

Kinetic and Equilibrium studies of the Removal of Ferrous ion from wastewater using PCPUF

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Abstract— In this work, the efficiency of Pyrochatechol polyurethane foam (PCPUF) for the removal of Fe(II) from wastewater was studied through an adsorption process. The effects of various parameters such as solution pH, initial Fe(II) concentration and contact time were examined. Adsorption kinetics followed Pseudo second order and adsorption isotherms followed Langmuir.

Index Terms— PCPUF, Ferrous ion, removal, wastewater, isotherm, kinetic.

1 INTRODUCTION

Water pollution is contamination of water by foreign matter that deteriorates the quality of the water. In normal situation, organic pollutants are biodegraded by microbes and converted to a form that brings benefits to the aquatic life. And for the inorganic pollutants, in the same situation, don't bring to much hazards because they are widely dispersed and have almost no effect to the environment which they are released to. Some of the pollutants like lead (Pb), arsenic (As), mercury (Hg), chromium (Cr) specially hexavalent chromium, nickel (Ni), barium (Ba), cadmium (Cd), cobalt (Co), selenium (Se), vanadium (V), oils and grease, pesticides, etc are very harmful, toxic and poisonous even in ppb (parts per billion) range. There are some minerals which are useful for human and animal health in small doses beyond which these are toxic. Zinc (Zn), copper (Cu), iron (Fe), etc fall into this category. For agriculture, some elements like zinc, copper, manganese (Mn), sulphur (S), iron, boron (B), together with phosphates, nitrates, urea, potassium, etc are useful in prescribed quantities[1,16]. Adsorption is favored by its efficiency and universally applicable, for the remediation of organic and inorganic compounds, even at low concentration. Adsorption has advantage of its relative ease of operation both in batch and continuous operation, regeneration and reusability of adsorbent[17,18]. Adsorption by polyurethane foam is considered is widely used nowadays. Its low cost and availability make it an alternative adsorbent for other highly cost adsorbents [19,20].

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The aim of the study was to evaluate the adsorption activity of PCPUF for simultaneous removal of ferrous ion(Fe(II)) from aqueous solution. The removal behavior of PCPUF was studied to optimize the conditions for the optimal removal of Fe(II). Kinetic, thermodynamic and equilibrium data was obtained[21,22].

2 Experimental

2.1 Preparation of PCPUF

5gm of commercial polyurethane foam is cutted into 1 cm³ cubes and boiled in 1M HCl for 1 hr with stirring, then washed well by dist. Water. The washed foam is soaked in 0.1M HCl for 30 minutes in ice bath. After that we put the 2M NaNO₂ by drop wise stirring to make the diazonium salt. Finally, we put the 1M pyrocatechol/1M NaOH by drop wise stirring and the resulted dyed foam is soaked and washed in the next day[23]. It is leaved to dry in the air, then blended by food blender.

2.2 Characterization

Morphology of PCPUF was investigated using a JEOL (JSM-6510LV, USA) scanning electron microscope. FT-IR spectra were performed by a JASCO (FTIR-410 spectrometer) in the 4000-400 cm⁻¹ spectral range.

The absorbance measurements were performed using a JASCO (V-630 UV-VIS Spectrophotometer, Japan). UV-Vis absorption spectra of PCPUF was recorded in the solid state.

The crystallinity was determined using an XRD Bruker D8 diffractometer equipped with a Cu K α radiation ($\lambda=1.5418 \text{ \AA}$) with 40 kV voltage and 40 mA current. Surface area and Pore size were determined by BET and BJH techniques using a NOVA 3200 (USA).

