Kinetic, Equilibrium and Thermodynamic studies for the extraction of iron from Aqueous Solution using Lignin-biosorbent

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Abstract—. The adsorption of Fe(III) from aqueous solution onto lignin was studied using batch process. The maximum adsorption of Fe (~100%) was obtained in a pH range of 3–6 with a shaking time of 5 min. The kinetics were best described by the pseudo-second-order model (R^2 = 0.999). The adsorption capacity of lignin was 0.32 mmol/g for Fe(III). The isotherms exhibit good correlation (R^2 = 0.999) with a zero intercept (0.002). Successful application was obtained for pharmaceutical samples.

Index Terms— Iron; Lignin; pharmaceutical; Extraction; equilibrium

1. Introduction

Iron (Fe) is an essential microelement for biological organisms (1); it plays main functional roles in several biological activities including enzymatic process (2), synthesize of hemoglobin, myoglobin and electron transfer. Excess of iron may cause some kinds of cancers (3), chronic liver disease and Alzheimer's. Also, low iron content is the most common cause of defective erythropoiesis and anemia (4). Direct determination of Fe in different pharmaceutical samples is to some extent a problem because of the high concentration of interfering matrix components (5,6). Separation and determination procedures of Fe to eliminate such interference prior to their detection are necessary (7,8).

Separation by using biosorbent originated from a plant is cheap, abundant, and environmental-friendly (9,10). Lignin is the second most abundant biological material on the planet (11–13), where it serves as a binding agent for cellulose and hemicellulose (14). Lignin and lignin-based materials have been used in many fields, such as stabilizing agents, lubricants, surfactants, emulsifiers, and sorbents (15). It was the subject of much research due to its presence various functional groups including phenolic, hydroxyl, and carboxyl groups which anchored on its surface and serve as binding sites for different metal ions (16,17).

In this study, we use lignin extracted from orange tree as new stable biosorbent for separation and determination of Fe from pharmaceutical samples for increasing the sensitivity and selectivity of the spectrophotometric method.

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2. Experimental

2.1. Reagents and materials

Lignin of orange biosorbent: orange stem was cut into small pieces, washed with water to remove dust. The pieces were dried overnight in oven at 105 °C, followed by grinded in a food–processing blender. A 50 g of orange powder was soaked in 100 mL of H_2SO_4 (1:1) for 24 h, followed by washing with distilled water till neutral pH, filtrate and, then dried at 105 °C.

A stock solutions of iron(III), (1mg/ mL) was prepared by dissolving appropriate amounts of iron (III) chloride in distilled water containing 1 mL of concentrated HCl.

2.2. Apparatus

All spectrophotometric measurements were performed on a JASCO (V-630UV-VIS Spectrophotometer, Japan). The pH measurements were carried out using a Jenway 3510 pH-meter (Beacon Road, Stone, Staffordshire, ST15 OSA, UK).

2.3 Recommended procedures

Batch experiment, A 25 mL of iron solutions were shacked for 60 min with 100 mg of Lignin. The sorption percentages of iron and capacity of biosorbent was calculated using the following equations: $\%Sorption = (C_o - C) \times 100/C_o$ and and ($Capacity = C_oEV/m$).

Where, Co is the initial Fe concentration, C is the concentration of Fe in solution at equilibrium, V is the volume of iron solutions and m is the mass of sorbent.

3. Results and Discussion

3.2 Optimum condition for sorption of iron(III) using Lignin-biosorbent

3.1.1 pH

The sorption percentage of iron against the pH values (1-6) was tested (Fig. 1). It is noted that the maximum sorption per-

centages of Fe (III) ion were at pH values 3-6. Based on the behavior of Fe (III) ion extracted, it is speculated that the sorption process mainly depends cation chelation or ion exchange processes.

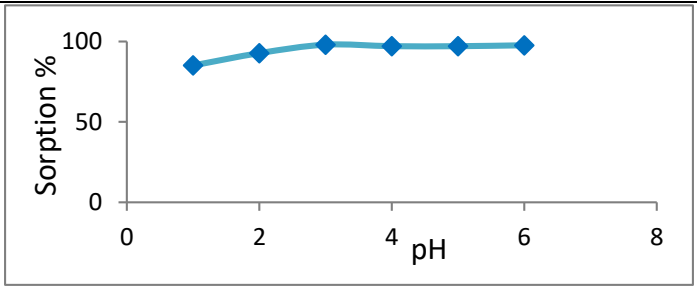

Fig.1 Effect of pH on the sorption of Fe(III) using Lignin-biosorbent.

