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Equilibrium and Kinetic Studies on Biosorption of Iron (II) and Iron (III) Ions onto Eggshell Powder from Aqueous Solution

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Abstract: As a consequence of modernization, industry is spread in the whole world, one of the industries that producing a wastewater as a by-product, iron and steel industry. The result is a huge amount of wastewater that contaminated with iron and steel. Biosorption techniques especially with a natural low cost adsorbent material, namely chicken eggshell is gaining an important goal for treating with a cost efficient material. This present investigation, eggshell (untreated natural eggshell and the treated one which is burned to 500°C) was applied for two types of iron removal from wastewater (Fe^{2+} and Fe^{3+}). The adsorption capacity of Fe^{3+} and Fe^{2+} verified 105.4 and 165.6 mg/g, respectively within 120 minutes for the unmodified eggshell, which enhanced to 129.7 and 181.3 mg/g, respectively, for the modified eggshell. Different parameters were studied such as initial iron concentration in wastewater, agitation speed and the mass of the biosorbent. The isotherm study revealed that the data well fitted for linearized forms of Langmuir. The kinetic study followed the pseudo-second order reaction rate.

Keywords: Biorbent, Chicken Eggshell By-Product, Iron, Wastewater

1. Introduction

At present, there is an increase in the wastewater effluents that containing heavy metals in Egypt. For instance, large quantities of wastewater are released from metal processing, mining, pesticides, rubber and organic chemicals. The release of toxic substances from such industries causes a series damage to the environment. Thus, the environmental pollution is an important issue facing the society as a result of this industrialization, which is increased to harmful levels to the living creatures. Toxic wastewater from industrial effluents containing heavy metals such as iron, lead, cadmium, copper and chromium could also contaminate ground water causing a series problems. Those heavy metals should be removed from wastewater before disposal [1-4].

Iron metal is considered, as a natural constituent of soils and rocks and it is normally present in highly insoluble forms. However, it could be brought into a solution during anaerobic conditions or by the presence of carbon dioxide. The result is unfavorable conditions such as nuisance conditions that could occur when the iron concentration is exceeds than 0.3 mg/L. The presence of iron in excessive quantities cases a risk to water bodies, ground water and soil in the long-term. This metal could accumulate in the water and soil causing a ultimate harmful effect on the living organisms [5].

According to this industrialization activities a large amounts of wastewater from all these sources are thrown directly to freshwater bodies. An urgent needs to treat such wastewater before disposal. For several decades, the much research has been done on removing heavy metals by the conventional physico-chemical treatment methods. For instance, such techniques are membrane separation, evaporation chemical precipitation and ion exchange. However, those available treatment facilities, which providing proper treatment are expensive, inefficient and difficult to manage. Therefore, nowadays searching for an innovative low cost technique consuming low energy and easy to manage is a research topic [1, 4]. Hence, the adsorption technique is considered a potential alternative method as it is technically easy and cheap methods especially when it is based on economic cost effective biomass materials that cause bio-sorption. For instance, chicken eggshell is considered one of the simple bio-sorption techniques, the main component in this eggshell is the calcium carbonate besides some traces of other elements makes the substance is capable of the sorption behavior [2, 3]. This innovative technique in comparison with the other conventional techniques is easy to operate and after the treatment there is no secondary treatment as there is no chemical sludge produced [3]. Moreover, according to the literature [2], in some countries, annually there are a large amount of eggshells are produced as a waste products and managed by landfilling. Bhumik [2] used this waste product chicken eggshell for he fluoride removal from aqueous solution. In addition, Zulfikar et al., [6] applied the powdered eggshell in adsorption of anionic polyelectrolyte polymers, namely ignosulfonate. Furthermore, Rohaizar et al. [3], in 2013 used the chicken eggshell for chromium removal and recovery from wastewater. Rubcumintara [4] used the chicken eggshell for chromium removal from wastewater. Additionally, Ikram et al., [7] used the eggshell on the sorption of oxalic acid.

The objectives of this work are to study the effects of different operating parameters including agitation rate, adsorbent mass, initial load of iron in the wastewater and contact time on the adsorption efficiency of Fe^{2+} and Fe^{3+} from water by two types of chicken eggshell, raw and treated one. Besides, the present study is also aimed to evaluate the equilibrium of adsorption process using Langmuir and Freundlich isotherms. Meanwhile, the kinetics of Fe^{2+} and Fe^{3+} adsorption on two types of chicken eggshell adsorbent is also analyzed using different models including the pseudo-first-order and pseudo-second-order kinetic models.

2. Materials and Methods

2.1. Materials

2.1.1. Biosorbent Collection and Preparation

Natural chicken eggshells with its membrane were collected from local restaurants and washed with distilled water followed by drying at ambient conditions. Consequently, the dried eggshell with membrane was grounded by house mill to prepare a powdered eggshell. Some of the powder material was tested for its adsorbent qualities without further chemical or physical treatment.

However, for the object of comparison, other samples are subjected for 500°C treatment for 2 hrs (because protein component in egg shell can denature at high temperature). The predominant constituents of eggshell are presented in Table 1 [8].