2.3 Recommended procedures

The adsorption of Fe(II) onto PCPUF was investigated using a batch experiments. 0.05 g of PCPUF, was added to 25 mL of the Fe(II) solution and measured spectrophotometrically at $\lambda_{max} = 470 \text{ nm}$, then the solution was shaken, filtered and the remaining Fe(II) concentration in solution was analyzed at $\lambda_{max} = 470 \text{ nm}$. Best condition for removal of Fe(II) can be determined by studying effects of pH, contact time and initial Fe(II) concentration. Concentration of pollutants is measured before and after time of shaking 0.05 (q_e) were calculated from the following equations:

$$\%E = ((C_0 - C_e)/C_0) \times 100 \quad (1)$$

$$q_e = (C_0 - C_e) V/m \quad (2)$$

Where, C_0 is the initial SA concentration, C_e is the concentration of Fe(II) in solution at equilibrium, V is the volume of Fe(II) solutions and m is the mass of adsorbent.

3 RESULTS AND DISCUSSION

3.1 Optimum conditions for SA removal using 10ZAC

3.1.1 pH

The effect of the pH on the removal of Fe(II) (12 mg/L) using PCPUF was studied (Fig.1). The removal rates of Fe(II) onto PCPUF not influenced by pH.

3.1.2 Contact time

The effect of contact time on Fe(II)(12 mg/L) removal using PCPUF was investigated at pH=2.5 (Fig. 2). The removal rate of Fe(II) increases from , where 30-40% of the total amount Fe(II) was removed within 10 min. Then the rates become slower with increase in time until reaching about 50% within 30 min.

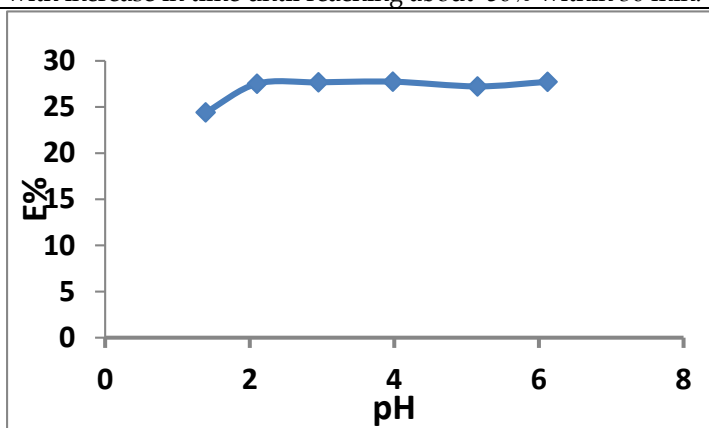


Fig.1 Effect of pH on Fe(II) removal using PCPUF

3.1.3 Initial Fe(II) concentration

The effect of initial Fe(II) concentration was studied for different Fe(II) concentrations at pH=3.5.(Fig. 3). The removal rates of Fe(II) using PCPUF increased with increase in Fe(II) concentration within a range from 2 to 32 mg/L. The maxi-

imum adsorption capacity of PCPUF is found 1.5 mg/g.

