liquid adsorption process, the solute transfer is usually characterized by either external mass transfer or intraparticle diffusion or both. Generally three types of mechanisms are involved in the adsorption process, mentioned as follows:[11]

(1) Film diffusion, which involves the movement of adsorbate molecules from the adsorbent.
(2) Particle diffusion, where the adsorbate molecules move in the interior of the adsorbent particles.
(3) Adsorption of the adsorbate molecules on the interior of the porous adsorbent.

Weber and Morris model[12,13]

The Lagergren first-order and pseudo-second-order models connot identify the diffusion mechanism. For this reason, the kinetic results were then subjected to analyze by the intraparticle diffusion model. According to this model, the plot of uptake (q_t) versus the square root of time ($t^{1/2}$) should be linear if the intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step. The initial curved portion of the plots seems to be due to boundary layer adsorption and the linear portion to intrapartile diffusion, with the plateau corresponding to equilibrium.

Intraparticle diffusion model is of major concern because it is rate-modeling step in the liquid adsorption systems. During the batch mode of operation, these was a possibility of transport of adsorbate species into the pores of sorbent, which is often the rate controlling step.

Metal uptake in the adsorption processes

The study of adsorption kinetics describes the solute uptake rate and evidently these rate controls the residence time of adsorbate uptake at the solid-solution interface including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process[14]

The amount of metal ion adsorbed per unit mass of the adsorbent (q_e) (mg/g) was evaluated by using the following mass balance equation:

$$q_e = \frac{C_0 - C_e}{m} V \quad \ldots\ldots (8)$$

Where (C_o) and (C_e) are the concentrations (mg l^{-1}) in the solution at time (t = 0) and at equilibrium time (t), (V) is the volume of solution treated adorbate (l) and (m) is the weight of the adsorbent (g). the percent removal of metal ion was calculated by the following equation:

$$\text{Removal}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad \ldots\ldots (9)$$

RESULTS AND DISCUSSIONS

Studies of adsorption processes for the removal of Ferric ion (Fe^{3+}) by DOWEX™ HCR-S/S

Effect of pH on the Fe^{3+} adsorption

The pH of the heavy metal solution is an important controlling parameter in the adsorption process. Variation in the pH value of soluble heavy metal solution would not only affect on the electronic status of the present functional groups but it may also affect or alter the form of the metal ions present in the medium. The effect of pH on the adsorption amount of Fe^{3+} on DOWEX™ HCR-S/S was investigated within pH ranges between 0.7 and 4.5.

The data of heavy metal ion adsorption which affected on pH are shown in Figs. (1, 2). From these figures shows that at low pH values, the DOWEX™ HCR-S/S acquire high adsorption. By increasing pH of the medium, the adsorption amount decreased dramatically to reach the maximum amount at pH values which depend on the metal ion type. The low absorption at high pH values (pH >1) could be referred to transform the dissolved metal into precipitated hydroxide form which as a result the adsorption is decreased.[15]

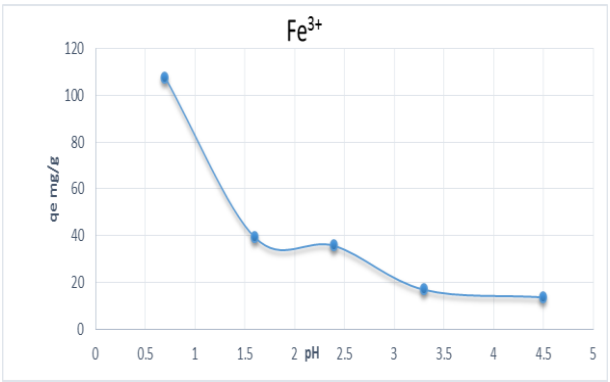

Fig. 1: Effect of the Fe^{3+} adsorption efficiency by DOWEX™ HCR-S/S at different pH.

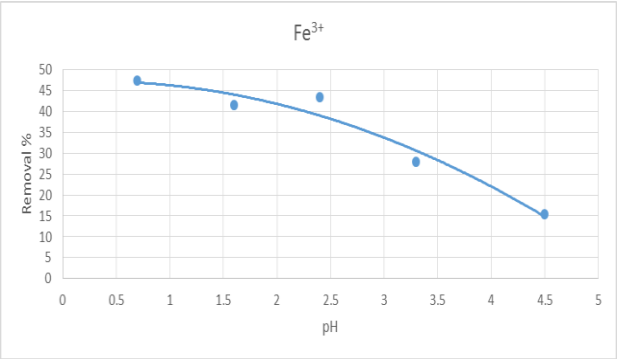

Fig. 2: Effect of the removal of Fe^{3+} by DOWEX™ HCR-S/S at Different pH.

