Scientific Research

Improvement of Fe(II)-Adsorption Capacity of FeOOH-Coated Brick in Solutions, and Kinetics Aspects

Saint Charles Dehou[1], Joseph Mabingui[1], Ludovic Lesven[2], Michel Wartel[2], Abdel Boughriet[2,3*]

[1]Chaire Unesco sur la Gestion de l'Eau, Laboratoire Hydrosciences Lavoisier,
Faculté des Sciences, Université de Bangui, Bangui City, République Centrafricaine
[2]Université de Lille1 Laboratoire Géosystèmes Equipe Chimie Analytique et Marine,
CNRS UMR 8217, Villeneuve d'Ascq, France
[3]Département de Chimie, Université Lille Nord de France, I.U.T de Béthune,
Rue de l'Université, Béthune, France
Email: *abdel.boughriet@univ-lille1.fr

ABSTRACT

The adsorbent, iron oxy-hydroxide coated brick, was used in the present work for removal of iron(II) from aqueous solutions. The adsorption performances of this composite were significantly improved when brick pellets (as a support material) were pre-treated in a 6 M HCl solution at 90°C for 6 hours, when compared to untreated ones and those pre-washed in a 1 M HCl solution at RT for 1 day. This phenomenon was attributed to larger surface areas measured for modified brick by BET, thus enabling a better FeOOH deposition. The ability of this new composite to better adsorb Fe^{2+} ions from synthetic solutions was evidenced from fixed-bed column experiments: data were compared to those obtained from raw brick and iron oxides-coated sand columns. The adsorption mechanism followed better pseudo-second-order reaction kinetics, suggesting a chemisorption process, and the rate constant increased with a temperature increase, revealing the endothermic nature of Fe(II) adsorption. Furthermore, the equilibrium data fitted the Langmuir isotherm model with a maximum monolayer sorption capacity $Q_{max} = 0.669$ mg/g and a Langmuir constant $K_L = 0.659$ L/mg at room temperature. The activation energy (Ea) of Fe(II) adsorption and the changes in entropy (ΔS), enthalpy (ΔH) and free energy (ΔG) of activation were determined, with values suggesting the involvement of an activated chemical adsorption and an associative mechanism.

Keywords: Brick; Ferrous Ion; Iron Oxyhydroxide; Acid Activation; Adsorption; Kinetics; Activation Energy; Water Treatment

1. Introduction

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 [1]. 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. On this view, many works demonstrated the beneficiary effects of surface coatings of iron oxide(s)/hydroxide(s) on the sorption behavior towards metal ions onto, for instance: 1) silica and $Al(OH)_3/SiO_2$ [2-8]; 2) aluminosilicate minerals such as zeolite [9,10]; and 3) hydrated magnesium silicate

mineral, sepiolite [11]. One possible solution to this problem is to use the brick material which is composed predominantly of sand and clays. Recently published works had allowed us to show that brick pellets recovered with FeOOH represented an appropriate material for removing soluble iron from ground waters [12].

The first objective of the present work had been to improve the Fe(II)-adsorption capacity performances of the brick made by craftsmen in Central African Republic. The adsorption capacity of a new absorbent (FeOOH deposited onto 6 M HCl-treated brick pellets) was investigated by carrying out column experiments, and data were compared to those obtained with untreated brick grains and ones that were previously gently treated in a 1 M HCl solution at RT before their FeOOH coating.

The second objective of this work had been to investigate the adsorption kinetics and isotherm models of iron(II) removal from aqueous solutions by this new composite, and to elucidate the resulting Fe(II)—adsorp-

tion mechanism .

2. Materials and Experiments

2.1. Materials

Bricks were made by craftsmen and used for construction activity by local people in Bangui region (Central African Republic). Bricks makers extracted starting material directly near their homes at ≥0.2 m below ground. Briefly, extracted soils were mixed with water and the obtained mud was shaped manually; Resulting air-dried (48 h) bricks were placed in efficient stackings in order to ensure a continuous air flow through a setting up assimilated to a basic oven (that was built simply on ground), heat treated with dry wood for a period of about three days at temperatures ranging from 500˚C to 800˚C and finally cooled progressively up to ambient temperature during two/three days. In order to increase the surface area of the brick material, this latter was broken in grains manually by using a hammer. The brick particles were afterwards sieved with a mechanical sieves and the fraction containing particles sizes which varied from 0.7 to 1.0 mm, was kept for our experiments. This fraction was washed with Milli-Q water and then decanted; After settling, the water was eliminated and brick grains were dried at 105˚C. The dried solid particles thus obtained were ready for two leaching procedures: the first one consisted of washing brick pellets with a 1 M HCl solution for one day and with Milli-Q water several times, and finally dried them at 105˚C; the second one consisted of leaching the material in a 6 M HCl solution at a constant temperature of 90˚C for six hours. Afterwards, a deposition of FeOOH onto modified brick grains was performed by the precipitation of a 0.25 M ferric nitrate solution in the presence of a 6 NaOH solution followed by a 1 M NaOH solution in order to adjust pH at 6 - 7; and finally, the resulting pellets were washed several times with Milli-Q water in order to eliminate the excess of FeOOH not attached to grains.

Specific surface areas pore volumes of brick pellets before and after chemical treatments were determined by nitrogen adsorption isotherm analyses (BET) using Sorptomatic 1990 Carlo Erba at −196˚C.

2.2. Column Experiments

All the experiments were conducted in a glass column with an inner diameter of 1.4 cm, a height of 25 cm, and a medium—porosity sintered—pyrex disc at its bottom in order to prevent any loss of material. This column was packed with an absorbent composite (14.1 g) which contained either sand or brick as the support material. The adsorption capacity of these different absorbents was investigated for a bed height of about 10 cm. The iron(II)-containing influent ($[Fe^{2+}]$ = 9.6 mg/L) passed at room temperature through the column downward using a peristaltic pump at a flow rate of 10 mL per minute. Before being used in every experiment, about 5 bed volumes of Milli-Q water were passed through the column: 1) first in order to remove any unbound and thin particles/iron oxide(s)/hydroxide(s); 2) second to check the absence of soluble iron in the effluent by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy); and 3) third to confirm the stability of the FeOOH coating on brick grains. Effluent samples were collected at various time intervals, and the concentration of soluble iron in the effluent was analyzed with time using an ICP-AES spectrometer model: Varian Pro axial view.