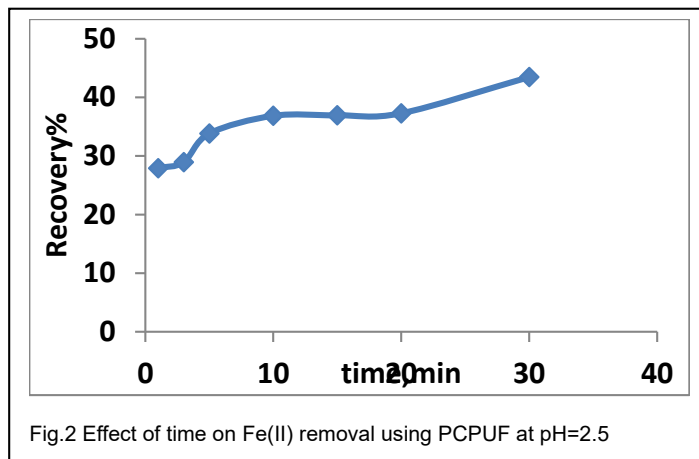


Fig.2 Effect of time on Fe(II) removal using PCPUF at pH=2.5

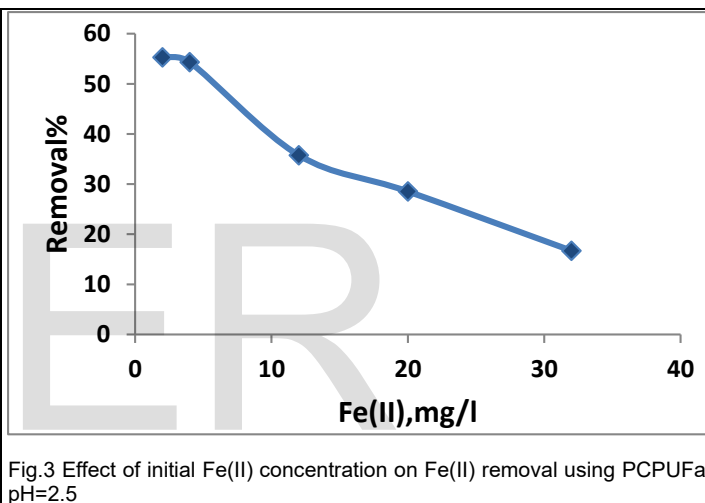


Fig.3 Effect of initial Fe(II) concentration on Fe(II) removal using PCPUF at pH=2.5

3.2 Kinetic studies

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

$$\log(q_e - q_t) = \log q_e - (K_1 t / 2.303) \quad (3)$$

$$t/q_t = (1/K_2 q_e^2) + t/q_e \quad (4)$$

Where q_e and q_t is the sorption 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 R^2 of the Pseudo second order is higher than that of the first order (Table 1). Also, higher rate constant and faster half-life times suggests that the adsorption is followed Pseudo second order which controlled by chemisorption mechanism and depended on both Fe(II) and PCPUF[25].

Kinetic modeling of the experimental data allows us to gain insight into the potential rate-controlling steps involved in the

adsorption process. Two kinetic models (i.e., Pseudo first order $[\log(q_e - q_t) = \log q_e - (k_1 t/2.303)]$ and Pseudo second order $[t/q_t = (1/K_1 q_e^2) + (t/q_e)]$ models) were tested to fit the experimental data for the adsorption of Fe(II) onto PCPUF.

The diffusion mechanism was investigated using the Morris-Weber $[q_t = K_i \sqrt{t}]$, Reichenberg $[Bt = -0.4977 - \ln(1-F)]$ and $[F = (6/R)(D_i t/\pi)^{1/2}]$ equations. Where q_t is the amount of Fe(II) adsorbed at time t , K_i is the intraparticle diffusion rate constant ($\text{mg/g min}^{1/2}$), C_o is the initial concentration of Fe(II) in solution, V is the volume of the Fe(II) solution and m is the mass of PCPUF. The Bt value is a mathematical function of $F = q_t/q_e$. D_i is the effective diffusion coefficient and α and K_o are constant.

A plot of q_t as a function of $t^{1/2}$ should be a straight line ($R^2 = 0.9208$) that does not pass through the origin. The diffusion rate of Fe(II) is rapid in the initial stages and decreases with the passage of time. The average values of K_i for Fe(II) adsorption was $0.05 \text{ mmol/g min}^{-1/2}$.

The relationship between Bt and t for Fe(II) adsorption was investigated, which indicates that a partial film formed along with intraparticle diffusion. The slope of the linear plots of F as a function of $t^{1/2}$ provide the numerical value of the effective diffusion coefficient (D_i).