Effect of Initial Concentration on the Fe^{3+} adsorption

Initial concentration varied from 126 to 900 ppm., time, adsorbent dosage, temperature was kept constant. The variation of efficiency with change in the initial concentration varies from 31.5 mg/g in the low concentration then raise to 137.25 mg/g at equilibrium then the efficiency decreased to 105.2 mg/g as shown graphically as show in Fig.(3). Even though removal efficiency and Fe^{3+} uptake decreases with increase in initial concentration, the change is only very less. This shows that initial concentration has only a very little effect on adsorption. Similarly, it means that the adsorption process is highly concentration dependent, Fig.(4).

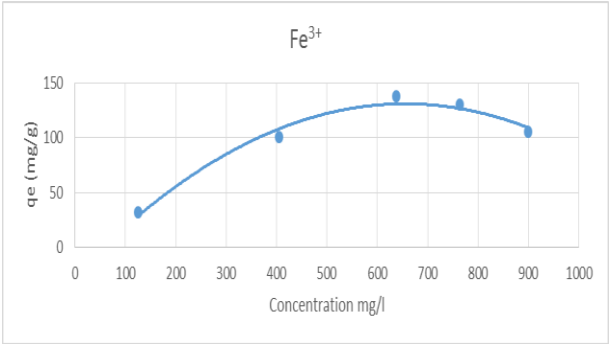

Fig. 3: Effect of the efficiency of Fe^{3+} adsorption by DOWEX™ HCR-S/S at different Concentrations of Fe^{3+}.

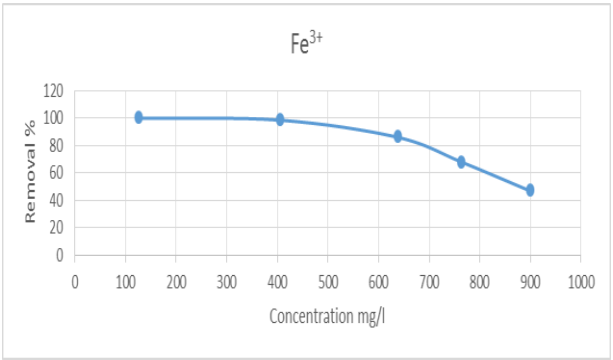

Fig. 4: Effect of the removal of Fe^{3+} by DOWEX™ HCR-S/S at different Concentrations of Fe^{3+}.

Effect of adsorbent dosage on the Fe^{3+} adsorption

As adsorbent dosage increases keeping all the other parameters at constant value removal efficiency first increases, reaches maximum and then decreases. As adsorbent dosage increases Iron uptake decreases as shown in the Fig.(5). At lower adsorbent concentration number of active sites is higher. With the increase in adsorbent dosage aggregation of particles take place, as a result efficiency and Fe^{3+}uptake decreases. But when we see to metal uptake it increase with increase the dosage as in Fig.(6).

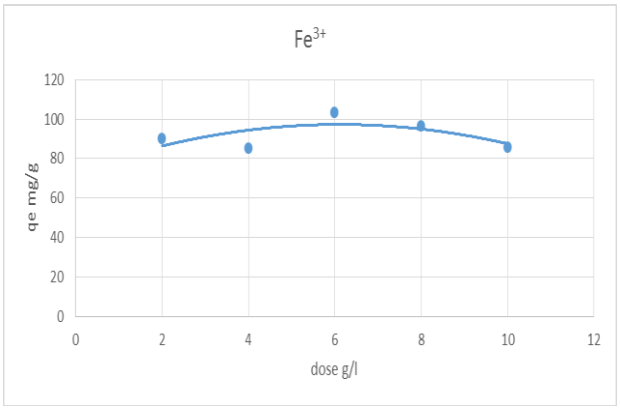

Fig. 5: Effect of the efficiency of DOWEX™ HCR-S/S dose on the Fe^{3+} adsorption.

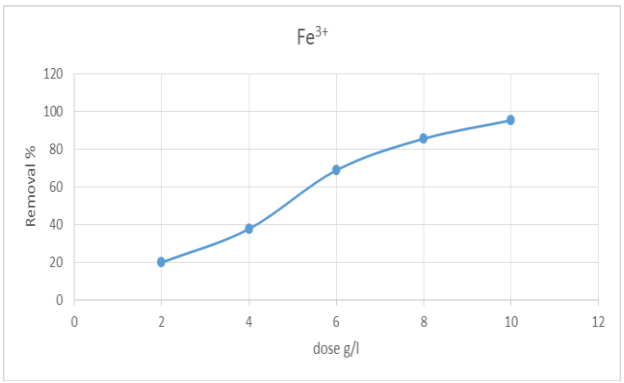

Fig. 6: Effect of the efficiency of DOWEX™ HCR-S/S dose on the Fe^{3+} adsorption.

Effect of Time and Temperature on the Fe^{3+} adsorption

As equilibrium time is one of the important parameters for selecting a wastewater treatment system, the time consumed for wastewater disposal should be considered. It is also essential to evaluate the effect of contact time on the adsorption prior to the kinetic study of the adsorption.

As shown in Fig.(7) the adsorption of Fe^{3+} ions onto the DOWEX™ HCR-S/S strong acid cation exchange resin at 25^0C was rapid for the first 30 min for Fe^{3+} and equilibrium was reached within 300 min.