2.3. Adsorption Experiments

Kinetics studies on Fe(II) adsorption onto Bangui brick were carried out with brick grains with 0.7 - 1.0 mm sizes that were first pre-treated with a 6 M HCl solution at 90˚C for six hours, and second coated with FeOOH. Experimental data were afterwards compared to those found for FeOOH-brick composites that were prepared directly from raw brick grains and from ones pre-washed in a 1 M HCl solution for 24 hours. 50 mL of a Fe^{2+} ions solution [prepared from the salt: $Fe(NH_4)_2(SO_4)_2, 6H_2O$] at a concentration of 30 mg of iron per liter were transferred into a cell containing 4 g of brick pellets (with average diameters varying from 0.7 to 1.0 mm). The mixture thus prepared was shaken gently at a constant speed of 120 rpm using a mechanical shaker (Model: IKA Labortechnik KS 250 basic). 1 mL of the supernatant (which was filtered through a 0.45 μm pore diameter cellulose nitrate filter) was collected at various time intervals from 0 to 30 minutes and analyzed for the determination of iron level by using an ICP-AES spectrometer (Inductively Coupled Plasma Atomic Emission Spectroscopy; Model: Varian Pro axial view). The reproducibility of concentration measurements was ensured by repeating three times the same experiments under identical experiment conditions. This procedure permitted us to determine average values of iron content in the reaction solution, and standard deviations of these analyses were evaluated to be within ±3%. The Fe(II) adsorption capacity of brick was calculated by using the following equation: $Q_e = (C_o - C_e)V/m$, where Q_e represented the adsorption capacity of iron(II) on FeOOH-coated brick (in mg/g); C_o was the initial content of iron(II) in the cell (in mg/L); C_e represented the equilibrium solute concentration (in mg/L); and m and V corresponded to the mass of brick used (g) and the volume of Fe(II) solution used (L), respectively.

Adsorption-isotherms studies were performed in ten 100 mL-flasks each one containing 2 g of brick pellets in which were added 50 mL of an iron(II) solution having a concentration ranging from 2 to 20 mg/L. These flasks

were placed on a mechanical shaker (as mentioned above) and gently shaked at a speed of 120 rpm. Preliminary sorption experiments showed that a reaction time of 4 hours at a temperature of 17°C ± 1°C was sufficient for the system to attain thermodynamic equilibrium. Afterwards, suspensions were filtered and the recovered solution was analyzed to determine Fe^{2+} ions concentrations using ICP-AES. The quantity of iron adsorbed onto brick pellets, noted Q_e (in mg/g), was assessed from the difference between the initial and the equilibrium contents of iron(II) in the liquid phase. It should be noted that all these experiments were at least triplicated and data were averaged.

3. Results

3.1. Improvement of Adsorption Performances of Brick

There was evidence in the literature [13-16], that clay minerals could be chemically modified to enhance their adsorption capacity, particularly, when amorphous meta-kaolinite (which is a mineral present in the study brick [12]) was thermally treated with concentrated inorganic acids. In our case, this suggestion was clearly confirmed, indeed, the surface area (S.A.) and pore volume (V_{pore}) of crushed brick increased notably after acid leaching from: S.A. = 31.2 cm^2/g and V_{pore} = 0.15 cm^3/g in 1 M HCl-washed brick pellets at room temperature for 24 hours, to: S.A = 76 cm^2/g and V_{pore} = 0.23 cm^3/g in 6 M HCl-treated ones at 90°C for 6 h. Recently, more exhaustive studies (not reported here) revealed that HCl concentration and reaction temperature/time induced dramatic morphological, compositional, textural, and surficial modifications of Bangui-brick grains, resulting in more microporous structures in which clay minerals played a predominant role [17].

On the other hand, the effects of contact time on the adsorption of Fe^{2+} ions onto FeOOH-coated brick pellets were examined in the present work. Overall, it can been seen in **Figure 1** that Fe(II) adsorption was found to be a more rapid process when pellets were previously pretreated with a 6 M HCl solution at 90°C for 6 hours than when they were simply washed with a 1 M HCl solution for 1 day. This observation confirmed the importance of medium acidity and temperature on the chemical treatment of the brick in order to improve its properties as a support material. Thus, owing to the acid pre-activation of Bangui brick more than 80% of the reaction occurred within the first 8 min, and the solid-liquid equilibrium was attained in less than 25 min.

Finally, Fe(II)-adsorption capacities of different adsorbents in aqueous media were investigated in a fixed-bed column. The influent with a Fe(II) concentration of 9.5 mg/L was continuously passed through a glass column at
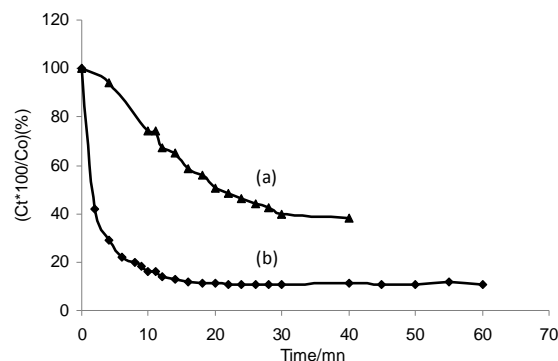

Figure 1. Variation of Fe^{2+}-ions concentration versus contact time at room temperature during Fe(II) adsorption onto the composite FeOOH-coated brick: (a) With brick previously washed in a 1 M HCl solution for 24 h; (b) With brick previously pre-activated in a 6 M HCl solution at 90°C for 6 h. C_o represented the initial concentration of iron(II) in the medium, and C_t was the Fe(II) content at the adsorption time, t.

a flow rate of ~10 mL/mn and at a pH range 5.5 - 5.9. As a whole, for either raw sand or iron oxides-coated sand, barely 40% of Fe^{2+} ions in this influent were adsorbed by these adsorbents at the beginning of the experiments (**Figure 2**), and these quantities decreased rapidly up to reach Fe(II) levels close to those initially measured in the influent. As for raw brick, its iron(II) removal process was found to be better than that observed for raw sand and modified sand, and increased drastically when brick pellets were previously recovered with FeOOH (**Figure 2**).