Table 1

The Kinetic parameters for removing of Fe(II) using PCPUF

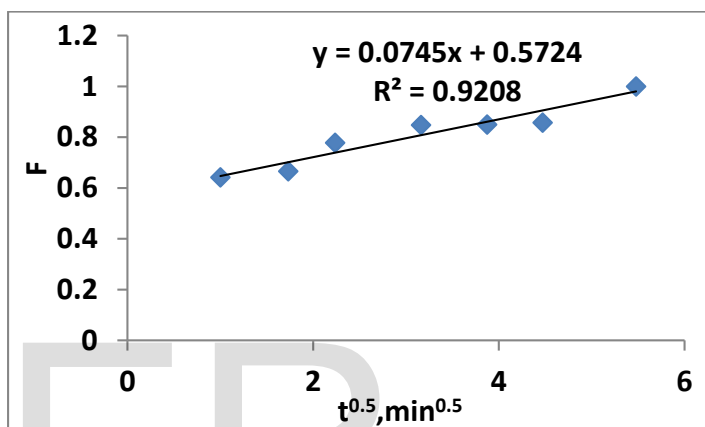
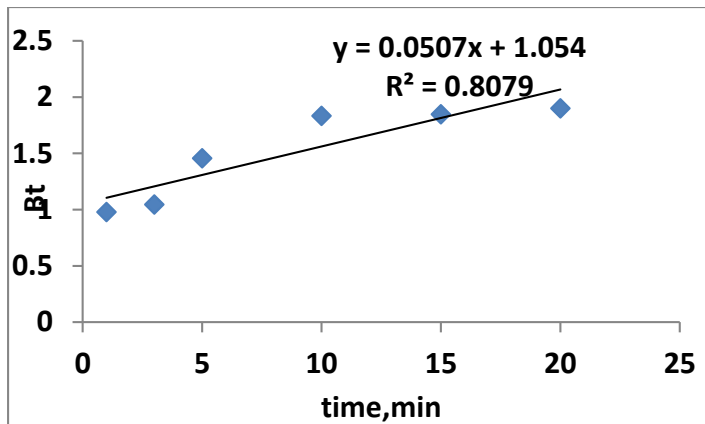
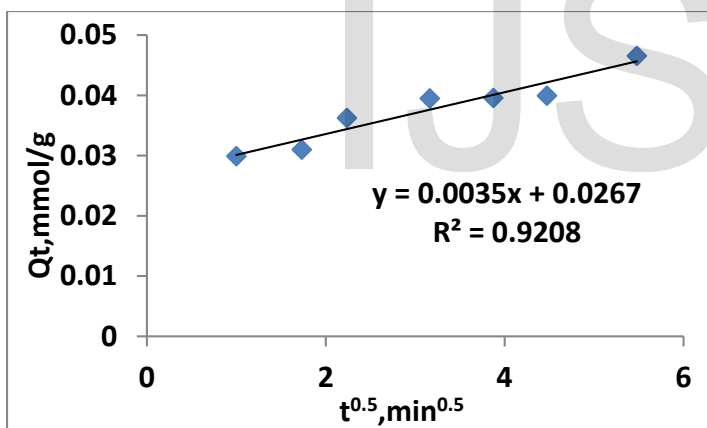


Fig.5: Diffusion models of Fe(II) removal using 10ZAC (a)Weber-Morris kinetics (b)Reichenberg diffusion (c)Boyed diffusion

3.3 Equilibrium studies

Langmuir(5) and Freundlich (6) isotherms were applied to study the removal behavior of Fe(II) using 10ZAC.

$$C_e/q_c = (1/K_L b) + (C_e/K_L) \quad (5)$$

$$\log q_c = \log K_F + 1/n \log C_e \quad (6)$$

Where q_c is the amount of dyes adsorbed at equilibrium and C_e is the Fe(II) concentration at equilibrium. K_L and b are Langmuir constants, while K_F and n are Freundlich constants.

The results showed that the R^2 of Langmuir is higher than that of Freundlich (Table 2). Suggesting for monolayer adsorption over heterogeneous surfaces. Also, the values of $1/n$ are less than 1, referring to a favorable chemisorption process (Fig. 4) [25].