Table 1. *Approximate Composition of Eggshell.*

arameter	Content
Moisture	0.46%
Protein	3.92%
Ash	94.61%
Fat	0.35%
Calcium	34.12%
Magnesium	0.29 ppm
Phosphorous	0.04 ppm
Potassium	0.03 ppm
Sodium	0.05 ppm
Copper	<1ppm
Iron	22 ppm
Manganese	<1ppm

2.1.2. Preparation of Adsorbate Solution

A simulated heavy metals contaminated wastewater containing iron was synthesized. Stock solution of iron-contaminated wastewater was prepared by dissolving certain amounts of $FeCl_2$ or $FeCl_3$ (Sigma-Aldrich) in 1L of distilled water. The required concentration of the solution was prepared by serial dilution of 1000 mg/L iron stock solution in range of 5- 300 mg/L. Thereafter, this iron-contaminated wastewater was submitted to a different bottles at different conditions and concentration to check the adsorption process.

2.2. Methodology

Two series of batch-type experiments were carried out. Adsorption equilibrium was derived from small-scale batch experiments and kinetic data were derived from larger scale contact time experiments. Kinetics of adsorption was carried out using agitated batch adsorber.

2.2.1. Equilibrium Experiments

Bio-sorbent Eggshell in contact with 50 ml of iron solutions which were prepared in distilled water at concentrations ranging from 5 to 300 mg/L was used to investigate the equilibrium uptake of iron ions (Fe^{3+} or Fe^{2+}) at 303 K with a sorbent mass of 0.1g. The solution with the adsorbent was mechanically shaken using an electrical shaker (Model: WBT-400) at 600 rpm and 303 K for 120 and 60 minutes for Fe^{3+} or Fe^{2+}, respectively. Thereafter, the samples were analyzed for the iron remaining in the solution. The results founded that equilibrium was established within 3hr; however, all equilibrium experiments were allowed to run for 180 and 120 min for Fe^{3+} or Fe^{2+}, respectively to ensure uniformity.

Adsorption isotherms were determined by using the following procedure. The experiments were carried out at different temperatures of 25, 35, 45 and 55 ± 2°C. The experiments were carried out with shaker containing water bath with electrical heater and thermometer. The bottles were shaken submerged in water bath, controlled at ±2°C. The experiments were started when the temperature of the solution reached to the required value. After 300 min. samples were taken and remaining iron was analyzed.

2.2.2. Isotherm Experiment

In this study, the adsorption data were analyzed using

Langmuir and Freundlich adsorption isotherm models to describe the sorption equilibrium.

The Langmuir isotherm is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir isotherm is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L a_L} + \frac{1}{K_L} C_e \quad (1)$$

where C_e is the equilibrium dye concentration (mg L^{-1}), q_e is the mass of dye adsorbed per unit mass of adsorbent (mg g^{-1}), K_L and a_L are the Langmuir constants related to the adsorption capacity and rate of adsorption, respectively.

The Freundlich isotherm model is applicable to a highly heterogeneous surface:

$$\ln(q_e) = lnK_F + \frac{1}{n} lnC_e \quad (2)$$

where K_F relates to the adsorption capacity of the adsorbent and n is a measure of the adsorption intensity. The magnitude of the coefficient, 1/n, gives an indication of how favourable the adsorption is; values of $n > 1$ represent favourable adsorption conditions [9].

2.2.3. Kinetic Study

The study of the adsorption kinetics describes the resistance to solute transfer from the solution to the boundary layer at the solid-liquid interface to the pore water and then to the solid. It is well known that the following steps mainly control adsorption kinetics:

1. Solute molecules transfer from the solution to the boundary film; 2. Solute molecules transfer from the film to the surface of the sorbent (external diffusion); 3. Diffusion from the surface to intra-particle sites and 4. Interaction of solute molecules with the available sites on the internal surface [10]. The evolution of the adsorption process can be followed by measuring the number of particles adsorbed per unit time. Many kinetic models have been proposed for the adsorption of solutes on solids, such those models were employed to fit the kinetic data [11-13].

2.3. Analytical Methods

The residual dye concentrations of the samples were measured after the reaction time using a spectrophotometer (SHIMADZU-UV 1601, Model TCC-240A) using iron kit for analysis and the calibration curves for the two types of iron salts were done and the maximum wavelength which is 510 nm was determined.

3. Results and Discussions

3.1. Preliminary Adsorption Studies: Effect of Contact Time

Generally, for designing the batch adsorption experiments, it is crucial to inspect the effect of contact time required to reach the equilibrium. The iron removal capacity q_t (mg/g) on the eggshell powder was determined by varying contact time. Figure 1 (a) and (b) shows the effect of contact time on the adsorption of Fe^{3+} and Fe^{2+} onto eggshell, respectively. It is evident from the Figure that the adsorption capacity of Fe^{3+} and Fe^{2+} increase with the rise in contact time and attains equilibrium in 120 and 60 minutes but all experiments run to 180 and 120 min, respectively to ensure completely adsorption. However, further increase in contact time did not enhance the iron adsorption process. It could be noted that in the initial stage, there is a fast adsorption behavior attained which is explicated by availability in the number of active binding sites on the biosorbent, eggshell surface [2]. The adsorption is rapidly happens and is controlled by the process of diffusion from bulk to the surface. Similar findings were reported in the literature [5] for the adsorption of iron from aqueous solution onto Pongamia pinnata and for eggshell as an unconventional biosorbent.