It was further shown that, before FeOOH coating, the pre-treatment of the brick in a 6 M HCl solution at 90°C for 6 hours contributed to enhance strongly its Fe(II)-adsorption capacity (see **Figure 2**). The maximum column capacity, q_{max} (in mg), for a given feed concentration and flow rate was calculated from the equation: q_{total} = $FC_oA/10^5$, where F was the volumetric flow rate (in ml/min), and A represented the area under the plot of the adsorbed Fe(II) percentage versus time that was evaluated from: $A = \int_{t=0}^{t=tfinal} Fe\% \cdot dt$ [where Fe% = $(C_o - C) \cdot 100/C_o$, with C_o = influent Fe(II) concentration (in mg/L) and C = effluent Fe(II) concentration(in mg/L)]. We found: q_{total} = 9.9 mg for FeOOH-coated brick, and q_{total} = 22.6 mg for FeOOH-coated (pre-activated) brick (q_{total} values were determined for a brick mass of 14.1 g inside the glass column). The equilibrium uptake (Q_e) representing the amount of iron(II) adsorbed onto brick surfaces per unit mass of dry material in the column was calculated from the equation: Q_e = q_{total}/m_{brick}, where m_{brick} (14.1 g) corresponded to the total mass of dry adsorbent inside the column. We found: Q_e = 0.7 mg/g for FeOOH-coated brick, and Q_e = 1.6 mg/g for FeOOH-coated (pre-activated) brick. These values indi-
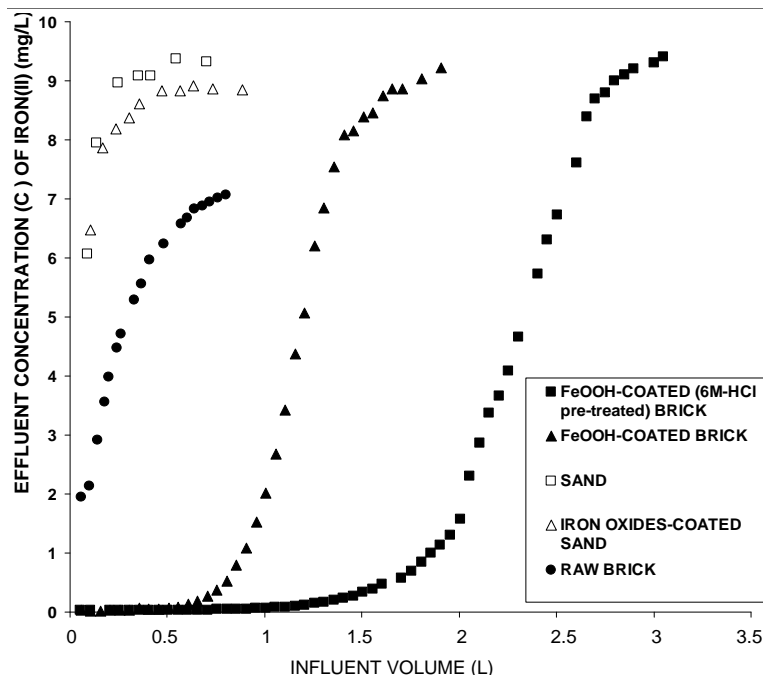
Figure 2. Evolution of Fe(II) concentration in the effluent (in mg/L) as a function of influent volume (containing 9.6 mg of iron per liter)) passed through a glass column (which was packed with different adsorbents at a bed height of 10 cm) at a flow rate of 10 mL/mn: raw sand (□); iron oxides-coated sand (△); raw brick (●); FeOOH-brick composites prepared with brick pellets treated in a 1 M-HCl solution at room temperature for 24 hours (▲), and in a 6 M-HCl solution at 90°C for 6 hours (■).

cated clearly that the acidic and thermal treatment of the brick contributed to generate a better support material (with greater surface areas, as evidenced above) for FeOOH deposition and, as a consequence, to improve the Fe(II)-adsorption characteristics of FeOOH-brick composite.

3.2. Adsorption Kinetics Characteristics

The kinetics of Fe(II) adsorption onto Bangui brick was studied by carrying out a batch of experiments at several constant temperatures ranging from 17°C to 45°C, and by monitoring the content of adsorbed Fe^{2+} ions with time. The kinetic mechanism involved in the study system was examined in terms of different kinetic models: 1) pseudo-first order kinetics; 2) pseudo-second order kinetics; 3) Elovich equation; and 4) intra-particle diffusion (for more details, consult e.g. [18] and references therein). The rates of Fe(II) adsorption onto FeOOH-coated brick in aqueous media were then examined by plotting the following curves: 1) $Ln(Q_e - Q_t)$ versus time for a pseudo-first order kinetics; 2) t/Q_t versus time for a pseudo-second order kinetics; 3) Q_t versus $Ln(t)$ according to Elovich equation; and 4) Q_t versus $(t^{1/2})$ in case Fe^{2+} ions were assumed to be transported from the liquid phase towards the brick surface according to an intraparticle diffusion phenomenon [where Q_e and Q_t represented the contents of Fe(II) adsorbed (mg/g) at equilibrium and at time t (min), respectively]. In order to find the best

kinetic model, the fitting of experimental data to kinetic equations was tested, and kinetic constants and correlation coefficients were determined (**Table 1**). In this table, Q_e^{exp} which represented the quantity of iron deposited onto brick pellets was determined experimentally from the equation $[(C_i - C_e) \cdot V]/(1000 \cdot m_{brick})$, where C_i was the initial concentration of Fe^{2+} ions in contact with brick pellets, C_e was that obtained when the system reached the equilibrium state, and m_{brick} was the mass of brick pellets in interaction with a V(mL) volume of Fe(II) solution; and Q_e^{calc} was calculated from the mathematiccal treatment of the first-order and second-order kinetics plots drawn.