The linear plot of $\ln q_e$ as a function of \mathcal{E}^2 (Dubinin-Radushkevich isotherm $(\ln q_e = \ln K_{D-R} - \beta \mathcal{E}^2)$ and $E = 1/\sqrt{2\beta}$, $R^2 = 0.92$) is shown in figure 7. K_{D-R} is the maximum amount of Fe(II) adsorbed onto PCPUF, β is a constant related to the transfer energy of the Fe(II) from the bulk solution to the PCPUF, and \mathcal{E} is the Polanyi potential. Values of K_{D-R} and β were calculated as 20.73 mg/g and $0.0138 \text{ mol}^2/\text{KJ}^2$, respectively. The adsorption energy E was determined to be 6.19 KJ/mol for Fe(II). This result showed that the removal of Fe(II) onto PCPUF was an adsorption mechanism (Fig. 5).

Method	Pseudo first order			Pseudo second order		
	R ²	k ₁ (min ⁻¹)	t ^{1/2} (min)	R ²	k ₂ (g/mg min)	t ^{1/2} (min)
pH 2.5	0.8079	0.05	13.86	0.9883	13.613	1.59

Table 2

The equilibrium parameters for removing of SA using 10ZACat pH=3.5

Method	Langmuir		Freundlich	
	R ²	b (L mmol ⁻¹)	R ²	1/n
pH=2.5	0.9871	16.846	0.9249	0.4753

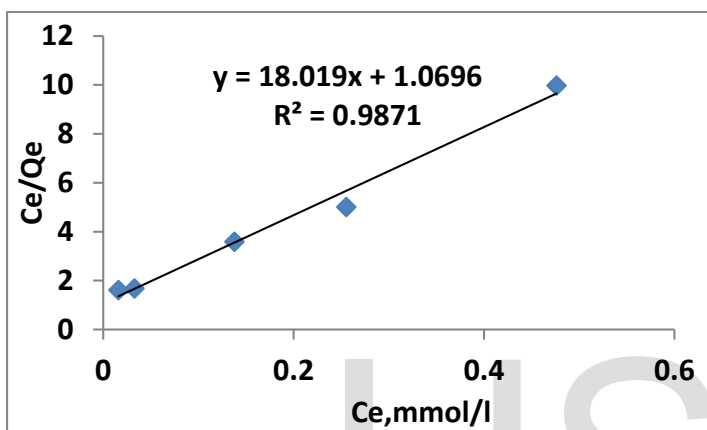


Fig.4 Langmuir isotherm of SA removal using 10ZAC

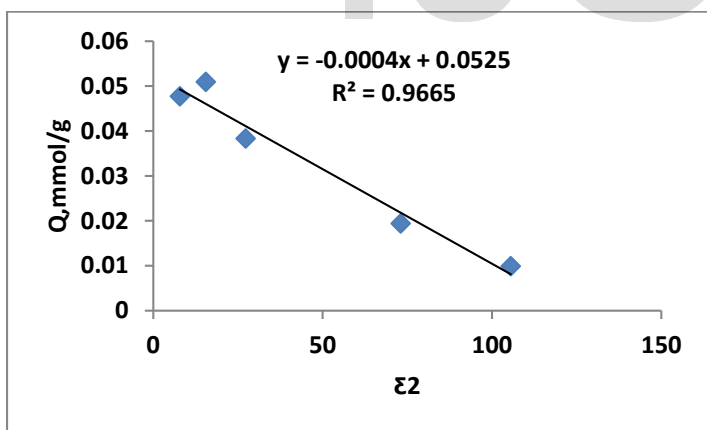


Fig. 5: Dubinin- Radushkevich isotherm of SA removal using 10ZAC

4 CONCLUSION

PCPUF was successfully prepared as identified by SEM, XRD, BET, FTIR and UV-Vis spectroscopy. PCPUF was tested for the removal of Fe(II) at pH=2.5. The maximum adsorption capacities of PCPUF are found 0.046 mmol/g within 30min over a wide pH range (2-6). 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. Thermodynamic parameters demon-

strate the spontaneous and the exothermic nature of adsorption process. PCPUF proved its efficiency in the removal of ferrous ion from wastewater under optimum conditions.

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