The time profile of metal uptake is a single, smooth, continuous curve leading to saturation. This figure shows the adsorption performance, expressed as pollutant removal (in percentage) of DOWEX™ HCR-S/S strong acid cation exchange resin versus contact time (in minutes) toward the Fe^{3+} toxic metal present in these studies Table (2).

To compare the adsorption behavior of metals, the mass of adsorbent was kept constant (4 g/l) and the metal ion concentration of Fe^{3+} was 191 ppm at 25^oC. The short time necessary to reach the plateau, for all the Fe^{3+} toxic metal, besides indicating strong interactions between metals and the resin network, suggests this toxic metal have a similar affinity for the DOWEX™ HCR-S/S

strong acid cation exchange resin surface exceptionally for Fe^{3+}, Fig.(7).

The affinity between the adsorbent and the adsorbate is the main interaction force controlling adsorption.[16] Reported that the adsorption mechanisms are complex because a large number of interactions, such as ion exchange, physical adsorption, hydrogen bonding and hydrophobic interactions, are involved. In Fig.(8) it can be seen that pollutant removal rapidly increases within the contact time due to fast interactions between metals and the surface of the material, and keeps increasing gradually until equilibrium is reached and then remains constant. The raise in Temperature led to increase in metal uptake due to increase in the size of the adsorbent and the pores increase and increase in temperature led to increase in chemical bonding occur.

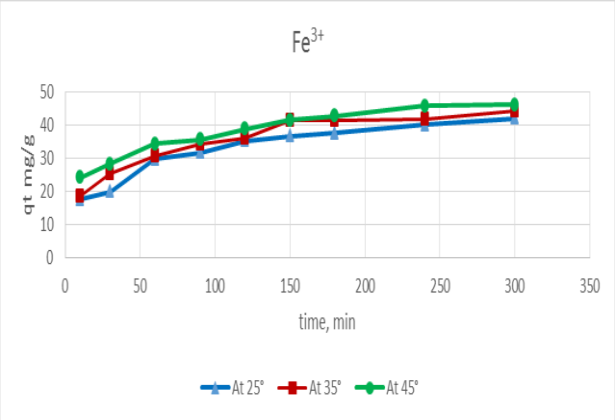

Fig. 7: Effect of the efficiency of Fe^{3+} by DOWEX™ HCR-S/S at different.

Times and Temperatures

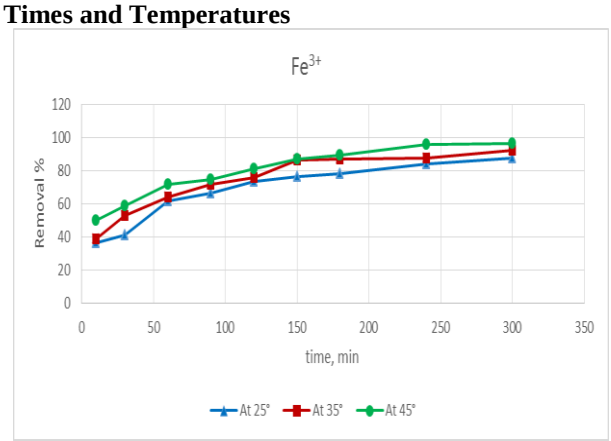

Fig. 8: Effect of the removal of Fe^{3+} by DOWEX™ HCR-S/S at different.

Times and Temperatures

Table 2: The summary of the results from removal of Fe^{3+} by DOWEX™ HCR-S/S.

		At 25°C		At 35 °C		At 45 °C	
C_o	Time (min)	C_t	Removal%	C_t	Removal%	C_t	Removal%
191	10	121.2	36.54	117.2	38.6	95	50.26
	30	111.8	41.47	90.2	52.77	78.2	59
	60	72.6	61.99	69	63.87	54	71.73
	90	64.4	66.28	53.6	71.94	48.6	74.55
	120	50.2	73.72	46.6	75.6	36.2	81.05
	150	44.6	76.65	26.2	86.28	25	86.91
	180	41.2	78.43	25.1	86.86	20.74	89.14
	240	30.7	83.93	24.22	87.32	8.22	95.7
	300	23.4	87.75	14.8	92.25	6.8	96.44

Adsorption isotherm modeling using Langmuir isotherm for the Fe^{3+} adsorption by DOWEX™ HCR-S/S

Isotherms are the equilibrium relation between the concentration of adsorbate on the solid phase and its concentration in the liquid phase. From the isotherms the maximum adsorption capacity can be obtained. These data provide information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions. Data has been subjected to different adsorption isotherms. Langmuir, Freundlich, models are the most common isotherms describing solid-liquid adsorption system.