As a whole, our findings showed that: 1) the pre-activation of brick pellets with HCl contributed to enhance significantly the rate constants for Fe^{2+}-ions adsorption with values increasing at room temperature from 0.078 to 0.102 (1/mn) for the first-order kinetics and from 0.060 to 0.830 g/(mg·min) for the second-order kinetics; and 2) a rise in temperature from 20°C to 39.5°C led to an increase of the pseudo-first order kinetic constant k_1 (from 0.102 to 0.159 1/min) and the pseudo-second order kinetic constant k_2 (from 0.830 to 1.315 g/(mg·min)). It could also be noticed that: 1) second-order plots (t/Q_t vs time) had better linearity with correlation coefficients $0.997 \leq R^2 \leq 0.998$ than those obtained for a first-order kinetics [$Ln(Q_e - Q_t)$ vs time] : $0.907 \leq R^2 \leq 0.994$; 2) the calculated Q_e values (where Q_e represented the amount of

Table 1. Kinetics constants obtained for Fe(II) adsorption onto FeOOH-coated (pre-activated) brick pellets at different temperatures.

Temperature (°C)	Q_e^{exp} (mg/g)	Pseudo-first-order			Pseudo-second-order		
		Q_e^{calc} (mg/g)	K_1 (1/min)	R^2	Q_e^{calc} (mg/g)	K_2 (g/(mg·min))	R^2
17	0.292	0.301	0.097	0.994	-	-	-
20	0.393	0.185	0.102	0.947	0.423	0.830	0.998
25	0.349	0.276	0.122	0.991	-	-	-
30	0.380	0.236	0.1	0.985	0.408	1.085	0.997
35	0.352	0.226	0.157	0.985	0.376	1.12	0.998
39.5	0.358	0.248	0.165	0.907	-	-	-
39.5	0.355	0.237	0.159	0.992	0.385	1.315	0.998
45	0.315	0.230	0.167	0.980	-	-	-

Fe^{2+} ions adsorbed onto brick per mass unit at equilibrium) which were obtained from second-order kinetics plots, were closer to the experimental ones than the calculated Q_e ones found from first-order kinetics plots (see **Table 1**); and 3) consequently the pseudo-second order model exhibited lower χ^2 values ($0.0012 \leq \chi^2 \leq 0.0020$) than those determined for the pseudo-first-order model ($0.0070 \leq \chi^2 \leq 0.0087$), where χ represented a generalized error function, defined as: $\chi^2 = (1/N)\sum_{i=1..N} (Q_e^{exp} - Q_e^{calc})^2$, with Q_e^{exp} corresponding to the experimental values of adsorbate per gram of adsorbent and Q_e^{calc} being the calculated ones. These observations suggested that Fe(II) adsorption onto brick might be approximated to the pseudo-second order kinetics model. This finding indicated that a chemisorption process or an activated reaction occurred more predominantly in the rate controlling step. Such a model then assumed that one iron ion was sorbed onto two sorption sites (noted 2A) on the brick surface according to:

$$2A_{(brick)} + Fe^{2+}_{(solution)} \rightarrow A_2Fe_{(brick)}$$
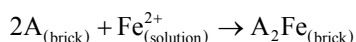
Also, in the assumption that solid surfaces in this modified brick were energetically heterogeneous, we could apply to our pseudo-second-order kinetic system Elovich equation defined as: $Q_t = [Ln(\alpha\beta)]/\beta + [Ln(t)]/\beta$, where Q_t was the sorption capacity at time t; α (in mg/(g·min)) was the initial sorption rate of Elovich equation; and the parameter β (in g/mg) was dependent upon the extent of surface coverage and activation energy of the considered chemisorption reaction. From our experimental data, Elovich plots were drawn, and the lines were found to be linear at different temperatures ranging from 25°C to 45°C ($0.968 \leq R^2 \leq 0.991$). **Table 2** lists the kinetic constants obtained from Elovich equation under the following experimental conditions: the initial concentration, C_i, was 30 mg of iron per liter, and the brick mass, m_{brick}, was 4 g in 100 mL of Milli-Q water.

Overall, it can be seen that the initial adsorption rate, α, and the β coefficient do not change significantly with

Table 2. Kinetic parameters determined from Elovich equation.

Temperature (°C)	α (mg/(g·min))	β (g/mg)	R^2
25	0.480	15.36	0.991
35	0.445	13.40	0.978
39.5	0.434	12.58	0.973
45	0.517	16.13	0.968

temperature: α varying from 0.434 to 0.517 mg/(g·min) and β from 12.58 to16.13 g/mg.

On the other hand, in order to check whether or not the overall kinetics of Fe(II) adsorption reaction was controlled by surface/intra-particle diffusion, the intra-particle model developed by Weber and Morris [19] was also tested to our system by plotting Q_t against $t^{1/2}$ (not shown here). The obtained curves at the beginning of the kinetic process were roughly linear; however, their straight lines did not pass through the origin, what meant and confirmed that the intra-particle diffusion was not the rate-controlling step. Instead, we believed that the formation of solid solutions as: $Fe(II)_xFe(III)_y(OH)_z$ at the external surface of brick pellets might be responsible for this adsorption, thus preventing the sorbate molecules to move into the interior of sorbent particles (FeOOH coatings), and thereby limiting any binding of Fe^{2+} ions on / with interior sites of the sorbent by diffusion.

3.3. Adsorption Isotherms Characteristics

In order to gain more information about Fe(II) adsorption mechanism and surface characteristics and affinities of Bangui brick, three adsorption isotherm models were applied to our system (for more details, see e.g. [20] and references therein): 1) C_e/Q_e versus C_e (Langmuir adsorption isotherm); 2) $Log(Q_e)$ versus $Log(C_e)$ (Freundlich adsorption isotherm); and 3) Q_e versus $Ln(C_e)$ (Temkin adsorption isotherm). In this latter case, the plots obtained (not shown here) were badly linear with correla-

tion coefficients $R^2 \leq 0.85$, and this model was therefore excluded.

As for Freundlich and Langmuir models, all the plots were found to be linear with correlation coefficients $R^2 \geq 0.95$ (see **Figure 3** and **Table 3**).

