Adsorption kinetic and mechanistic view of aqueous ferric ion onto bio-natural rice grains

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Abstract.   Adsorption kinetics of aqueous ferric ion (Fe^{3+}) onto bio-natural rice grains (BRG) have been studied in a batch system. The influence of contact time (0-180 minutes), the dosage of BRG adsorbent (10, 20, 40, and 60 g L^{-1}), and ambient temperature (27, 37, 47, and 57 ℃) for the adsorption system have been reported. The equilibrium time achieved after 20 minutes of adsorption contact time. The maximum removal of ferric ion is 99% by using 60 gL^{-1} of BRG, T=37 ℃, and 50 mg L^{-1} ferric ion solution. Adsorption kinetic and diffusion models, such as pseudo-first order, pseudo-second order, and Weber-Morris intra-particle diffusion model, have been used to describe the adsorption rate and mechanism of the ferric ion onto BRG surface. The sorption data results are fitted by Lagergren pseudo-second order model (R^2=1.0). The kinetic parameters, rate constant, and sorption capacities have been calculated. The new information in this study suggests that BRG could adsorb ferric ion from water physiosorption during the first 5 minutes. Afterward, the electrostatic interaction between ferric ion and BGR-surface could take place as a very weak chemisorptions process. Thus, there is no significant change could be noticed in the FTIR spectra after adsorption. I recommend producing BGR as a bio-natural filtering material for removing the ferric ion from water.

Keywords: ferric ion; bio-natural rice; adsorption; pseudo-second order; kinetic

1. Introduction

   Iron is present in water largely in some Middle East regions. The aqueous iron ion is found as ferrous and/or ferric ion. Ferrous ion can be dissolved in the water and watching without color. The ferric ion can be in the form of solid particles suspended in the water in the form of oxides or hydroxides. But, ferric ion can be soluble in water either in the case of iron complex or in strong acidic solution (pH=1-2) (Hem and Cropper 1959). There is a great interest regarding the removal of iron ion from the aqueous medium. This is because that the dissolved iron ion in water has a direct impact on human health, as well as the industry (Lauffer 1992, Guidelines 1996). Therefore, it is important to find a way of removing the high concentration level of iron ion from water safely with low cost materials. Herein, it lays the talk about using adsorption technique using natural materials. There are many research works published on this aspect, using natural materials. However, these adsorbents are high cost or they are not abundant. This study is aimed at

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understanding both the adsorption capacity of this adsorbent for iron and the mechanism of the iron binding onto the surface of adsorbent.

Some natural adsorbents used to remove iron and other toxic metals from the aquatic systems are granular activated carbon and activated tea waste (Ramous, Flores *et al.* 2005, Ouki, Neufeld *et al.* 1997, Kim 2004, Mondal 2009, Monser and Adhoum 2002), pulp and industrial-waste of paper (Suthepong and Siraneem 2009), thioglycolic acid modified oil-palm (Akaninwor, Wegwu *et al.* 2007), wild cocoyam biomass (Horsfall, Jnr *et al.* 2004), coconut husk (Oyedeji and Osinfade 2010), chitosan coated oil palm shell charcoal (Nomanbhay and Palanisamy 2005), lignite (Mohan and Chander 2006), chitosan (Burke, Yilmaz *et al.* 2002), Bengal gram husk powder (Senthil Kumar 2010), activated carbon (Edwin Vasu 2008, Lakshmi Narayanan Rao, Krishniah *et al.* 1994, Zawani, Luqman *et al.* 2009), egg shells (Yeddou and Bensmaili 2007), biogenic wastes (Babalola, Olowoyo *et al.* 2016a), Nauclea diderrichii seed epicarp doped with MnO_2 nanoparticles (Omorogie, Babalola *et al.* 2016a), N. diderrichii seed biomass (Omorogie, Babalola *et al*. 2016b), *Cedrela odorata* Seed Chaff (Babalola, Koiki *et al*. 2016b), Nauclea diderrichii agrowaste-nanoscale titania hybrid adsorbent (Omorogie, Babalola *et al*. 2015) and low-cost papaya-clay combo adsorbent (Unuabonah, Adedapo *et al*. 2015). We have recently been able to use a significant number of natural adsorbents to remove the ferric ion where these studies achieved good results, such as, zeolite (Al-Anber and Al-Anber 2008a, Al-Anber 2007), olive cake (Al-Anber and Al-Anber 2008b), quartz and bentonite (Al-Anber 2010), deffatted jojoba (Al-Anber, Al-Anber *et al*. 2014a), feldspar (Al-Anber 2015a), cotton (Al-Anber 2014b), cypress seeds (Al-Anber 2016a) and coal of Date Palm seeds (Al-Anber, Abu-Rayyan *et al*. 2016c). These studies focus in the thermodynamic and kinetic study. These sorption studies approved that the most important mechanistic aspects follow the pseudo-second order. The most related contributions in the adsorption kinetics for the adsorption of the ferric ion can be encountered through using polycarbamide grafted carbon (El-Zahhar 2013); In addition, some examples are listed in the Table 1.