Langmuir isotherm is often used to describe adsorption of solute from liquid solutions and this model assumes monolayer adsorption onto a homogeneous surface with finite number of identical sites and expressed by the following (eq. (1)).

$$q_e = \frac{Q_o k_L C_e}{1 + k_L C_e} \quad \text{.....(1)}$$

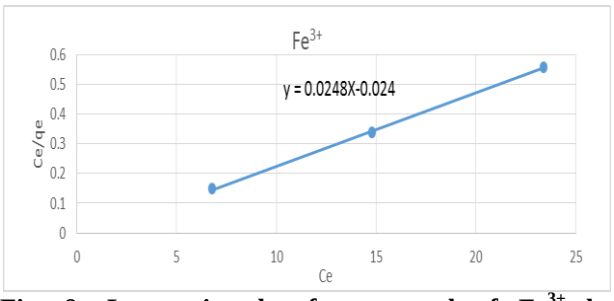

Fig. 9: Langmuir plot for removal of Fe^{3+} by DOWEX™ HCR-S/S.

Characteristic constants of Langmuir equation, Q_o the theoretical maximum adsorption capacity and k_L related to affinity of the binding sites, Q_o and k_L Langmuir isotherm constants can be determined from the linearized of Eq(1) as Eq(2):

$$\frac{C_e}{q_e} = \frac{1}{bQo} + \frac{C_e}{Qo} \quad \text{.....(2)}$$

The slope and intercept of the linear plot (Fig.9) of (C_e/q_e) Verses (C_e) give the values of Q_o and b respectively. In order to know the feasibity of the isotherm, the essential features of Langmiur model can be expressed in the terms of separation factor or equilibrium parameter R_L, which was defined by Eq(3):

$$R_L = \frac{1}{1+bCo} \quad \text{.....(3)}$$

The values of R_L indicate the shapes of isotherms to be either unfavorable (R_L>1), linear (R_L=1), favorable (0< R_L<1) or irreversible (R_L=0).[17] The R_L values for Fe^{3+} were calculated and indicated that adsorption is even favorable for the higher metal ion concentration that have been investigated. The data of R_L values the adsorbent is suitable adsorbent (DOEX HCR S/S) for the adsorption of Fe^{3+}ions from aqueous solutions.

Adsorption isotherm modeling using Fruendlich isotherm for the Fe^{3+} adsorption by DOWEX™ HCR-S/S

The Freundlich model is expressed as follows (Eq. 4):

$$q_e = k_f C_e^{1/n} \text{----------(4)}$$

The linearized form of Freundlich equation are given by (Eq. 5):

$$\text{Ln}q_e = \text{Ln}\ k_f + (1/n)\ \text{Ln}\ C_e \text{----(5)}$$

Where k_f and 1/n are characteristic constants representing the adsorption capacity and adsorption intensity of the system respectively. The linear plot between (ln q_e) verses (ln C_e) gives a slope which is equal to the value of (1/n) and intercept is (ln k_f). The magnitude of 0<n<1 indicates the favorability of process of adsorption.

The experimental data were fitted well with Langmiur isotherm suggesting that the Fe^{3+} adsorbed from monolayer coverage on the adsorbent surface. To lesser extent, the equilibrium data were also well described with the Freundlich model probably due to the real heterogeneous nature of the surface sites involved in the process of adsorption, Fig.(10)

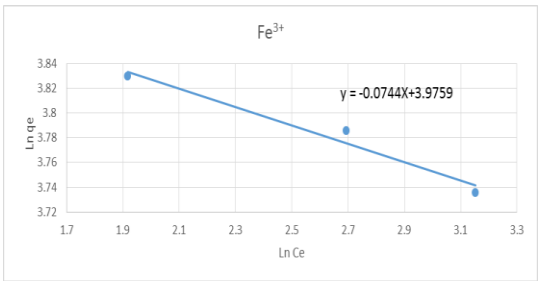

Fig. 10: Freundlich plot for removal of Fe^{3+} by DOWEX™ HCR-S/S.

The correlation co-efficient (R^2) value indicates that Langmiur model is favorable to describe the adsorption process. Our data of (n) values more than 1 indicating that the adsorption of Fe^{3+} on to the adsorbent DOWEX™ HCR-S/S. is non favorable to **Freundlich** model at the studied conditions. This can be attributed to the fact that, when the Fe^{3+} ions present in the solution, may diffuses to the surface sites slowly or rapidly, however, diffusion might be retarded when the Fe^{3+} ions are hydrated. It is possible that with fewer weakly bonded water molecules they tend to move faster to the potential adsorption sites, when compared to the cations with higher hydrated ionic radii.[18]

On the other hand, the equilibrium data were analyzed using Freundlich isotherm model and (R^2) values were estimated. The value of (n) generally indicates that the adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the adsorbent by Fe^{3+} ions.

It can be concluded that the Langmuir isotherm was more suitable than Freundlich one as in most cases the correlation co-efficient was higher thus indicating the applicability of monolayer coverage of the Fe^{3+} ions on the surface of adsorbent. This can be explained by the fact that the adsorbent have a high surface area for Fe^{3+} ions adsorption. Therefore only monolayer adsorption occurred on their surface.