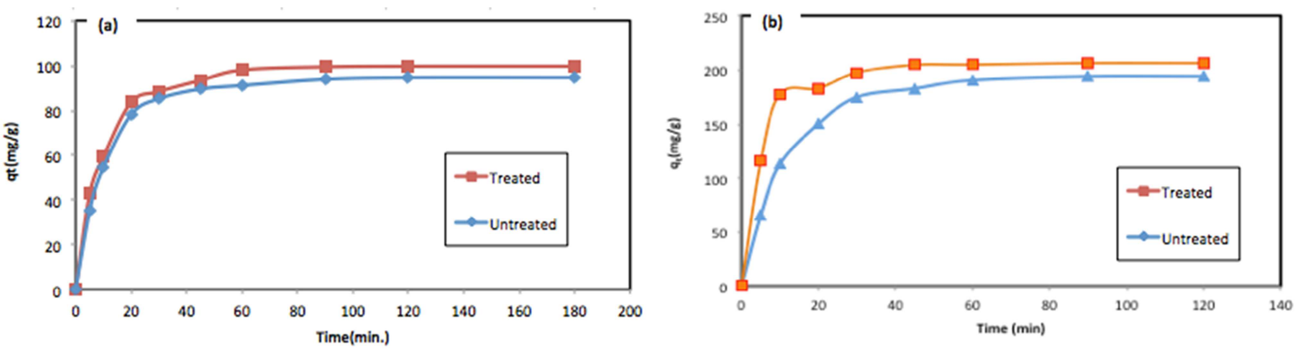


Figure 1. *Effect of (a) Fe^{3+} and (b) Fe^{2+} adsorption on untreated and burned (modified) eggshell.*

3.2. Adsorption Isotherms

The adsorption isotherm is the relationship between the amount of a substance adsorbed and its concentration in the equilibrium solution at a constant temperature. In this investigation, the Freundlich and the Langmuir were used to describe the equilibrium data acquired at different temperatures (in the range from 298-328K). The results are shown in Table 2 and the modeled isotherms are plotted in Figure 2. According to Table 2, firstly, for both types of iron, namely Fe^{2+} and Fe^{3+} the treated iron with burning at 500°C showed higher adsorption capacity than the untreated one according to the q_t(mg/g) values which is higher in the case of the treated eggshell than the untreated one as shown in Figure 1. In addition, the Langmuir isotherm model showed excellent fit to the experimental data (R^2>0.9) with high correlation coefficients at all temperatures for Fe^{3+} removal from wastewater compared to the Frendlich isotherm (R^2 ranged from 0.3 to 0.9). The empirical Langmuir model also showed a fairly good fit to the experimental equilibrium data at all temperatures studied (R^2>0.9). The values of K_F and q_{max} increased with increase in temperature (Table 2), the magnitude of the Langmuir constant K_L has small values (0.012–0.02 L/mg), which indicates a low adsorption capacity [14, 15]. The constant K_L, represents the affinity between the adsorbent and adsorbate.