The slope and intercept of these curves were used to calculate relevant parameters: 1) first Freundlich ones, K_F and n, which are two constants indicative of the relative adsorption capacity and adsorption intensity, respectively; and 2) second Langmuir ones, K_L being the equilibrium adsorption constant and Q_{max} representing the maximum amount of Fe^{2+} ions per unit mass of brick. Considering Freundlich adsorption model data, the n values were found to be higher than 1, and further the Freundlich constant K_F increased with temperature. All these findings suggested that: 1) Fe(II) ions interacted favorably with brick according to a chemisorption mechanism and 2) this process was endothermic. The isotherm plots of $Log(Q_e)$ vs $Log(C_e)$ at room temperature showed clearly that, when attaining the equilibrium state, FeOOH-coated (pre-activated) brick possessed better adsorption characteristics of Fe(II) ions than those observed in original (untreated) brick: indeed the extent of adsorption in percentage and the Fe(II) content adsorbed per unit mass of modified brick pellets (Q_{max}) were found to increase appreciably (see **Table 3**).

Thus, from the linear Freundlich plots obtained for no-activated brick (with correlation coefficients $0.95 \leq R^2 \leq 0.98$), the Freundlich isotherm capacity, K_F, varied from 0.036 to 0.050 mg/g and the adsorption intensity, n, ranged from 1.581 to 2.170 (see **Table 3**); whereas from the linear Freundlich plots obtained for activated brick (with $R^2 \approx 0.88$), K_F and n were found to be: 0.348 and 4.531, respectively (see **Table 3**).

Langmuir isotherm plots found for our system had also good linearity with regression coefficient, R^2, ranging from 0.990 to 0.993, indicating strong monolayer chemisorption. It is also worth noting that the Langmuir equilibrium coefficient, K_L, was indicative of the way in which the presumed equilibrium reaction was displaced:

$$brick + Fe(II)_{(in\ aqueous\ phase)} <=> brick - Fe(II)$$
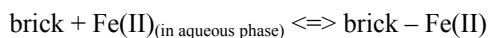
As a whole, when brick pellets were pre-treated by HCl at 90°C, larger K_L values were found and confirmed better association between brick and Fe(II) ions. Also, acid activation was found to have further positive effect on the maximum adsorption capacity, Q_{max} increasing from 0.179 - 0.264 mg/g to 0.669 mg/g by enhancing the Langmuir capacity of brick by about 300%. This phenomenon can be explained by the generation of a great number of additional adsorption sites through the HCl treatment of brick pellets preceding their FeOOH coating.

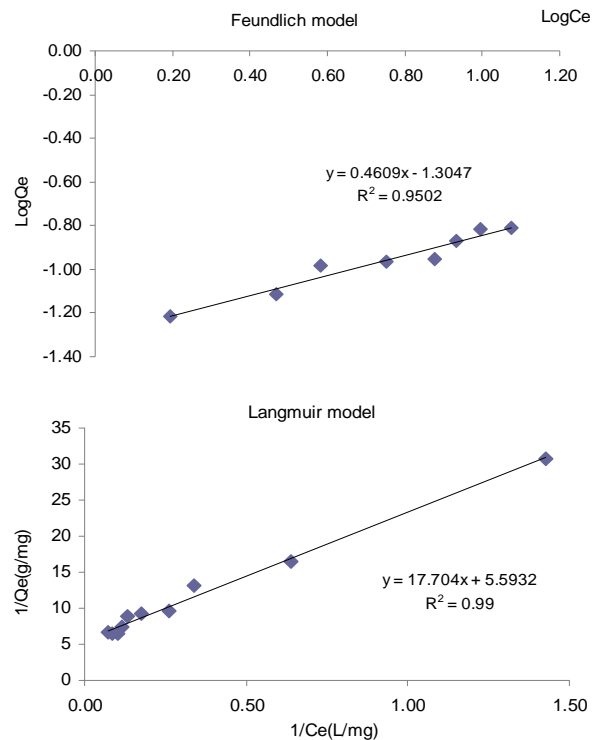The essential features of Langmuir isotherm can be expressed by the dimensionless constant separation fac-

Figure 3. Typical Langmuir and Freundlich isotherms obtained for Fe(II) adsorption on to FeOOH-coated (pre-activated) brick pellets at room temperature. The initial concentration of Fe(II) solution was 30 mg of iron per liter; and the amount of brick grains, m_{brick}, in the medium was 4 g in 100 mL.

Table 3. Adsorption parameters determined from Langmuir and Freundlich isotherms.

Adsorbents	Langmuir constants			Freundlich constants		
	Q_{max} (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2
FeOOH-coated brick pellets	0.179	0.3159	0.990	0.050	2.170	0.950
(brick grains were previously washed with HCl 1 M at RT for 24 hours)	0.264	0.2297	0.993	0.036	1.581	0.981
FeOOH-coated brick pellets						
(brick grains were pre-activated with HCl 6 M at 90°C for 6 hours)	0.669	0.659	0.919	0.348	4.531	0.881

tor or equilibrium parameter: $R_L = 1/(1 + K_L C_o)$, where K_L is the Langmuir isotherm constant, and Co represents the initial Fe^{2+}-ions concentration in the study aqueous medium [21]. The values of R_L calculated for Fe(II) adsorption on to FeOOH coated-brick pellets were found to be, in all cases, within 0 and 1, suggesting a highly favorable adsorption process, in addition, with a more elevated adsorption efficiency when Fe(II) content in-

creased in solution [raw brick pellets: $0.14 \leq R_L \leq 0.68$; and pre-treated (activated) brick : $0.04 \leq R_L \leq 0.08$].

3.4. Effect of Temperature and Activation Parameters for Fe(II) Adsorption onto Modified Brick

The above kinetic investigations by considering either a pseudo-first-order or a pseudo-second-order allowed us to show that: 1) the adsorption was controlled by chemical sorption; and 2) an increase in temperature favored Fe(II)-adsorption onto brick pellets, and consequently, that this process was endothermic.