Recently, we have reported the use of bio-natural rice grains (BRG) as a low-cost adsorbent for adsorbing ferric ion from aqueous solution (Al-Anber 2016b). Sorption thermodynamics and equilibrium studies have been obtained. Wherein, the maximum removal has been found by using low concentrations of Fe^{3+} ions (10 mg L^{-1}), high BRG dosage (60 g L^{-1}), 37°C, 180 minutes of adsorption time, and 300 rpm. The maximum homogeneity adsorption capacities represent the fitting data into the Langmuir model. The adsorption of ferric ion on BRG is spontaneous, favorable, and endothermic in nature. Results that have been obtained through the FT-IR and Dubinin-Kaganer-Radushkevich (DKR) isotherm proved that the mechanism for the adsorption process is a weak chemisorption process. We have indicated that this approach can be applied and recommended for preparing a natural membrane of rice.

To the best of my knowledge, up to date, we do not find any study related to the adsorption kinetics and the mechanistic aspects of aqueous ferric ion onto bio-natural rice grains (BRG), neither Fe^{2+} nor Fe^{3+} ion. Therefore, it is important to study the kinetic and mechanistic aspects of the adsorption process, which are evaluated for different dosage and temperature. In this contribution, bio-natural rice grains (BRG) particles can be used for removing high-level concentration of ferric ion from the aqueous medium. Several models were applied in this study such as pseudo-first order and pseudo-second order. Sorption diffusion model, such as Weber-Morris intra-particle diffusion model, have been used to describe the adsorption rate of the ferric ion onto rice particles.

Table 1 Selected examples and Adsorption Kinetic models for adsorbing Fe^{3+} onto variant adsorbents

Natural Adsorbent	Pseudo-first order		Pseudo-second order			Ref.
	$k_1 \, (\text{min}^{-1})$	R^2	$k_2 (\text{g mg}^{-1} \text{min}^{-1})$	q_e	R^2	
Natural bentonite (NB)	0.066	0.89	0.337	0.649	0.99	(Al-Anber 2010)
Natural quartz (NQ)	0.057	0.76	0.552	0.746	0.99	(Al-Anber 2010)
Olive cake (OC)	0.061	0.89	0.018	15.97	0.99	(Al-Anber and Al-Anber 2008b)
Natural zeolite (NZ)	0.045	0.88	0.040	20.00	1.0	(Al-Anber and Al-Anber 2008a, Al-Anber 2007)
Feldspar(NF)	0.378	0.83	0.035	8.85	1.0	(Al-Anber 2015a)
Defatted Jojoba seeds (DJS)	0.053	0.773	0.181	6.45	1.0	(Al-Anber, Al-Anber *et al.* 2014a)
Natural Cotton Fibers (NCF)	0.035	0.826	0.657	8.93	1.0	(Al-Anber 2014b)
Carbon			0.048	13.04	1.0	(Edwin Vasu 2008, Lakshmi Narayanan Rao, Krishniah *et al.* 1994, Zawani, Luqman *et al.* 2009)
Eggshells			0.403	1.92	1.0	(Yeddou and Bensmaili 2007)
Chitosan	0.0306	0.96	0.032		1.0	(Burke, Yilmaz *et al.* 2002)
Natural Cypress Seeds (NCS)	0.085	0.666	0.197	7.69	1.0	(Al-Anber 2016a)
EGR		<0.25	4.6013	2.50	1.0	This study

2. Material and methods

2.1 Bio-natural rice grains (BRG)

Bio-natural rice grains (BRG) (Egyptian rice grain) were ground and then screened into a size fraction of 180 μm using standard Tyler screen series. Rice grains were washed with excessive amounts of double de-ionized water. The washing process of grains was done by using hot de-ionized water (less than 90°C) and then the same process was done by using cold water (20°C), which was repeated three times for each. The physicochemical properties of BRG were reported (Badawi 1997).

2.2 Reagents

All chemicals were used as received as analytical grade. $Fe(NO_3)_3.6H_2O$ was purchased from Fluka AG (Buchs, Switzerland). HNO_3 (0.1 mol L^{-1}), was purchased from Merck (Darmstadt, Germany). A stock solution of ferric ion ions was prepared by dissolving an exact amount of $Fe(NO_3)_3.6H_2O$ (±0.01 g) in 990 mL of ultra-pure deionised water (18 Ω cm), and then 10 mL of HNO_3 must be added to complete the total volume of solution to 1000 mL. Standard ferric ion solutions of 10, 20, 30, 40, and 50 mg L^{-1} were prepared by appropriate dilution. An "initial" pH and its subsequent adjustment for all experimental runs were conducted less than 1.20 at the maximum value. The initial pH of the solution was adjusted using 1% HNO_3 for all experiment runs.

2.3 Apparatus and instruments

The metal concentration in the solution was measured using the atomic absorption spectrophotometer, AAS, (Perkin Elmer Analyst 300). The chemical functional group of the rice grains is detected by FTIR (Thermo Scientific Nicolet IR200 FT-IR). The mixtures were mixed by a thermostatic mechanical shaker at constant temperature (27, 37, 47 and 57℃ (±1℃), Isothermal Gefellschaft Fur 978). To ensure accuracy in the preparation, analytical balance is used (Sartorius, CP324-S/ management system certified according to ISO 9001).