Adsorption isotherm modeling using Temkin and Pyzhev isotherm for the Fe^{3+} adsorption by DOWEX™ HCR-S/S

The model assumes the following facts: (i) The heat of the adsorption of all molecules of the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and then (ii) The adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy. The derivation of the Temkn in isotherm assumes that the fall in the adsorption is linear rather than logarithmic, as implied in the Freundlich equation.

The Temkin ana Pyzhev isotherm has commonly been applied in the following (Eq. 6).

$$q_e = (RT/b)\ \ln(AC_e) \text{----------(6)}$$

$$q_e = B_T \ln A_T + B_T \ln C_e \text{------(7)}$$

$$B_T = RT/b_T \text{----------(8)}$$

Where (A_T) (L/g) and (b_T) (J/mol) are Temkin isotherm constants, (R) is the gas constant (8.314 J/mol) (T) is the absolute temperature.

The Temkin and Pyzhev isotherm for the Fe^{3+} ions as shown in Fig.(11).

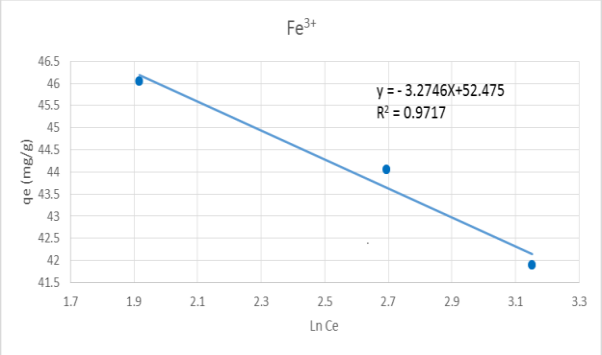

Fig. 11: Temkin plot for removal of Fe^{3+} by DOWEX™ HCR-S/S.

The related parameters (b_T) related to heat of adsorption. Values higher than 8 indicates strong interaction between Fe^{3+} and adsorbent. However, higher value indicates presence of relatively stronger cohesive forces in between the adsorbent and Fe^{3+}.

Although the Frenudlich isotherm provides the information about the surface heterogeneity and the exponential distribution of the active sites and their energies, it does not predict any saturation of the surface of the adsorbent by the adsorbate. Hence, infinite surface coverage could be predicted mathematically. In contrast, Dubinin-Radushkevich (D-R) isotherm the heterogeneity of energies closes to the adsorbent surface. If a very small sub region of adsorption surface is chosen and assumed to be approximately by the Langmuir isotherm, Fig.(12).

The Dubinin-Radushkevich isotherm[19] was also employed to find out the adsorption mechanism based on the potential theory assuming a heterogeneous surface. Dubinin-Radu-shkevich isotherm is expressed as follows (Eq.9):

$$q_e = X_m e^{-\beta\varepsilon 2} \text{----------(9)}$$

The liner form was (Eq. 10):

$$\text{Ln}q_e = \text{Ln}\ X_m - \beta\varepsilon^2 \text{----------(10)}$$

Where (X_m) is the Dubinin-Radushkevich monolayer capacity (mg/g), (β) is a constant related to adsorption energy, and (ε) is the Polanyi potential[20] which is related to the equilibrium concentration as follows in (Eq. 11):

$$\varepsilon = RT \ln (1+(1/C_e)) \text{---------(11)}$$

Where (R) is the gas constant (8.314 J/mol K) and (T) is absolute temperature.

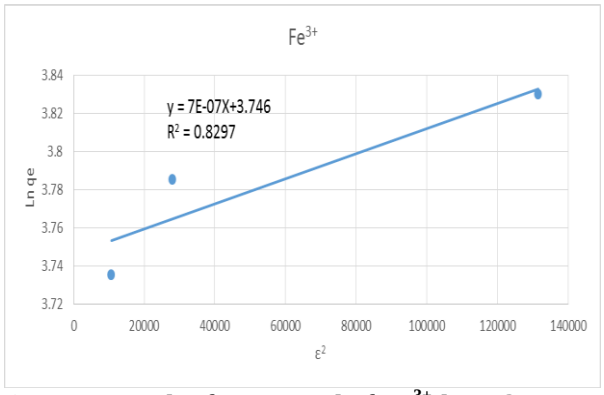

Fig. 12: D-R plot for removal of Fe^{3+} by DOWEX™ HCR-S/S.

A plot of (ln q_e) Vs (ε^2) as in Fig.(12), gave a straight line of slope, (β) and intercept, (X_m) of different systems were evaluated. The difference in the free energy between the adsorbed phase and the saturated liquid adsorbate is referred to as the potential, a term first advanced in.[20]

Thus the adsorption space in the vicinity of the solid surface may be characterized by a series of equipotential surfaces with a given adsorption potential. The adsorption potential is independent of temperature but varies according to the nature of the adsorbent and adsorbate.