The linear form of Arrhenius equation as: $Lnk = -E_a/RT + Cst$ was used successfully in the temperature range 17°C - 45°C in order to assess the activation energy for Fe^{2+} ions adsorption onto brick grains: Lnk_1 and Lnk_2 were plotted against $1/T$, and the corresponding curves yielded straight lines with regression coefficient values of $R_1^2 = 0.95$ and $R_2^2 = 0.97$, respectively (see **Figure 4**). It should be noted that the curve Lnk_1 vs $1/T$ contained more experimental aligned dots and in addition its regression coefficient was found to be better than that determined from the curve Lnk_2 vs $1/T$, suggesting that the pseudo-first-order model correlated better with Arrhenius equation. The activation energies, E_{a1} and E_{a2}, were evaluated from the slope $-E_a/RT$: we found $E_{a1} = 16.20 \pm 0.40$ kJ/mole and $E_{a2} = 16.93 \pm 0.85$ kJ/mole. These positive values of activation energy were found to be closer each other and further revealed that the rise in the solution temperature enhanced Fe(II) adsorption onto treated brick according to an endothermic process. In other words, a rise in temperature then led to help more Fe^{2+} ions to overcome this energy barrier, E_a, and thereby to get attached to brick surfaces/sites. On the other hand, the activation energies for Fe(II) adsorption onto modified brick exceeded largely 4.2 kJ/mole. This E_a value is usually considered as the maximum one measured for physical adsorption since the forces involved in such a process are low [22].

Accordingly, the involvement of a physical adsorption process in our system should be excluded. Instead, E_{a1} and E_{a2} were found to be in the range of activation energies obtained for activated chemical adsorptions, *i.e.*: 8.4 –83.7 kJ/mole [22-24].

To provide a better understanding of the adsorption thermodynamics of Fe^{2+} ions onto FeOOH-coated brick pellets, the thermodynamic activation parameters of this process were assessed using Eyring equation: $Ln(k/T) = Ln(k_B/h) + \Delta S/R - \Delta H/RT$, where k_B is the Boltzmann constant (1.3807×10^{-23} J·K^{-1}); h is the planck constant (6.6261×10^{-34} J·s); and ΔS and ΔH are the changes in entropy and enthalpy of activation, respectively. $Ln(k_1/T)$ and $Ln(k_2/T)$ were plotted against $1/T$, see **Figure 5**, and the slopes allowed us to determine $-\Delta H_1/R$ and $-\Delta H_2/R$,
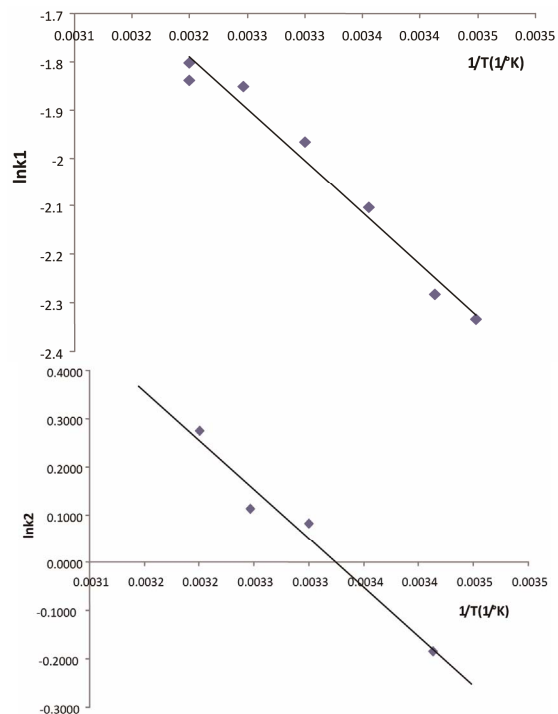

Figure 4. Activation energies measured for adsorption kinetics of soluble ions on to FeOOH-coated (activated) brick pellets by plotting Ln(k) versus 1/T, where k represents the pseudo-first order (k_1) and pseudo-second order (k_2) kinetics constant, and T is the reaction temperature.
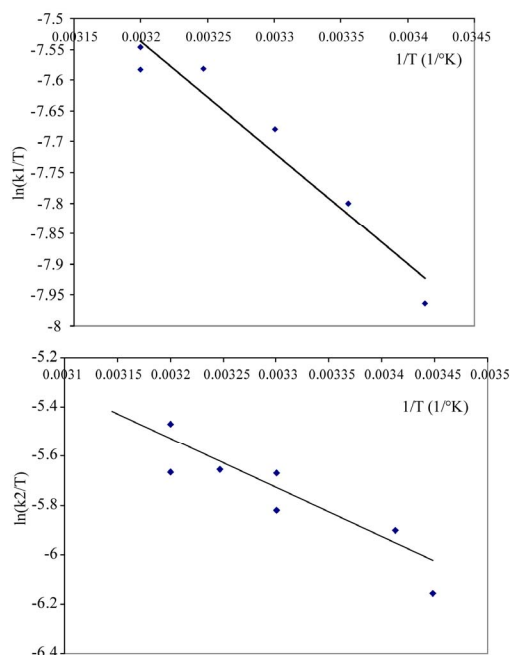

Figure 5. Thermodynamic parameters obtained for adsorption kinetics of iron(II) on to FeOOH-coated (activated) brick pellets by plotting Ln(k/T) against 1/T, where k represents the pseudo-first order (k_1) and pseudo-second order (k_2) kinetics constant, and T is the reaction temperature.

and the intercepts $[Ln(k_B/h) + \Delta S_1/R]$ and $[Ln(k_B/h) + \Delta S_2/R]$; And from these results, the changes in entropy of activation (ΔS_1 and ΔS_2) and in enthalpy of activation (ΔH_1 and ΔH_2) were evaluated and reported in **Table 4**. Also, the free energies of activation, ΔG_1 and ΔG_2 for this process were calculated at different temperatures ranging from 17°C to 45°C from the equation: $\Delta G = \Delta H - T\Delta S$ (see **Table 4**).

It should be noted that ΔS_1 and ΔS_2 were negative, suggesting that Fe^{2+} ions at the solid-solution interface were more organized than those located far in the bulk solution phase, and consequently, their degree of freedom decreased [25-28]. The magnitude and sign of ΔS_1 and ΔS_2 were good indicators to know whether the study reaction is an associative or dissociative mechanism [29-31]. Our ΔS values did confirm that Fe(II) adsorption onto this treated brick was an associative mechanism. As for the changes in enthalpy of activation, ΔH, they were found to be largely lower than $-T\Delta S$ in all cases, which meant that the reorientation step was mainly entropy controlled at the activation state. The values of free energy indicated that the adsorption reaction was not a spontaneous one and instead the system consumed energy from an entropic source that resulted from the structural organization of Fe^{2+} ions at the brick surface; and this free energy further increased with an increase in temperature (see **Table 4**).