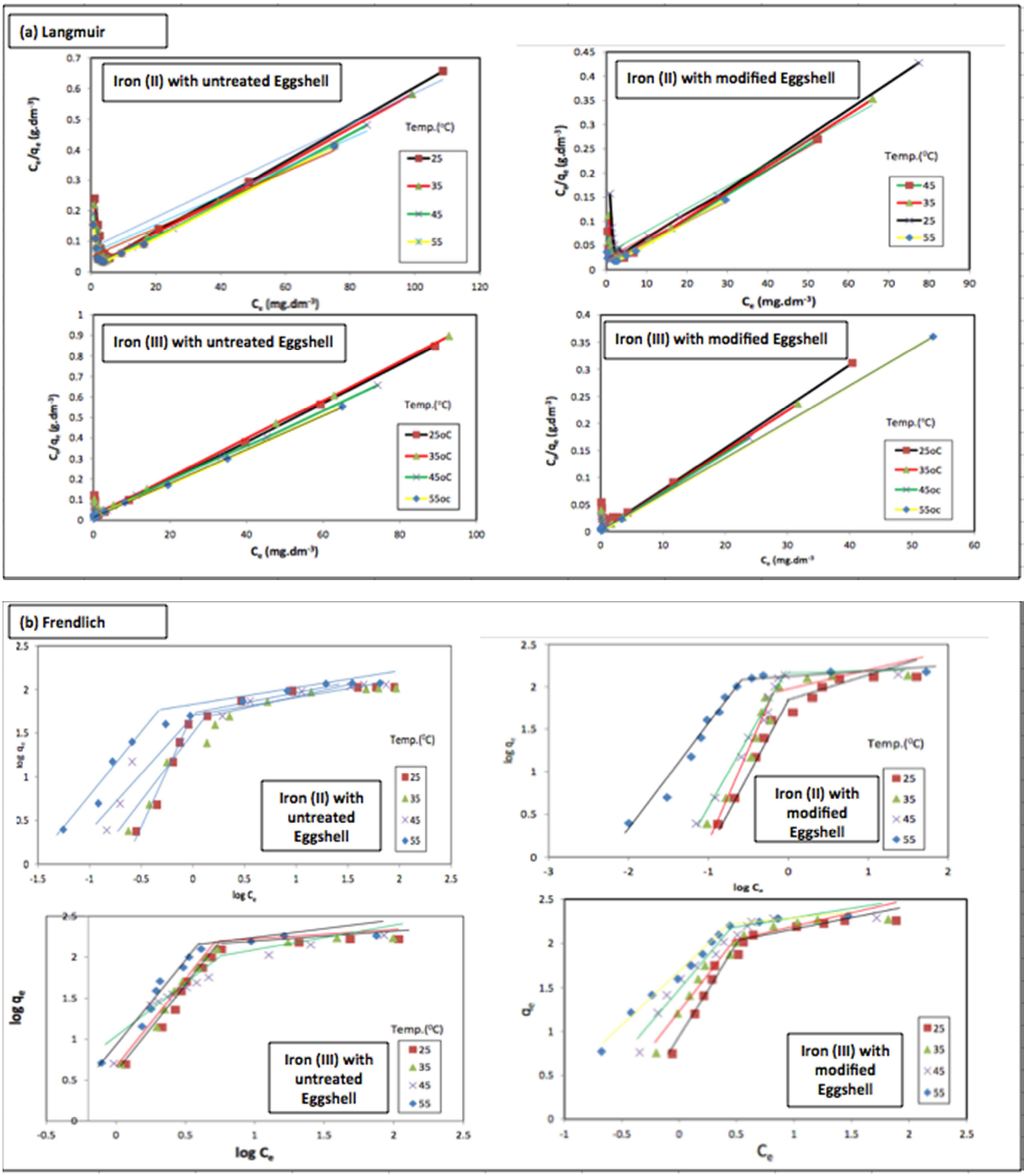


Figure 2. *(a) Langmuir; (b) Freundlich isotherms for iron adsorption onto Eggshell at different temperature.*

Table 2. *Adsorption isotherm constants for adsorption of iron onto eggshell powder at different temperatures.*

Adsorbent		*Temp. (K)*	*Langmuir isotherm parameters*			*Frendlich isotherm parameters*			
			$_LK$ *(dm^3/g)*	*K (mg/g)*	^2R	$_FK$ *(dm^3/g)*	q_{max} *(mg/g)*	*n*	^2R
Iro (II)	Untreated Eggshell	298	24.691	105.382	0.9841	55.86	89.2	6.14	0.824
		308	22.624	103.565	0.9934	79.415	92.87	16.33	0.959
		318	36.496	112.874	0.9963	74.508	74.25	9.779	0.932
		328	70.922	117.483	0.9989	55.757	65.03	4.75	0.916
	Modified Eggshell	298	55.249	129.792	0.9997	55.86	6.143	6.14	0.658
		308	82.645	134.163	0.9629	112.23	15.11	15.11	0.576
		318	96.154	138.071	0.9654	107.795	11.00	11.00	0.308
		328	476.191	148.3	0.9997	55.757	4.757	4.75	0.548
Iron (III)	Untrearted Eggshell	298	24.691	105.382	0.9841	125.632	15.949	15.94	0.763
		308	22.624	103.565	0.9934	127.908	14.992	14.99	0.716
		318	36.496	112.874	0.9963	53.113	3.506	3.50	0.969
		328	70.922	117.483	0.9989	142.594	16.313	16.31	0.514
	Modified Eggshell	298	21.786	212.766	0.8705	65.207	77.43	4.16	0.658
		308	30.675	212.766	0.9018	112.23	65.98	15.11	0.576
		318	45.455	217.391	0.9195	107.795	52.32	11.00	0.309
		328	81.967	227.273	0.9425	127.174	29.54	18.62	0.548

Additionally, for Fe^{2+} removal, Langmuir isotherm model is well fitted the data. The maximum iron (Fe^{2+}) sorption capacity of eggshell powder was found to be 148.3 mg/g at 328 K. From the Table 2, the sorption capacity (K_F) and (K_L) increased with increase in temperature which implies the sorption process as endothermic in nature and lower value for K_F indicates that the rate of adsorbate removal is low of (Fe^{2+}). The 'n' should have values lying in the range of 1–10 for classification as favorable adsorption [16, 17]. A higher value of n (Table 2) indicates a weaker bond between adsorbate and adsorbent [18, 19]. However, the correlation coefficient of the Frendlich isotherm is noted lower that of Langmuir one which means both types of the iron salts fitted with the Langmuir isotherm model.

Furthermore, as seen from Figure 2 the linear plots of Langmuir and Freundlich equations representing iron adsorption by the powdered eggshells. The value of R^2 is a measure of the goodness-of-fit of experimental data on the isotherm models. The adsorption constants of Langmuir and Freundlich equations and their correlation coefficients (R^2) which are presented in Table 2 confirm the fitness of Fe^{2+} and Fe^{3+} removal with Langmuir isotherm removal model.