The magnitude of (β) is used to determine the type of adsorption mechanism. When one mole of Fe^{3+} ions is transferred the adsorbent surface, its value is higher than 8.0 KJ/mol which indicates chemical adsorption, the calculated values of (E) for the present study is higher than 8.0 KJ/mol for the adsorption of Fe^{3+}, which suggest that adsorption process onto the surface of the adsorbent DOWEX™ HCR-S/S is following chemical adsorption type.

Adsorption kinetics modeling for the Fe^{3+} adsorption by DOWEX™ HCR-S/S

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid/solution interface. The data of the kinetics of Fe^{3+} adsorbed from aqueous solution onto DOWEX™ HCR-S/S as illustrated in Fig. (13-15) were analyzed using pseudo first order, pseudo second order intra particle diffusion kinetic models, respectively. The conformity between experimental data and each model predicted values was expressed by the correlation coefficient (R^2). A relatively high (R^2) values indicated that the model successfully describes the kinetics of Fe^{3+} ions adsorption removal.

The adsorption kinetics of Fe^{3+} ions from liquid phase to solid is considered as a reversible reaction with an equilibrium state being established between two phases. A simple pseudo first-order model was therefore used to correlate the rate of reaction and expressed as follows (Eq. 12):

$$dq_t/dt = k_1(q_e-q_t)\text{----------(12)}$$

Where (q_e) and (q_t) (mg/g) are concentration of Fe^{3+} ions in the adsorbent at equilibrium and at time (t), respectively integration and applying boundary conditions (t=0 to t=t) and (q_t=0 to q_t=q_t), the integrated from of (Eq. 12) becomes (Eq. 13):

$$\log (q_e-q_t)=\log q_e -(kt/2.303)t\text{----(13)}$$

Plots for (Eq. 13) were made for the Fe^{3+} ions adsorption at different studied temperature, and shown in Fig. (13). Approximately linear fits were observed for the Fe^{3+} ions, over the entire range of shaking time explored and at all temperatures with low correlation coefficient as in Fig. (13), indicating that the pseudo first order kinetic model is not valid for the present systems.

A pseudo second-order rate model is also used to describe the kinetics of the adsorption of Fe^{3+} ion adsorbent materials. The differential equation for chemisorptions kinetic rate reaction is expressed as (Eq. 14):

$$dq_t/dt = k_2(q_e-q_t)^2\text{----------(14)}$$

Where k_2 is the rate constant of pseudo second-order equation, for the boundary conditions (t=0 to t=t) and (q_t=0 to q_t=q_t), the integrated from of (Eq. 14) becomes (Eq. 15):

$$1/(q_e-q_t) = 1/q_e\ t\text{----------(15)}$$

Eq. (15) can be rearranged to obtain a linear form equation as Eq. (16):

$$(t/q_t) = (1/k_2q_e^2) + (1/q_e)\ t\text{----(16)}$$

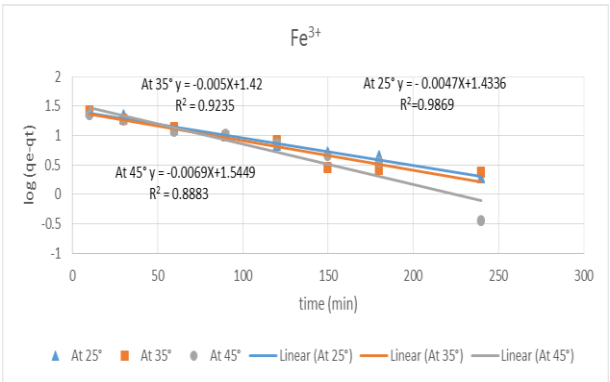

Fig. 13: Pseudo first order plot for removal of Fe^{3+} by DOWEX™ HCR-S/S.

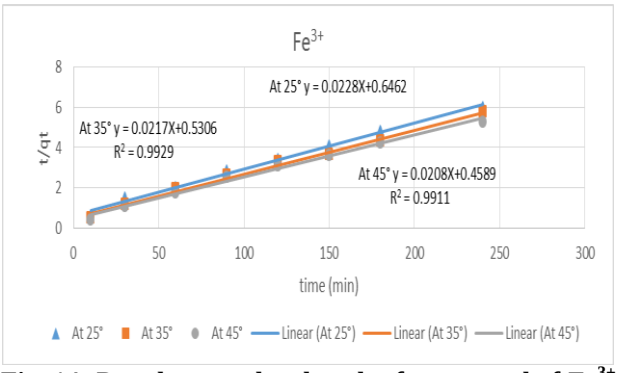

Fig. 14: Pseudo second order plot for removal of Fe^{3+} by DOWEX™ HCR-S/S.

The kinetic plots of (t/q_t) versus (t) for Fe^{3+} ions adsorption at different temperature are present in Fig.(14). The relationships are linear, and the values of correlation coefficient (R^2), suggest a strong relationship between the parameters and also explain that the process of adsorption of Fe^{3+} ions follows pseudo second order kinetic model.