3.1.2 Contact time

The effect of shaking time on the sorption of Fe (III) ions using lignin was tested (Fig. 2). The sorption rate of Fe (III) was initially rapid, where 80% of total Fe (III) were extracted within the first 30 sec. Then the rate became slower with increasing in time until reaching 100% at 3-5 min.

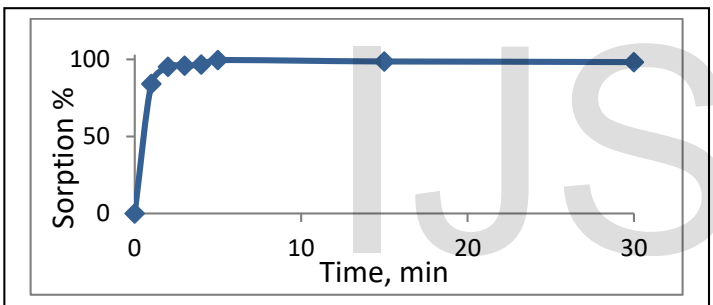

Fig.2 Effect of time on the sorption of Fe(III) using Lignin-biosorbent.

3.1.3 Initial dye concentration

The effect of initial Fe(III) concentration was studied for the sorption of Fe(III) ions using Lignin biosorbent (Fig. 3). It is obvious that the increase Fe(III) ions concentrations followed by a subsequent increase in the sorption capacities of biosorbent. The maximum capacity of Lignin was 0.32 mmol/g.

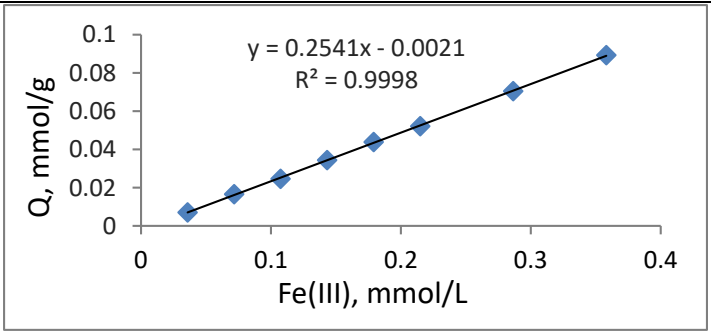

Fig. 3 Effect of initial concentration on the sorption of Fe(III) using Lignin-Biosorbent.

3.2 Kinetic studies

. The pseudo first-order (3) and pseudo second-order (4) were used to investigate the mechanism of the adsorption and the rate controlling steps involved in the sorption.

$$\log(Q_e - Q_t) = \log Q_e - (k_1 t/2.303) \quad (3)$$

$$t/Q_t = \left(1/k_2 {Q_e}^2\right) + t/Q_e \quad (4)$$

Where Q_e and Q_t is the adsorption capacity at equilibrium and at time t. k_1 and k_2 is the pseudo first rate constant and the pseudo second order rate constant. The half-life times ($t^{1/2}$) of Pseudo first order are calculated by $t_{1/2} = 0.693/K_1$, while that of second order are calculated by $t^{1/2} = 1/Q_e K_2$.

The data showed that the average values of R^2 obtained for the pseudo-second-order sorption model (1.0) are higher than that obtained for the pseudo-first-order kinetic first-order kinetic (0.91), which indicates that the pseudo-second-order sorption is predominant (Fig. 4).

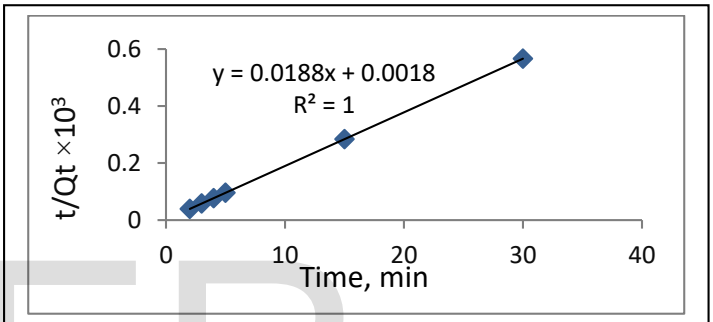

Fig. 4: Pseudo second-order for sorption Fe(III) using Lignin-biosorbent.