2.4 Equilibrium studies

The removal of ferric ion was calculated from the mass balance, which was stated as the amount of ferric ion adsorbed onto the BRG. It equal the amount of ferric ion removed from the aqueous solution. Mathematically can be expressed by Eqs. (1)-(2)

$$q_e = \frac{(C_i - C_e)}{S} \tag{1}$$

$$q_t = \frac{(C_i - C_t)}{S} \tag{2}$$

Where
  q_e: Ferric ion amount adsorbed on the BRG surface at equilibrium (mg g^{-1}).
  q_t: Ferric ion amount adsorbed on the BRG surface at a specific time (mg g^{-1}).
  C_i: Initial concentration of ferric ion in the aqueous solution (mg L^{-1}).
  C_e: Equilibrium concentration or final concentration of ferric ion in the aqueous solution (mg L^{-1}).
  C_t: The final concentration of ferric ion in the aqueous solution (mg L^{-1}) at a specific time.
  S: Dosage (slurry) concentration of BRG and can be expressed by

$$S = \frac{m}{v} \tag{3}$$

Where v is the initial volume of ferric ion solution used (L) and m is the mass of BRG adsorbent. The percent adsorption (%) was also calculated by using the following equation

$$Percentage\ of\ Removal\ = \frac{C_i - C_e}{C_i} \times 100\% \tag{4}$$

2.5 Effect of the temperature

The adsorption experiments were carried out by shaking vigorously the stopper (plastic) flasks containing 50 mL of 30 mg L^{-1} of ferric ion solution (initial pH=1.28) and 60 g L^{-1} of BRG using thermostatic mechanical shaker at constant contact time (3 hours) and agitation speed (300 rpm) with varying temperatures (27, 37, 47 and 57℃). At the end of the equilibrium time, the flasks were removed from the shaker and then the solution was filtered using filter paper (Whatman No. 41). The filtrate samples were analyzed. All the reported results were the average of at least triplicate measurements.

2.6 Effect of dosage

Adsorption measurements were made by a batch technique at a temperature of 37 (±1℃). Different doses of BRG (2, 8, 16, 20, 40 and 60 g L^{-1}) were placed in a 100 mL stopper (plastic) flask containing 50 mL of 30 mg L^{-1} of ferric ion solution (initial pH=1.15). The solutions were shaken vigorously (agitation speed=300 rpm) using thermostatic mechanical shaker for 3.0 hours. At the end of the equilibrium, the flasks were removed from the shaker and then the solution was filtered using filter paper (Whatman No. 41). The filtrate samples were analyzed. All the reported results were the average of at least triplicate measurements.

3. Results and discussion

3.1 FTIR spectroscopy

FTIR spectra can provide direct evidence for the chemical and physical process that lead to adsorption onto BGR. The FTIR spectra have been reported and discussed elsewhere in our recent publication (Al-Anber 2016b). Generally, there is no significant change in the FTIR spectra regarding the stretching frequency of the BRG functional groups after sorption. Furthermore, we do not see any chemical bond formation. The absence of any change in the stretching frequency indicates the presence of either physiosorption or the existence of very weak chemisorptions. Physiosorption, we could say that the adsorption of ferric ion onto the rice grains prefers physical entrapment of ferric ion. The existence of chemisorptive bonds has been supported by the recent thermodynamic information. It indicates to the presence of chemisorptions interactions between ferric ion and BGR (Al-Anber 2015c). This could be explained by the suggestion of the presence of a very weak intermolecular interaction (or/and a very weak electrostatic interactions) between
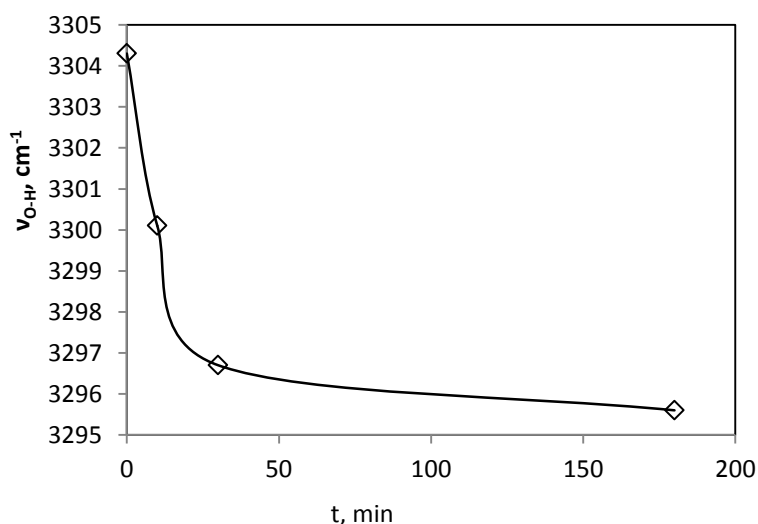

Fig. 1 Changing in the stretching frequency of the O-H bond in the starch framework vs. contact time of adsorption
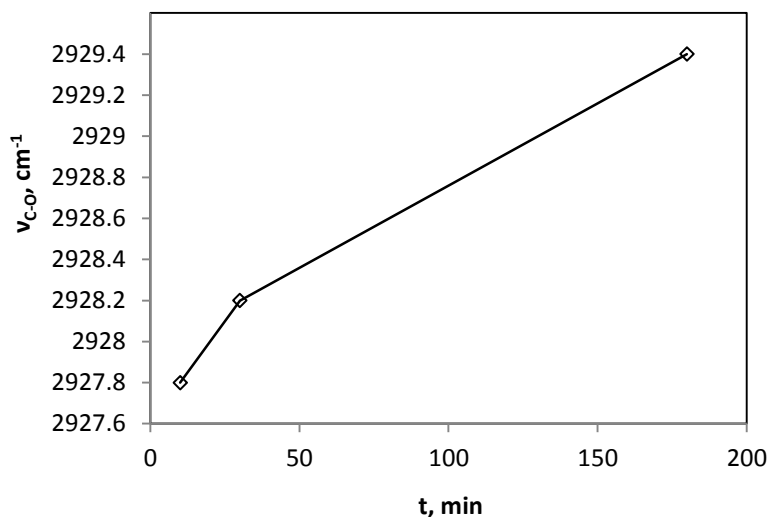
Mohammed A. Al-Anber