From the results, it can be shown that the value of the rate constant (k_2) were increased with increase in temperature the correlation coefficient (R^2) has an extremely high value, and theoretical (q_e) values agree with experimental ones. These results suggest that the pseudo second-order adsorption mechanism is predominant and that the overall rate constant of each Fe^{3+} ion appears to be controlled by the chemisorption process.

Intra-particle diffusion model (Weber-Marries) model for the Fe^{3+} adsor-ption by DOWEX™ HCR-S/S

The overall reaction kinetics for the adsorption of some toxic metal ions as: Fe^{3+} is a pseudo Frst-order process, however, this could not high light on the rate-limiting step. The rate limiting step (slowest step of the reaction) may be either the boundary layer (film) on intraparticle (pore) diffusion of solute on the solid surface from the bulk of the solution in the batch process. The probability of the intraparticle diffusion was explored by using the Marris's and Weber's pore–diffusion model.

At the present time Weber and Morris's and pore-diffusion is the most widely used models for studying the mechanism of adsorption. On the other hand, Weber and Morris's pore-diffusion model assumes that:

(i) The external resistance mass transfer is only significant for a very short period at the beginning of diffusion.
(ii) The direction of diffusion is radial and the concentration.
(iii) The pore diffusivity is constant and does not change with time, the pore diffusion parameter, k_{id} ((mg/g $min^{0.5}$) is expressed as (Eq. 17):

$$q_t = k_{id}t^{0.5} +C\text{----------(17)}$$

Where (q_t) is the amount adsorbed (mg/g) at time (t).
The (k_{id}) values were obtained from the slope of the linear portions of the curve of different initial concentration of the Fe^{3+} ions in aqueous solution and shown in Fig.(15). It can be seen that the plots possess multilinear portions; it indicates that the two or more steps influence the adsorption process. It was found that straight lines relate the points, the sharp first linear portion is due to the film diffusion and the second linear portion is due to the pore diffusion. Non-linearity of the plots had indicated the multi stage adsorption of toxic metal as Fe^{3+} by the adsorbent. The extrapolation of the first linear portion gives the intercept equal to the boundary layer thickness or film thickness. The values of intercept give an idea about the boundary layer thickness such as the layer the intercept, the greater the boundary layer effect.

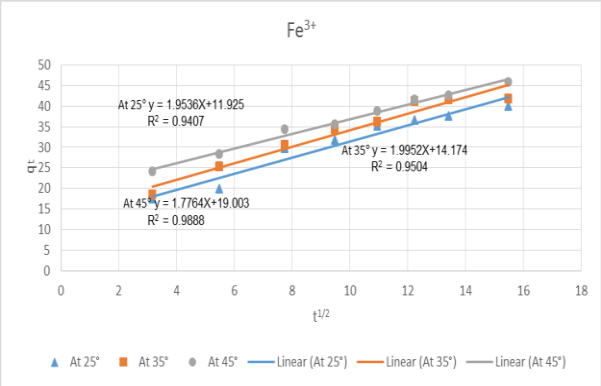

Fig. 15: The intra-particle diffusion model (Weber-Marries model) for removal of Fe^{3+} by DOWEX™ HCR-S/S.

Effect of temperature and calculation of activation energy (Ea) for the Fe^{3+} adsorption by DOWEX™ HCR-S/S

The thermodynamic assumptions of the best fitting isotherm provide insight into the surface properties and the mechanism of adsorption. The experi-mental results obtained as in Figs.(16,17) from a series of contact time studies for Fe^{3+} ion adsorption with an initial concentration of (191 ppm) in a solution in which temperature was varied from (25 to 45 ^{o}C).

The adsorption of Fe^{3+} ions has been found to increase with an increase in temperature from (298 to 318 ^{o}K).The increase in adsorption capacity of the adsorbent with temperature indicates an endothermic process as in Table (3).

The increase in adsorption with temperature may be attributing to either change in pore size of the adsorbent causing inter-particle diffusion within the pores or to enhancement in the chemical affinity of the Fe^{3+} ions to the surface of adsorbent leading to some kind of chemical interaction to take during adsorption process which results into increase in adsorption capacity. At higher temperature, the possibility of diffusion of solute within the pores of adsorbent may not ruled out as reposted by earlier workers.[21]

Since diffusion is an endothermic process, greater adsorption will be observed at higher temperature. Thus the diffusion rate of ions in the external mass transport process increases with temperature.

Table 3: Thermodynamic parameters for removal of Fe^{3+} by DOWEX™ HCR-S/S.

T	ΔG (KJ/mol)	ΔS (J/mol K)	ΔH (KJ/mol)	A	Ea (KJ/mol)
298	1443.300	179.71	52250.99	0.01048	6363.2
308	2792.969	-	-	-	-
318	5057.187	-	-	-	-

The above results were further substantiated by the various thermo-dynamic parameters. Enthalpy change (ΔH), Entropy change (ΔS), Gibbs free energy change (ΔG) and Activation energy (Ea) evaluated for adsorption.