4. Conclusion

The research described here was devoted to examine the Fe(II)-removal efficiency of FeOOH-brick composites in aqueous solutions following a thermal acid pre-treatment of the brick used as a support material. BET data revealed larger surface areas on the modified brick, favoring FeOOH coating. Column experiments indicated that Fe(II)-adsorption characteristics of the new composite were strongly improved when compared results to those obtained for raw brick, FeOOH-coated (no-treated) brick and iron oxides-coated sand. Fe(II) adsorption kinetics was found to be better described by the pseudo-second-order equation, showing that the chemical adsorption/

chemisorption was the rate-limiting step in the study system. Also, the equilibrium data were better described by the Langmuir equation, thus showing the involvement of a monolayer coverage of iron(II) onto brick-grains surfaces. The activation energy of this process was evaluated: $E_{a2} = 16.93 \pm 0.85$ kJ/mole. The magnitude of the Ea value indicated clearly that the adsorption was controlled by an activated chemical adsorption. Results from this study did suggested that FeOOH—coated brick could be used as an effective adsorbent for iron(II) removal from contaminated waters in developing countries, particularly when an acid pre-treatment of the support material "brick" was initially performed.

5. Acknowledgements

Table 4. Thermodynamic parameters for adsorption kinetics of iron(II) onto FeOOH-coated (pre-activated) brick.

Thermodynamic parameters	First order	Second order
ΔH (kJ/mole)	15.07	16.55
ΔS (J/mole/K)	−173.69	−152.25
ΔG (kJ/mole) at 20°C	65.96	61.16
ΔG (kJ/mole) at 25°C	66.83	61.92
ΔG (kJ/mole) at 30°C	67.70	62.68
ΔG (kJ/mole) at 35°C	68.57	63.44
ΔG (kJ/mole) at 39.5°C	69.35	64.13

REFERENCES

[1] D. van Halem, D. H. Moed, J. Q. J. C. Verberk, G. L. Amy and J. C. van Dijk, "Cation Exchange during Subsurface Iron Removal," *Water Research*, Vol. 46, No. 2, 2012, pp. 307-315. doi:10.1016/j.watres.2011.10.015

[2] R. P. Bailey, T. Bennett and M. M. Benjamin, "Sorption onto and Recovery of Cr(VI) Using Iron Oxide-Coated Sand," *Water Science & Technology*, Vol. 26, No. 5-6, 1992, pp. 1239-1244.

[3] S. Khaodhiar, M. F. Azizian, K. Osathaphan and P. E. Nelson, "Copper, Chromium and Arsenic Adsorption and Equilibrium Modeling in an Iron-Oxide-Coated Sand, Background Electrolyte System," *Water*, *Air*, *Soil Pollution*, Vol. 119, No. 1-4, 2000, pp. 105-120. doi:10.1023/A:1005109325539

[4] A. Joshi and M. Chaudhuri, "Removal of Arsenic from Ground Water by Iron-Oxide-Coated Sand," *Journal of Environmental Engineering*, Vol. 122, No. 8, 1996, pp. 769-800. doi:10.1061/(ASCE)0733-9372(1996)122:8(769)

[5] M. M. Benjamin, R. S. Sletten, R. P. Bailey and T. Bennett, "Sorption and Filtration of Metals Using Iron-Oxide-Coated Sand," *Water Research*, Vol. 30, No. 11, 1996, pp. 2609-2620. doi:10.1016/S0043-1354(96)00161-3

[6] M. M. Ahammed and K. Davra, "Performance Evaluation of Biosand Filter Modified with Iron Oxide-Coated Sand for Household Treatment of Drinking Water," *Desalination*, Vol. 276, No. 1-3, 2011, pp. 287-293. doi:10.1016/j.desal.2011.03.065

[7] B. Rusch, K. Hanna and B. Humbert, "Coating of Quartz Silica with Iron Oxides: Characterization and Surface Reactivity of Iron Coating Phases," *Colloids and Surfaces A*: *Physicochemical and Engineering Aspects*, Vol. 353, No. 2-3, 2010, pp. 172-180. doi:10.1016/j.colsurfa.2009.11.009

[8] M. M. Ahammed and V. Meera, "Metal Oxide/Hydroxide-Coated Dual-Media Filter for Simultaneous Removal of Bacteria and Heavy Metals from Natural Waters," *Journal of Hazardous Materials*, Vol. 181, No. 1-3, 2010, pp. 788-793. doi:10.1016/j.jhazmat.2010.05.082

[9] C.-S. Jeon, K. Back, J.-K. Park, Y.-K. Oh and S.-D. Lee, "Adsorption Characteristics of As(V) on Iron-Coated Zeolite," *Journal of Hazardous Materials*, Vol. 163, No. 2-3, 2009, pp. 804-808. doi:10.1016/j.jhazmat.2008.07.052

[10] R. Han, L. Zou, X. Hao, Y. Xu, F. Xu, Y. Li and Y. Wang, "Characterization and Properties of Iron-Oxide-Coated Zeolite as Adsorbent for Removal of Copper(II) from Solution in Fixed Bed Column," *Chemical Engineering Journal*, Vol. 149, No. 1-3, 2009, pp. 123-139. doi:10.1016/j.cej.2008.10.015

[11] E. Eren and H. Gumus, "Characterization of the Structural Properties and Pb(II) Adsorption Behavior of Iron Oxide Coated Sepiolite," *Desalination*, Vol. 273, No. 2-3, 2011, pp. 276-284. doi:10.1016/j.desal.2011.01.004

[12] S. C. Dehou, M. Wartel, P. Recourt, B. Revel, J. Mabingui, A. Montiel and A. Boughriet, "Physicochemical, Crystalline, and Morphological Characteristics of Bricks Used for Ground Waters Purification in Bangui Region (Central African Republic)," *Applied Clay Science*, Vol. 59-60, 2012, pp. 69-75. doi:10.1016/j.clay.2012.02.009