Fig. 2 Changing in the stretching frequency of the C-O bond in the starch framework vs. contact time of adsorption

O-H of the starch framework and ferric ion. These interactions can shift a little pet the stretching frequency of both O-H and C-O bonds as shown in Figs. 1 and 2. This behavior of adsorption agrees with the previous studies, such as: (i) biosorption of heavy metal onto *the Park Biolobosa biomass* (Ogbodu, Omorogie *et al.* 2015), and (ii) the adsorption of copper (II) ion from aqueous solution by starch-grafted polyacrylamide and cross linked starch grafted polyacrylamide (Tan, Wei *et al.* 2014).

3.2 Effect of contact time

The role of contact time was studied under the adsorption kinetic conditions; for instance, the pH of the solution was 0.98 by using 1% HNO_3, 300 rpm, the BGR dosage (60 gL^{-1}), 37 °C, and 50 mg L^{-1} of Fe^{3+} ion solution. Samples were collected at regular intervals and then analyzed after filtration.

The effect of contact time is shown in Fig. 3. At the initial stage, there is a sharp increase in the adsorption of Fe^{3+} ion onto BGR from 5-20 minutes of adsorption experiments. The equilibrium is reached the maximum adsorption after 20 minutes of the experiment time. The rate is very fast in the initial stages of adsorption. This may due to the availability of the uncovered surface area of the particles of BGR. This is because the adsorption kinetics depend on: (i) the surface area of the BGR particles, (ii) the nature and concentration of the surface active sites. These active sites, in the BGR, are responsible for the interaction with the ferric ion in aqueous medium even in the very limits of the weak interactions. Therefore, sorption onto BGR has an uncontrolled rate during the first 5 minutes indicating for the presence of physiosorption process. The final equilibrium of sorption starts after 10 minutes. The maximum adsorption (99%) can be obtained by using 50 mg L^{-1} (C_i), 60 g L^{-1} (dosage) at 37 °C. At the later stages, there slightly increases in adsorption efficiency within increasing the contact time. Wherein, this behavior is due to the decreasing number of active sites. Similar results have been reported in literature for the adsorption of dyes,
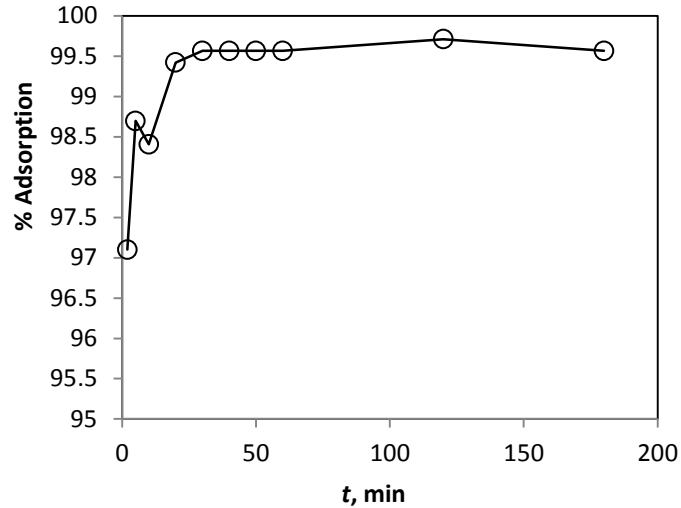
Fig. 3 The effect of contact time on the removal of aqueous Fe^{3+} ion in the interval of 5 to 180 minutes (Ci=50 mg L^{-1}, dosage=60 g L^{-1}, T=37°C, 300 rpm)
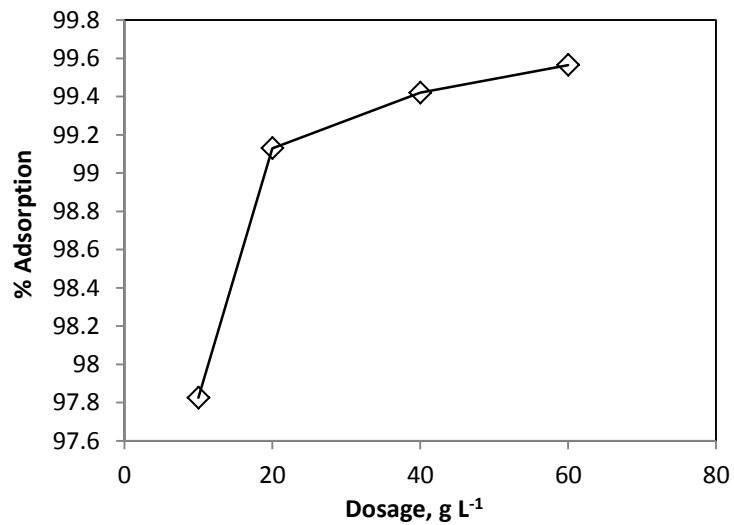

Fig. 4 The effect of dosage on the removal of aqueous Fe^{3+} ion (Ci=50 mg L^{-1}, dosage=10, 20, 40 and 60 g L^{-1}, T=37°C, t=10 min, 300 rpm)

organic acids and biosorption of heavy metal onto the *Parkia Biolobosa* biomass (Kannan and Meenakshisundaram 2002, Ogbodu, Omorogie *et al.* 2015).