The effect of temperature on adsorption is further confirmed by the vant Hoff plots as Fig. (16) based on the equations (18, 19, 20 and 21)[22]:

$$k_D = q_e/C_e \text{----------(18)}$$
$$\Delta G = -RT \ln k_D \text{----------(19)}$$
$$\Delta G = \Delta H - T\,\Delta S \text{----------(20)}$$
$$\ln k_D = (\Delta S/R) - (\Delta H/RT) \text{----(21)}$$

Where (T) is absolute temperature in Kevin (K), R is gas constant (8.314 J/mol K) and k_D is the distribution coefficient (ml/g). The thermodynamic parameters namely enthalpy change (ΔH) and entropy change (ΔS) can be calculated from the slope and intercept of straight line plotted by ($\ln k_D$) versus (1/T) as in Fig. (16). The Gibbs free energy change (ΔG) was determined. The obtained thermodynamic parameters (ΔH, ΔS, ΔG and Ea) were listed in Table (3).

By adsorption abundant Fe^{3+} ions onto the surface of the adsorbent, the number of H^+ ions attached to activate sites of the adsorbent decreased. Therefore the positive value of ΔS suggested some structure change in the adsorbent and adsorbate. In fact, the positive value of enthalpy (ΔH) further confirmed the endothermic nature of the processes, so increasing temperature supplied with a more favorable adsorption of Fe^{3+}ions onto the adsorbent. The positive Gibbs free energy (ΔG) value for the metal adsorption process on the adsorbent indicates the no spontaneous nature of the adsorption process.

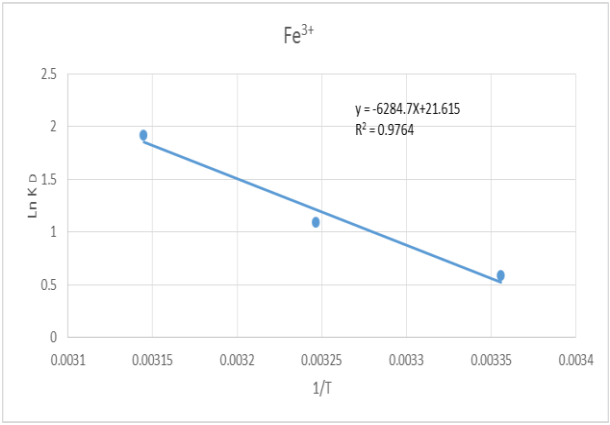

Fig. 16: The effect of the temperature on removal of Fe^{3+} by DOWEX™ HCR-S/S by The Vant-Holf polts study.

Generally, the values of the change in enthalpy (ΔH) indicated that adso-rption process of Fe^{3+} is chemical in nature.[22]

The activation energy (Ea) was calculated by the linearized Arrhenius equation (eq. 22):

$$\ln (k) = \ln (A) - (Ea/RT) \text{-----(22)}$$

where (Ea) is the activation energy of adsorption ($kJmol^{-1}$), (k) is the rate constant which control the process, (A) is Arrhenius constant, (R) is the ideal gas constant (8.314 J/mol K) and (T) is the absolute temperature (K).

From the pseudo second-order kinetic studies, k_2 is the rate constant which control the process, i.e (k) In this study, activation energy (Ea) value of different systems under study (KJ/mol) was obtained from the plot of (ln k_2) versus (1/T) as in Fig.(17).

In physical adsorption, the activ-ation energy (Ea) usually more than 8.0 $KJmol^{-1}$, since the forces involved in chemical adsorption is high.

Chemical adsorption involves forces much stronger than in physical adsorption and the activation energy (Ea) is between (8.4) and (83.7) $KJmol^{-1}$ [(209)] noted that chemical adsorption includes activated and non-activated forms. Activated chemical adsorption means that the rate varies with temperature according to finite activation energy (Ea) (between 8.4 and 83.7 $KJmol^{-1}$) in the Arrhenius equation, but the activation energy (Ea) for non-activation chemical adsorption is near zero.

The results shows that the process is one of activated chemical adsorption and the positive value of the activation energy (Ea) suggested that the rise in the solution temperature favors the Fe^{3+} ions adsorption onto the DOWEX™ HCR-S/S.

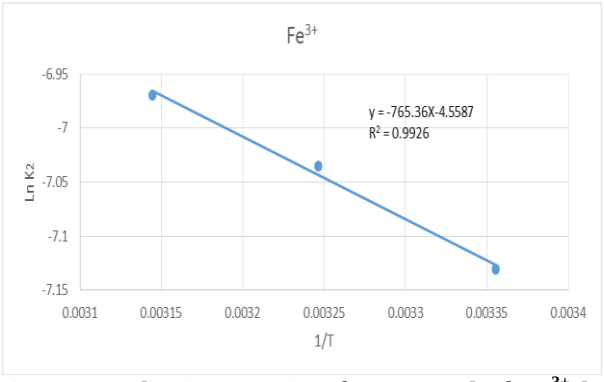

Fig. 17: Arrhenius equation for removal of Fe^{3+} by DOWEX™ HCR-S/S.

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