3.3. Adsorption Kinetics

Two kinetic models i.e. pseudo-first-order and Ho pseudo-second-order were applied to investigate the reaction pathways and potential rate limiting steps of the adsorption of iron onto eggshell powder.

The Lagergren pseudo-first-order rate constant, K_1 and the adsorption capacity, q_t at different agitation speeds, initial iron concentration or mass of eggshells were determined from the slope and intercept of the plots of log (1-q_t) versus t (time) and are listed in Table 3 along with the correlation coefficient (R^2). From the kinetic data in Table 3, a large difference between theoretical and experimental equilibrium adsorption capacity, q_e, is observed at all temperatures, indicating a poor fit of the pseudo- first-order equation to the experimental data.

Table 3. *First order kinetics parameters for adsorption of iron (II) onto untreated and modified eggshell powder at different operating conditions.*

Parameter Studied		Untreated Eggshell		Modified Eggshell	
		K_1 (min^{-1})	R^2	K_1 (min^{-1})	R^2
Agitation speed (rpm)	200	0.0543	0.93	0.0504	0.903
	400	0.0564	0.867	0.0532	0.91
	500	0.0564	0.835	0.0608	0.809
	600	0.0500	0.4845	0.0518	0.908
Initial conc. C_O (mg/L)	163	0.0534	0.851	0.0486	0.859
	244	0.0564	0.806	0.0527	0.91
	323	0.0509	0.932	0.0504	0.924
	440	0.0514	0.930	0.0509	0.93
Mass of eggshell (g)	0.5	0.0495	0.888	0.0530	0.899
	1.0	0.0903	0.886	0.0567	0.873
	1.5	0.0587	0.835	0.0490	0.927
	2.0	0.0555	0.857	0.0594	0.88

Table 4. *Second order kinetics parameters for adsorption of iron (II) onto modified eggshell powder at different operating conditions.*

Parameter Studied		Untreated Eggshell		Modified Eggshell	
		K_2 (g.mg^{-1}. min^{-1})	R^2	K_2 (g.mg^{-1}. min^{-1})	R^2
Agitation speed (rpm)	200	0.0007	0.991	0.0018	0.998
	400	0.0010	0.997	0.0011	0.996
	500	0.0012	0.998	0.0016	0.999
	600	0.0014	0.999	0.0021	0.9996
Initial conc. C_O (mg/L)	163	0.0015	0.999	0.0034	0.9998
	244	0.0022	0.997	0.0016	0.999
	323	0.0009	0.997	0.0013	0.999
	440	0.0001	0.995	0.0013	0.998
Mass of eggshell (g)	0.5	0.0005	0.981	0.0005	0.989
	1.0	0.0009	0.994	0.00084	0.995
	1.5	0.0010	0.997	0.0009	0.997
	2.0	0.0017	0.999	0.0012	0.998

The pseudo-second-order model constants were determined from the slope and intercept of the plot of t/q_t versus t. The plot of t/q_t versus t at different conditions was carried out (plots are not shown) and the values of K_2 are calculated and represented in Table 4. Contrary to the pseudo-first-order equation, the fitting of the kinetic data in the pseudo-second-order equation showed excellent linearity with high correlation coefficient (R^2> 0.999) over the experimental conditions.