3.3 Effect of dosage

Different dosages of BGR adsorbent were used for ferric ion adsorption from aqueous solution. This is just to detect the effect of BGR dosage on the kinetic studies and mechanistic aspects of

interaction between ferric ion and BGR. Fig. 4 shows the adsorption percentage by using different doses of BRG (10, 20, 40 and 60 g L^{-1}). This sorption experiment was applied at a temperature of 37°C. At the beginning of the equilibrium up to 10 minutes, it was found that the adsorption of Fe^{3+} slightly increases by increasing BGR doses, see Fig. 4. This is due to the availability of non reacted active sites for adsorbing Fe^{3+} ion. The maximum adsorption of Fe^{3+} ion onto BGR is 99%. Despite the presence of small amounts of BGR (10 g L^{-1}), the sorption rate and efficiency are high. For example, the maximum adsorption found 98% by using 10 g L^{-1}. This adsorption efficiency is almost equivalent to what has been recently published by using the polyacrylamide grafted activated carbon (El-Zahhar, Sharaf El-Deen *et al.*2013).

3.4 Effect of temperature

The effect of temperature on the adsorption of ferric ion onto BGR is performed through varying the temperature; they are in the range 27-57°C. Fig. 5 shows the plot curve of percentage adsorption against the ambient temperature of sorption. It shows that the maximum adsorption (99%) is achieved by using 37°C. But, there was no highly significant effect of temperature on the adsorption of Fe^{3+} onto BGR. Furthermore, the temperature seems not to influence the biosorption performance in the range 27-37°C. This plot confirms that the adsorption of Fe^{3+} ion onto BGR may be physiosorption in nature.

Herein, this could be explained by the suggestion that the increase in temperature may decrease the strength of intermolecular interactions between ferric ions and BGR. Furthermore, the increase in the temperature leads to increase the radius of pore inlets, which desorbs the ferric ion outside of BGR framework.

After adsorption equilibrium of each adsorption experiment, we noted that the final pH value of the solution is fixed between 0.98-0.99, as shown in Fig. 6. This indicates that the remaining ferric ion is still soluble in solution. In addition, it shows that the pH was not highly affected by the
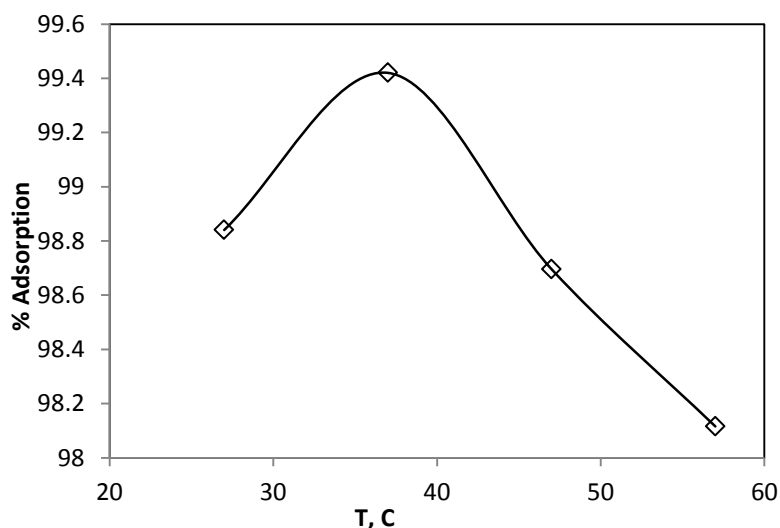

Fig. 5 The effect of dosage on the removal of aqueous Fe^{3+} ion (Ci=50 mg L^{-1}, T=27, 37, 47 and 57 C, t=20 min, 300 rpm)
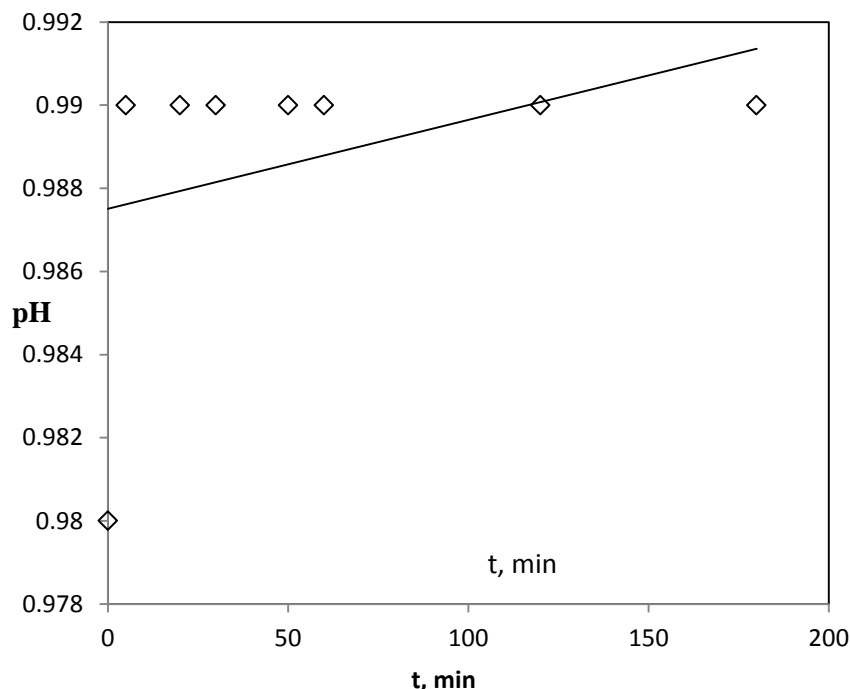
Fig. 6 pH and conductivity of ferric ion solution *vs.* contact time of adsorption in the interval of 5 to 180 minutes (C_i=50 mg L^{-1}, dosage=60 g L^{-1}, T=37°C, 300 rpm)