[13] G. Wang, X. Wang, X. Chai, J. Liu and N. Deng, "Adsorption of Uranium(VI) from Aqueous Solution on Calcined and Acid-Activated Kaolin," *Applied Clay Science*, Vol. 47, No. 3-4, 2010, pp. 448-451. doi:10.1016/j.clay.2009.11.003

[14] A. G. San Cristobal, R. Castello, M. A. M. Luengo and C. Viscayno, "Acid Activation of Mechanically and Thermally Modified Kaolins," *Materials Research Bulletin*, Vol. 44, No. 11, 2009, pp. 2103-2111. doi:10.1016/j.materresbull.2009.07.016

[15] K. Bhattacharyya and S. S. Gupta, "Removal of Cu(II) by Natural and Acid-Activated Clays: An insight of Adsorption Isotherm, Kinetic and Thermodynamics," *Desalination*, Vol. 272, No. 1-3, 2011, pp. 66-75. doi:10.1016/j.desal.2011.01.001

[16] G. Suraj, C. S. P. Lyer and M. Lalithambika, "Adsorption of Cadmium and Copper by Modified Kaolinites," *Applied Clay Science*, Vol. 13, No. 4, 1998, pp. 293-306. doi:10.1016/S0169-1317(98)00043-X

[17] S. C. Dehou, "Etude des Propriétés d'Adsorption des Oxyhydroxydes de fer Déposés sur un Support Naturel (la Brique): Application à l'Elimination du fer dans les eaux de Forages en République Centrafricaine," Thesis, University of Lillel, France, 2011, p. 157.

[18] S. S. Gupta and K. G. Bhattacharyya, "Kinetics of Adsorption of Metal Ions on Inorganic Materials: A Review," *Advances in Colloid and Interface Science*, Vol. 162, No. 1-2, 2011, pp. 39-58.

[19] W. J. Weber and J. C. Morris, "Kinetics of Adsorption on Carbon from Solutions," *Journal of the Sanitary Engineering Division*, Vol. 89, No. 2, 1963, pp. 31-63.

[20] K. Y. Foo and B. H. Hameed, "Insights into the Modeling of Adsorption Isotherm Systems," *Chemical Engineering Journal*, Vol. 156, No. 1, 2010, pp. 2-10. doi:10.1016/j.cej.2009.09.013

[21] K. R. Hall, L. C. Eagleton, A. Acrivos and T. Vermeulen, "Pore- and Solid-Diffusion Kinetics in Fixed-Bed Adsorption under Constant-Pattern Conditions," *Industrial & Engineering Chemistry Fundamentals*, Vol. 5, No. 2, 1966, pp. 212-213. doi:10.1021/i160018a011

[22] W. Zou, R. Han, Z. Chen, Z. Jinghna and J. Shi, "Kinetic Study of Adsorption of Cu(II) and Pb(II) from Aqueous Solution Using Manganese Oxide Coated Zeolite in Batch Mode," *Colloids and Surfaces A*: *Physicochemical and Engineering Aspects*, Vol. 279, No. 1-3, 2006, pp. 238-246. doi:10.1016/j.colsurfa.2006.01.008

[23] Z. Aksu, "Determination of the Equilibrium, Kinetic and Thermodynamic Parameters of the Batch Adsorption of Lead(II) Ions onto Chlorella Vulgaris," *Process Biochemistry*, Vol. 38, No. 1, 2002, pp. 89-99. doi:10.1016/S0032-9592(02)00051-1

[24] R. Han, W. Zou, Z. Thang, J. Shi and J. Yang, "Removal of Copper(II) and Lead(II) from Aqueous Solution by Manganese Oxide-Coated-Sand: I. Characterization and Kinetic Study," *Journal of Hazardous Materials*, Vol. 137, No. 1, 2006, pp. 384-393. doi:10.1016/j.jhazmat.2006.02.021

[25] M. M. Abu-Mesalam, "Sorption Kinetics of Copper, Zinc, Cadmium and Nickel Ions on Synthesized Silico-Antimonate Ion Exchanger," *Colloids and Surfaces A*: *Physicochemical and Engineering Aspects*, Vol. 225, No. 1-3, 2003, pp. 85-94. doi:10.1016/S0927-7757(03)00191-2

[26] R. S. Juang and J. Y. Chung, "Equilibrium Sorption of Heavy Metals and Phosphate from Single- and Binary-Sorbate Solutions on Goethite," *Journal of Colloid and Interface Science*, Vol. 275, No. 1, 2004, pp. 53-60. doi:10.1016/j.jcis.2004.01.035

[27] Z. Elouear, J. Bouzid, N. Boujelben, M. Feki, F. Jamoussi and A. Montiel, "Heavy Metal Removal from Aqueous Solutions by Activated Phosphate Rock," *Journal of Hazardous Materials*, Vol. 156, 2008, pp. 412-420. doi:10.1016/j.jhazmat.2007.12.036

[28] M. Waseem, S. Mustafa, A. Naeem, G. J. M. Koper and K. H. Shah, "Cd^{2+} Sorption Characteristics of Iron Coated Silica," *Desalination*, Vol. 277, No. 1-3, 2011, pp. 221-226. doi:10.1016/j.desal.2011.04.034

[29] M. Doğan and M. Alkan, "Adsorption Kinetics of Methyl Violet onto Perlite," *Chemisorption*, Vol. 50, No. 4, 2003, pp. 517-528.

[30] K. G. Scheckel and D. C. Sparks, "Temperature Effect on Nickel Sorption Kinetics of the Mineral-Water Interface," *Soil Science Society of America Journal*, Vol. 65, No. 3, 2008, pp. 719-728. doi:10.2136/sssaj2001.653719x

[31] M. Mohapatra, S. Khatun and S. Amand, "Kinetics and Thermodynamics of Lead(II) Adsorption on Lateritic

Nickel Ores of Indian Origin," *Chemical Engineering Journal*, Vol. 155, No. 1-2, 2009, pp. 184-190.   doi:10.1016/j.cej.2009.07.035