The diffusion mechanism was investigated using the Morris–Weber (1), Reichenberg (2) and Bangham (3) equations.

$$Q_t = K_M \sqrt{t} \quad (1)$$

$$B_t = -0.4977 - \ln(1-F) \quad (2)$$

$$\log\log(C_o/C_o - Q_{tm}) = \log(K_o m/2.33V) + \alpha \log(t) \quad (3)$$

Where Qt is the amount of Fe(III) sorbed at time t. K_M is the intraparticle diffusion rate constant (mmol/g $min^{1/2}$). The Bt value is a mathematical function of $[F = Q_t/Q_e]$. Di is the effective diffusion coefficient, and α, K_o are constant.

Plots of Q_t versus $t_{1/2}$ for diffusion of iron (III) onto Lignin-biosorbent according to Morris-Weber Model give straight lines, where R^2 value is 0.88 which does not pass through the origin. The value of diffusion rate constant is 0.0004 mmol/g $min^{1/2}$.

The double logarithmic plots of Bangham equation with the time yield linear curve. The correlation coefficient R^2 for the sorption of iron (III) onto Lignin-biosorbent is 0.96, this result show that the diffusion of iron (III) into pores of each sorbent is involved in the rate controlling step. The values of α is 0.013.

For Reichenberg diffusion model, relation between Bt and t,

give correlation coefficient is 0.85 for sorption Fe(III) using Lignin-biosorbent (Fig. 5).

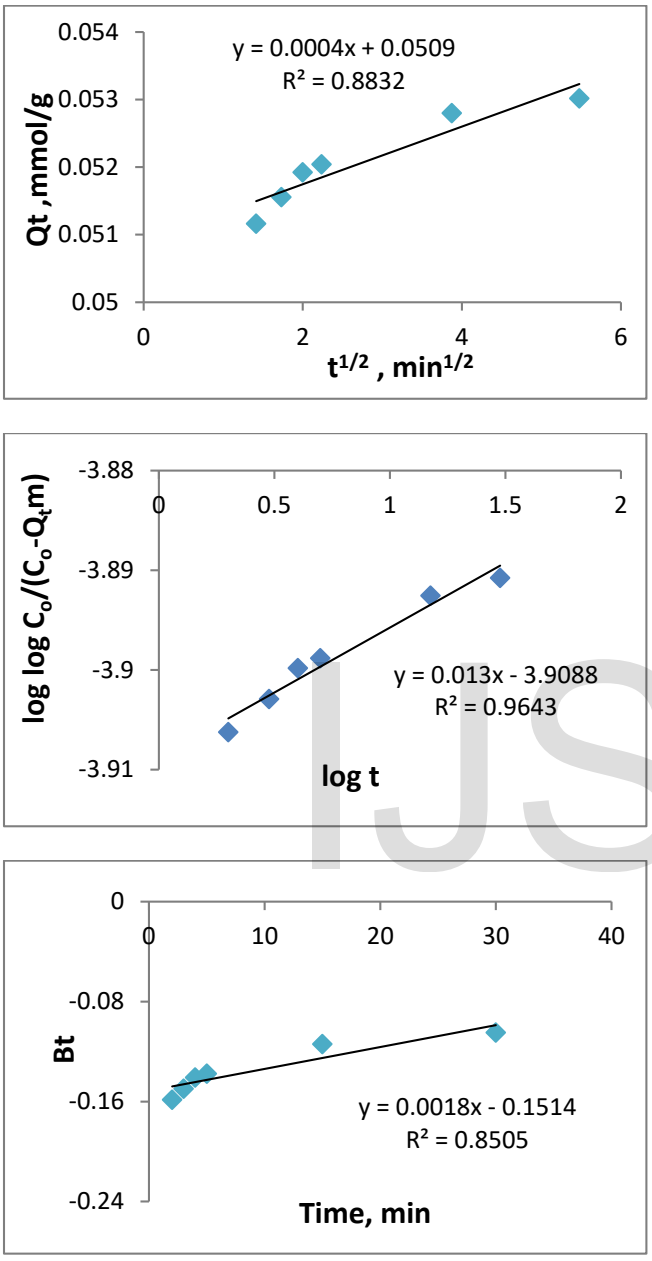

Fig. 5: Diffusion models for sorption of Fe(III) using Lignin-biosorbent.