amount of BRG. The conductivity of the solution decreases after each adsorption process as shown in Fig. 6. This is due to uptake of ferric ions from solution through adsorption process.

3.5 Kinetic modeling of Fe^{3+} sorption

The kinetics sorption of Fe^{3+} ion governs the rate using batch sorption systems. It determines the residence time and defining the efficiency of an adsorbent. Consequently, it is important to establish the time dependency of such systems for various pollutant removal processes. Therefore, the required contact time is important to give insight into a sorption process. This also provides information on the minimum time required for considerable adsorption to take place. In addition, it provides possible diffusion control mechanism between the Fe^{3+} ion as it moves from the bulk solution towards the rice surface.

In order to investigate the adsorption mechanistic aspects and rate controlling steps, include mass transfer of ion and chemisorptions and/or physiosorotion process, the pseudo-first-order and pseudo-second-order kinetic model is used.

The pseudo-first-order kinetic model and its integral can be discussed in some reports (Lagergren 1898, Aksu 2001, Ho and McKay 1999, Zamani, Shokri *et al.* 2013), wherein it can be represented by Eq. (5)

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

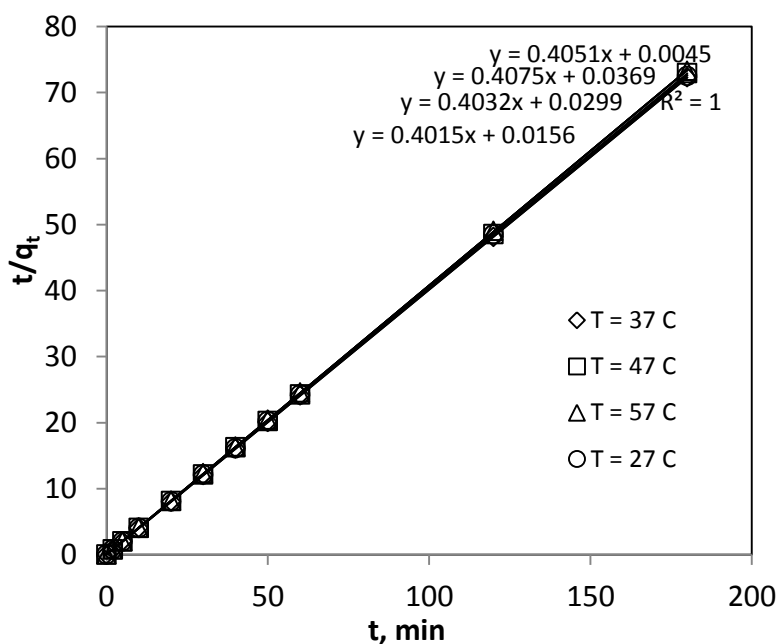Where q_e and q_t (mg g^{-1}) are the amounts of adsorbed Fe^{3+} ions at equilibrium and at times (*t*),

Fig. 7 Adsorption kinetics of Pseudo-second order model of aqueous Fe^{3+} ion by using different Temperature (27, 37, 47, 57°C), dosage=60 g L^{-1}, T=37°C, t=180 min, initial pH of 1% HNO_3, 300 rpm, and Ci=50 mg L^{-1}

respectively, k_1 (min^{-1}) is pseudo-first-order rate constant, and t (minutes) is the contact time. k_1 is the slope of the plot $\ln(q_e-q_t)$ versus t. The values of the model parameters k_1 and calculated q_e can be determined by plotting $\ln(q_e-q_t)$ versus t to produce a straight line of slope k_1 and intercept $\ln q_e$. The degree of goodness of a linear plot of this kinetic model can be judged from the value of the coefficient of determination of the plot, which can also be regarded as a criterion in the determination of the adequacy of kinetic model. The coefficient of determining value (R^2) is very low. Therefore, the fitting of the experimental data to the pseudo-first order was not so good.

The pseudo-second order kinetic model and its integral form are expressed by Eq. (6) (Ho and McKay 1999, Ho 2004)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

Where k_2 is the equilibrium rate constant of the pseudo-second order kinetic model (g mg^{-1} min^{-1}). The value of k_2 (g mg^{-1} min^{-1}) can be determined by plotting t/q_t versus t to obtain a straight line of slope $1/q_e$ and intercept of $1/(k_2 q_e^2)$ as shown in Fig. 7. From the determination coefficient value R^2=1 (approx.), the adsorption model can be regarded as a pseudo second order. Furthermore, the compression of q_e values of the experimental work ($q_{e, Exp}$=2.50 mg g^{-1}) and the calculated one (see Table 2) of pseudo-second order kinetic model (difference smaller) also shows the availability of this model.