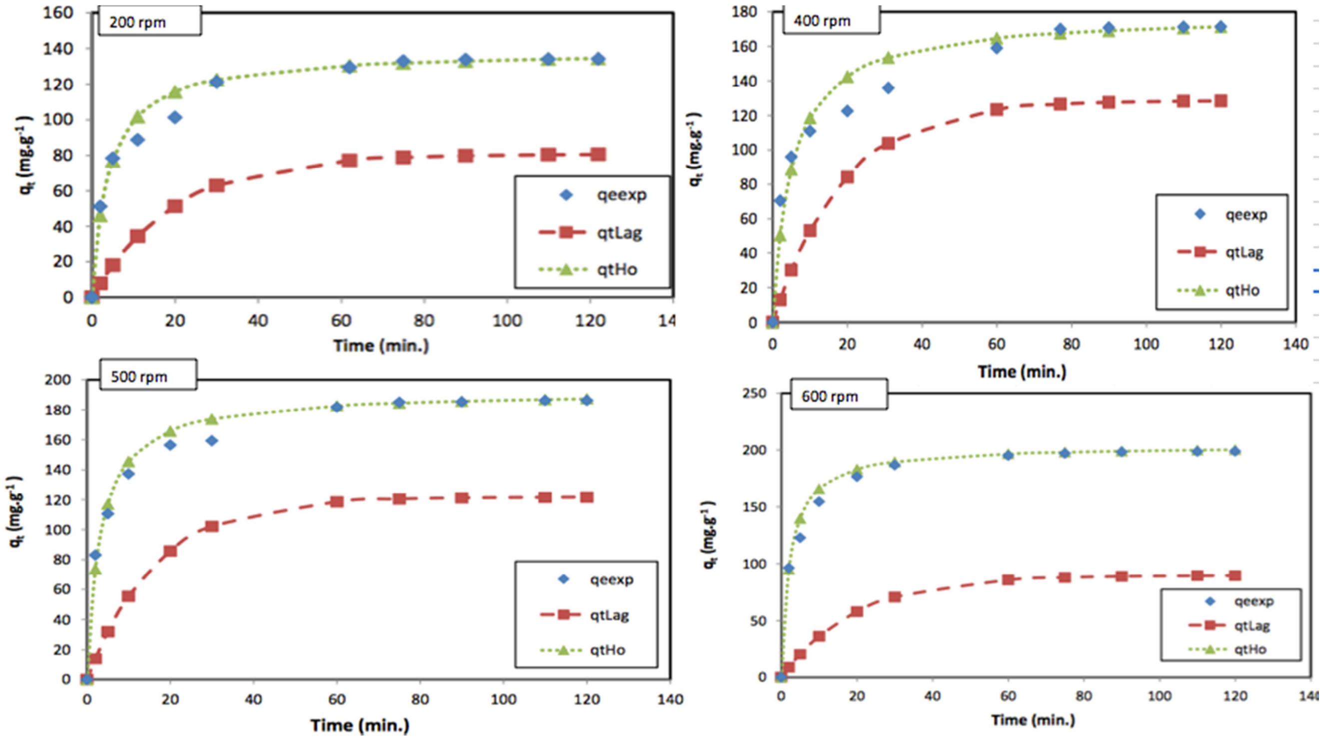


Figure 3. *Kinetic models comparison with the experimental data at different agitation speed.*

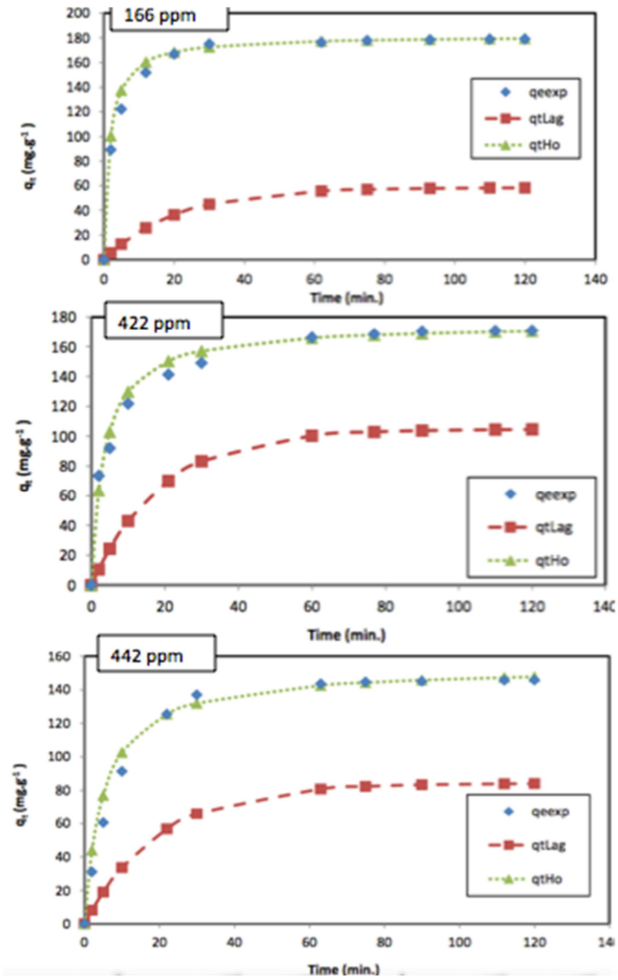


Figure 4. *Kinetic models comparison with the experimental data at initial iron (II) concentration.*