3.3 Equilibrium studies

Langmuir $[C_e/Q_c = (1/K_L b) + (C_e/K_L)]$ and Freundlich $[Log\ Q_c = Log\ K_F + 1/n\ Log\ C_e]$ models are mainly used to describe sorption equilibrium of Fe(III) using Lignin-biosorbent.. Langmuir isotherm is based on an assumption of monolayer sorption, independent energy of sorption and initially free sites. The Freundlich equation assuming heterogeneous surface energy. The average values of R^2 obtained from Langmuir model (0.82) is higher than that obtained from Freundlich model (0.62), indicated that the Langmuir model is a good fit to the adsorption experimental data and suggests monomolecular layer as well as a homogeneous distribution of active sites on lignin surface (Fig. 6).

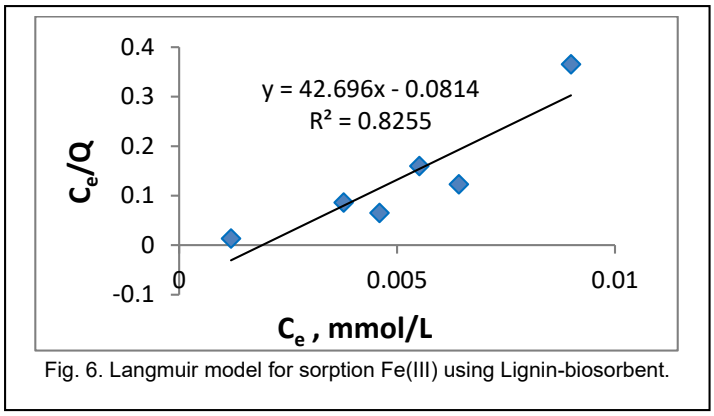

Fig. 6. Langmuir model for sorption Fe(III) using Lignin-biosorbent.

3.4. Thermodynamic studies

The effects of temperature (20–60 °C) on the sorption of Fe(III) ions using Lignin-biosorbent was studied. The sorption percentages of Fe(III) ions was plotted against temperature. The obtained results revealed that the sorption of Fe(III) ions were slight effecting with increasing of temperature.

Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) for the sorption of iron onto Lignin-biosorbent was evaluated. The enthalpy (ΔH) was 20.8 kJ/mol, the positive value of ΔH reveal to the sorption process of Fe(III) ions using Lignin-biosorbent is endothermic. The Gibbs free energy (ΔG) was -4.8 kJ/mol; these values attributed to the sorption process are spontaneous. Finally, the entropy (ΔS) of sorption Fe(III) ions onto Lignin-biosorbent was 86 J/K mol (Fig. 7).

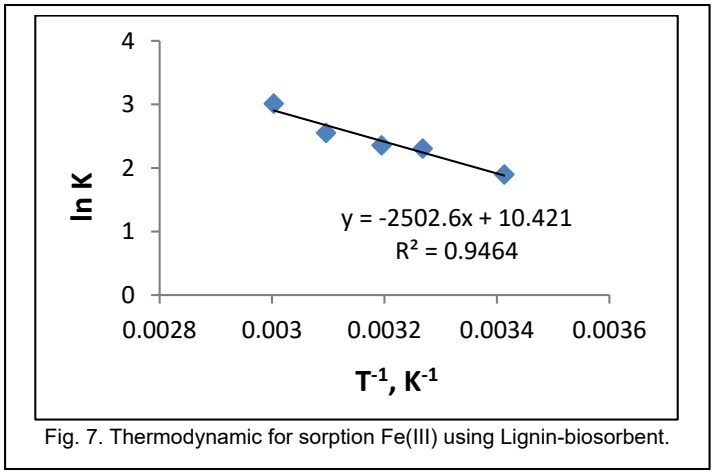

Fig. 7. Thermodynamic for sorption Fe(III) using Lignin-biosorbent.

4. Conclusion

Lignin was tested for the sorption of Fe(III). The maximum sorption capacity of lignin was found 0.32 mmol/g within 60 sec over a wide pH range (3-6). The kinetic studies were followed by pseudo-second-order model. The equilibrium isotherms showed that Langmuir model were have a good fit to the experimental data. The negative value of ΔG indicated that the spontaneous nature of the sorption process. Lignin proved its efficiency in the extraction of Fe(III) from pharmaceutical samples under optimum conditions.

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