Therefore, we can say that the adsorption system is chemisorption in nature. This can be supported by: (i) the thermodynamic information that was obtained from the study reported (Al-

Table 2 Pseudo second order parameters using different sorption temperature values

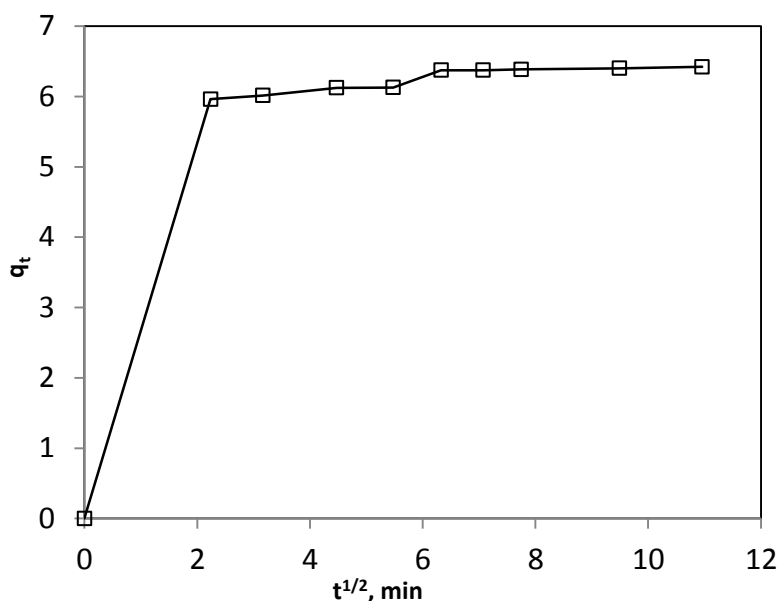| T (°C)	Pseudo second order			
	k_2 (g mg min^{-1})	$q_{e\ cal.}$ (mg g^{-1})	$q_{e\ Exp}$ (mg g^{-1})	R^2
27	5.6003	2.4813	2.50	1.00
37	10.72006	2.4937	2.50	1.00
47	41.00625	2.4691	2.50	1.00
57	4.6013	2.45700	2.50	1.00

Fig. 8 Weber-Moris intra-particular diffusion kinetic model at 37°C for adsorption of ferric ion on rice particles using different temperature values

Anber 2016b). Wherein, it concludes that the adsorption system depends almost on the BGR adsorbent capacity much more than the ferric ion concentration in solution. It is found that the adsorption process is controlled by an endothermic process. This phenomenon is characteristic of a chemical reaction or bonding being involved in the adsorption process. (ii) The q_{cal} approximately equal q_{exp} of adsorption system; and (iii) Plotting of percentage adsorption against the ambient temperature of adsorption experiment.

According to the information discussed in this article, it confirms that the adsorption of Fe^{3+} ion onto BGR may be not totally physiosorption. So, all these evidences support for considering the pseudo-second order instead of the first-second order kinetic model.

The kinetics results of this study are compared with other values as listed in Table 1. Apparently, the pseudo-second order model was found to be rate limiting, wherein the similar results have been observed using activated carbon (Edwin Vasu 2008), chitin (Karthikeyan, Andal *et al.* 2005), Chitosan (Wan, Ghani *et al.* 2005, Burke, Yilmaz *et al.* 2002), egg shells (Yeddou and Bensmaili 2007), olive cakes (Al-Anber and Al-Anber 2008b), zeolite (Al-Anber and Al-Anber 2008a, Al-Anber 2007), jojoba seeds (Al-Anber, Al-Anber *et al.* 2014a), natural cotton (Al-

Anber 2014b), quartz and bentonite (Al-Anber 2010).

To determine the diffusibility of the Fe^{3+} ions into the pores of the adsorbent, Weber-Moris intraparticule diffusion model (Weber and Digiano 1996) were used as in the Eq. (7)

$$q_t = k_{int}t^{\frac{1}{2}} + C \qquad (7)$$

Where C is constant, q_t the amount of ferric ion adsorbed at a time (mg g^{-1}) and k_{int} is the intra-particle diffusion rate constant (mg g^{-1} min$^{-0.5}$). A plot of q_t *vs.* $t^{\frac{1}{2}}$ gives straight line confirms intraparticle diffusion sorption as shown in Fig. 8. Due to the plot is not totally linear, and moreso do not pass through the origin, and then intraparticle diffusion could not be the only mechanism involved. Therefore, it, such plot, presents multi-linearity which indicates that two or more steps occur. The first, sharper portion (ca. $t^{\frac{1}{2}}$ range from 0 to 0.5 min$^{0.5}$; i.e., from 0 up to 1 minutes of adsorption period) is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage (ca. $t^{\frac{1}{2}}$ range from 0.5 to 0.84 min$^{0.5}$; i.e., from 1 up to 5 minutes of adsorption period), where the intraparticle diffusion is rate- controlled (k_{int}=5.9296 mg g^{-1} min$^{-0.5}$ and R^2=0.9993, see Fig. 8). The third portion is the final equilibrium state where the intraparticle diffusion starts to slow down due to extremely low solute concentrations in the solution and chemisorptions stage is taken part on the rice surface and pores (which already has been successfully explained by pseudo-second order kinetic model from 5 to 120 minutes of adsorption period).