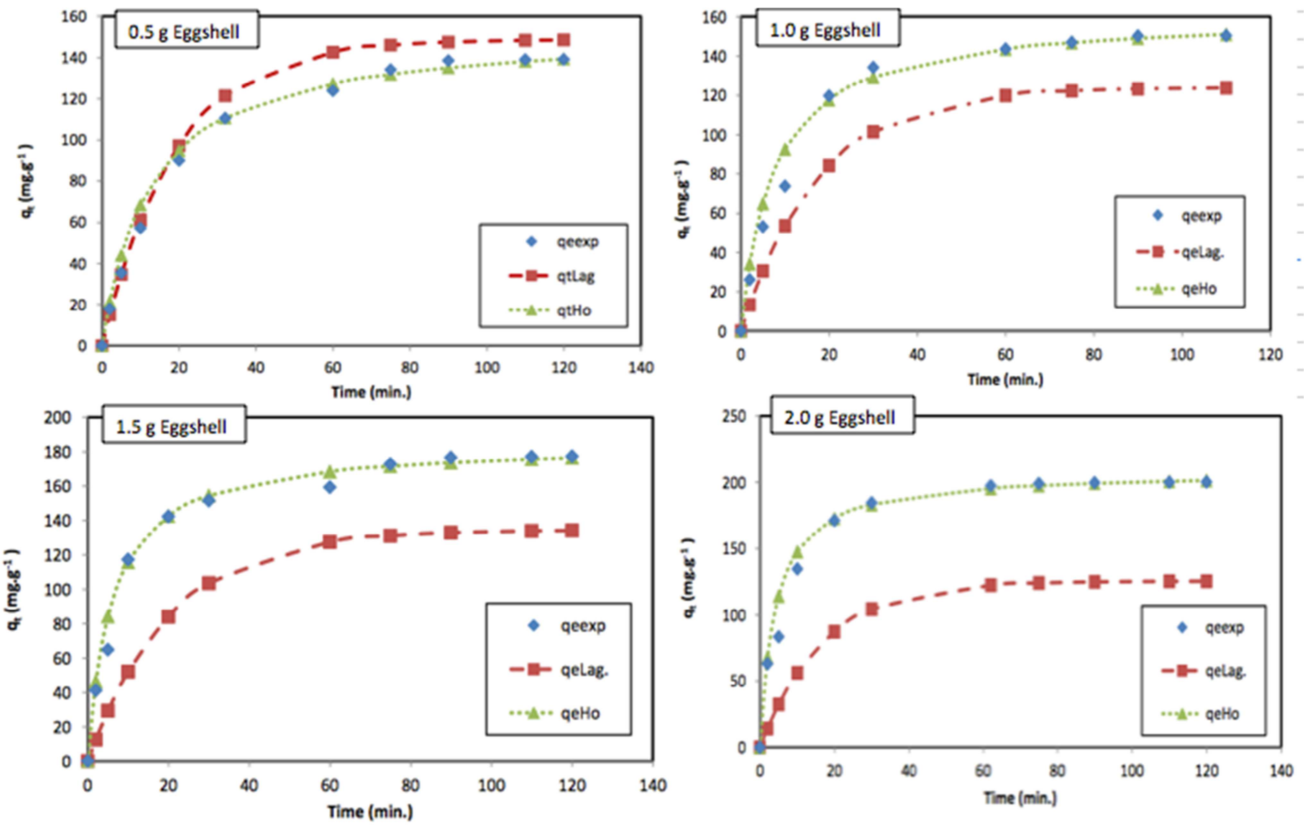


Figure 5. *Kinetic models comparison with the experimental data at different eggshell mass.*

It is also observed from the plots in Figures 3-5 that the calculated q_e values were found to be quite close to the experimental q_e values for all the parameters studied. So, it was inferred that the adsorption of iron onto eggshell followed pseudo- second-order kinetics. This finding suggests that the rate-limiting step of the adsorption system may be chemisorption.

3.4. Effect of System Variables on Adsorption of Iron

3.4.1. Effect of Agitation Speed

Studies on the effect of agitation speed were conducted by varying speeds from 200 to 600 rpm, at 310 ppm initial iron (II) concentration for 120 minutes of reaction time by using 1.5g of the untreated and modified eggshell at 313K. The influence of agitation speed on the extent of adsorption is shown in Figure 6. At a given time, iron removal increases with the increase in the speed of agitation. The reason for the increase in efficiency is that at higher speeds better contact between the adsorbent and adsorbate is possible [20]. Similar findings are reported in the literature for fluoride removal by using activated charcoal and have been reported by other investigator [20].

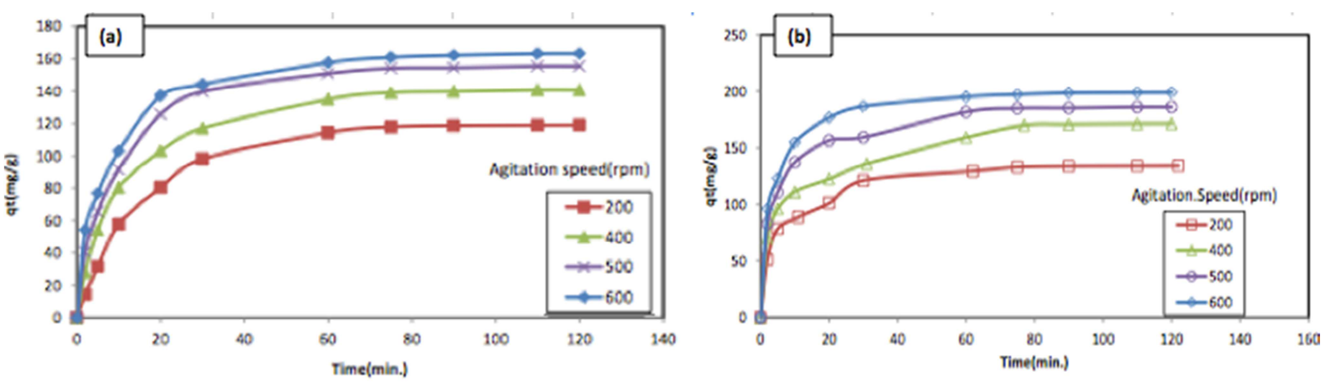
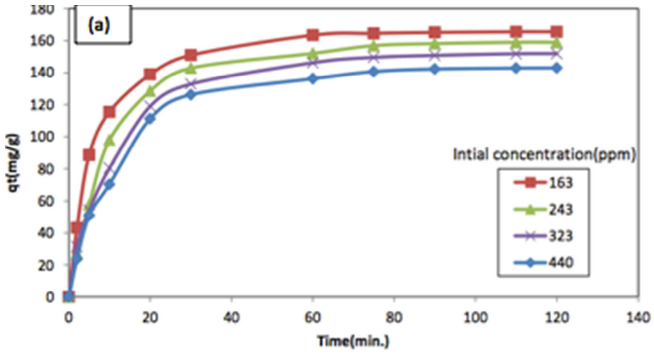