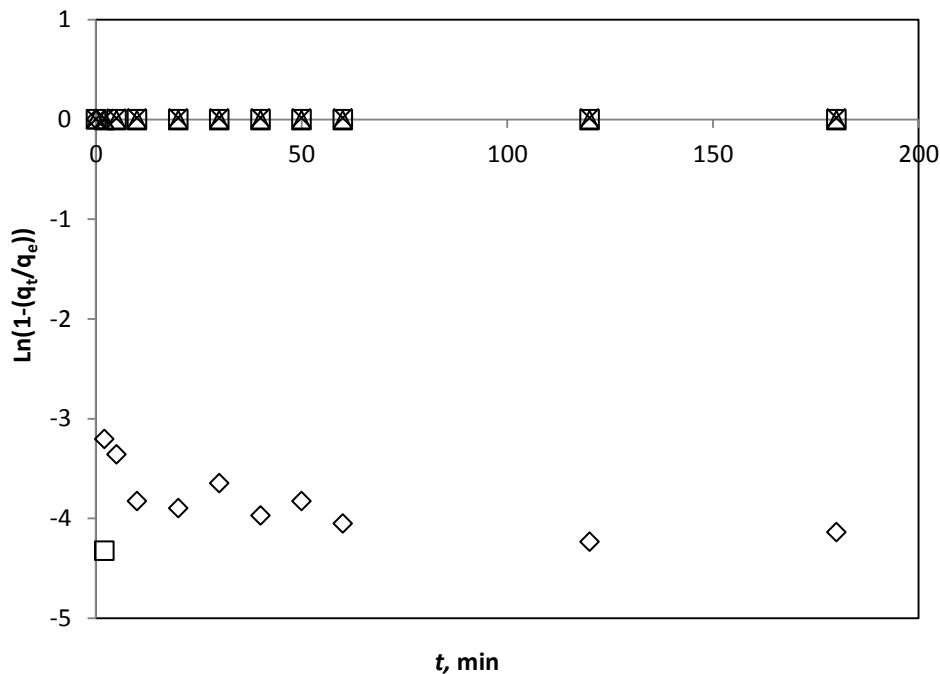Film diffusion mass transfer rate is presented by Eq. (8) (Boyd 1947)

Fig. 9 Film diffusion mass transfer kinetic models for the adsorption of ferric ion on rice particles using different dosages of rice particles

$$ln\left\{1 - \frac{qt}{qe}\right\} = -k\,t \tag{8}$$

Where, k (min^{-1}) is the liquid film diffusion constant. A plot of $ln\left\{1 - \frac{qt}{qe}\right\}$ *vs.* t should be a straight line with a slope $-k$ if the film diffusion is the rate limiting step. As shown in Fig. 9, it is found that the plot is non linear. Therefore, film diffusion mass transfer stage can be considered as the rate limiting step at the first period of adsorption (0 to 1 minutes) where, $k=7215$ min^{-1} and $R^2=0.9564$.

In summary, we can describe the adsorption mechanism of ferric ion onto BRG through three steps: (i) the external surface adsorption or instantaneous adsorption stage within 0 to 1 minutes of adsorption period. (ii) The intraparticle diffusion stage within 1 up to 5 minutes of the adsorption period (it is a physiosorption process). (iii) Chemisorptions stage and final equilibrium state within 5 to 180 minutes of adsorption period. Wherein, ferric ion binds with the O-H functional group of the starch framework in BGR particles. This interaction is considered as a very week chemisorptions interaction (or a very weak electrostatic interaction). This can be obtained from the FTIR, which support this idea in ref. (Al-Anber 2016b).

4. Conclusions

Recently, we have published the sorption thermodynamics and equilibrium of inorganic aqueous ferric ion onto Bio-natural Grain Rice (BGR) (Al-Anber 2016b). We have found that the adsorption process was favorable, endothermic and spontaneous in nature. Each BGR particle has monolayer coverage of ferric ion. This can be obtained by using low initial concentration and low temperature (37℃). It is found that the adsorption process is controlled by an endothermic process. This phenomenon is characteristic of a chemical reaction or bonding being involved in the adsorption process.

Subsequently to what has been published, herein, we get the mechanistic view of the sorption process through adsorption kinetic. Adsorption kinetic of aqueous ferric ion (Fe^{3+}) onto bio-natural rice grains (BRG) has followed the pseudo-second order model. The equilibrium time achieved within 20 minutes of adsorption process. The maximum removal of ferric ion is 99% upon the study conditions. The kinetic rate constant of sorption is 10.72006 g.mg min^{-1} (k_2).

Depending on the kinetic information that has been collected from this study and thermodynamic information (Al-Anber 2016b), we can determine the mechanistic aspects as follows: (i) the external surface adsorption or instantaneous adsorption stage within 0 to 1 minutes of adsorption period. (ii) The intraparticle diffusion stage within 1 up to 5 minutes of the adsorption period (it is a physiosorption process). (iii) The ferric ion binds to the O-H functional group within the starch framework in BGR particles. This adsorption reaction is done by forming a week electrostatic interactions or as a very weak intermolecular interactions.

The new information in this study suggests that BGR particles could adsorb ferric ion from water physically during the first 5 minutes. Afterward, the sorption of aqueous ferric ion (Fe^{3+}) onto bio-natural rice grains (BRG) has followed a very weak intermolecular interactions or electrostatic attraction between ferric ion and BGR-particles. Thus, I recommend for using BGR as bio-natural filtering materials for removing the ferric ion from water.

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