Figure 6. *Effect of agitation speed on Fe (II) adsorption onto (a) untreated eggshell; (b) modified eggshell.*

3.4.2. Effect of Initial Concentration

The efficiency of iron adsorption for different initial iron (II) concentrations ranging from 163 to 440 ppm was investigated by carrying out adsorption experiments at the best experimental conditions (600 rpm and 1.5g of eggshell) present in Figure 7. The adsorption capacity of iron decreased with increase in initial iron concentration. This is possibly due to the fact that for a fixed adsorbent dose, the total available adsorption sites are inadequate, which become saturated at a definite concentration. Due to increasing concentration gradient, acts as increasing driving force to overcome all mass transfer resistances of the iron between the aqueous and solid phase, leading to an increasing equilibrium sorption until sorbent saturation is achieved. Similar results have been reported for fluoride removal by activated charcoal [21].



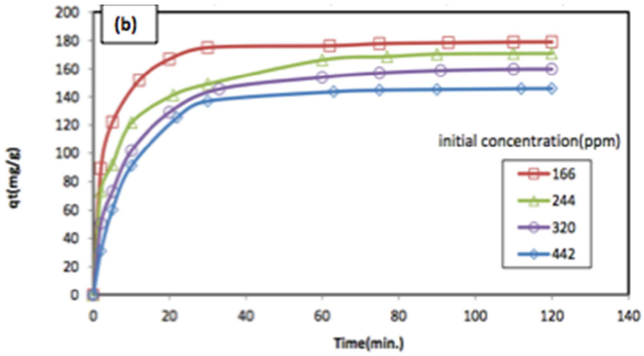
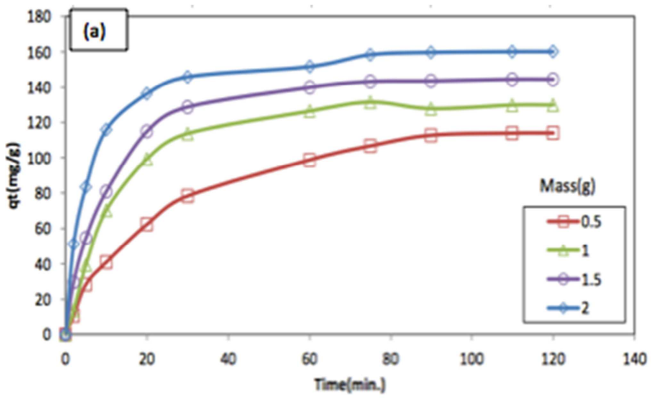


Figure 7. *Effect of initial Fe (II) concentration on Fe (II) adsorption onto (a) untreated eggshell; (b) modified eggshell.*

3.4.3. Effect of Adsorbent Mass

Adsorption process is mainly depends upon the particle size of the adsorbent. It is well established that the mass of the adsorbent is an additional factor greatly influence any adsorption process. The effect of eggshell mass was investigated at different concentrations of 0.5, 1.0, 1.5 and 2.0g. The results summarized in Figure 8, indicating the adsorption capacity increased with increase in eggshell mass. This result indicates high adsorbent mass addition favours the removal of iron by adsorption onto eggshell. This indicates that the surface area of the adsorbent is increased, so the iron adsorbed onto the eggshell. Similar trend were previously reported by Rubcumintara [4].



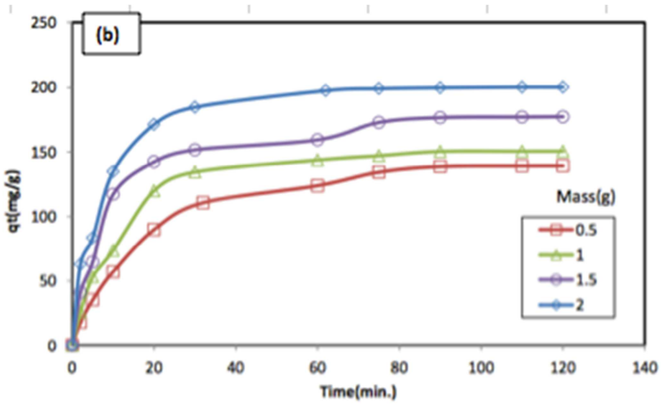


Figure 8. *Effect of agitation speed on Fe (II) adsorption onto (a) untreated eggshell; (b) modified eggshell.*

4. Conclusion

The present investigation of the possibility of Iron removal from aqueous solution by using adsorption technique into two types of eggshell (natural and burned eggshell at 500°C) as natural and low cost adsorbent which was carried out in batch adsorber with mechanical stirring column system. The results reveal that the treated eggshell shows better results than the untreated one. Moreover, the isotherm study showed the contaminated wastewater with iron (III) and (III) is well fitted with Langmuir isotherm. Finally, experimental data for the adsorption of Fe^{2+} onto both types of eggshell follows pseudo second- order model for all variables studied based on graphical presentation, and error functions values.

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