Detection, determination and removal of iron (Ⅲ) from wastewater

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Abstract— Polyurethane foam are white flexible polymer characterized with urethane group. PUF can be modified after different reactions to develop a new functional groups. Batch technique was studied at different pH, time and temperature to get best conditions for removal of pollutants. The best Isotherm models for adsorption of Fe3+ is D-R isotherm. Pseudo second order is the best fitted for kinetic studies for adsorption process. Thermodynamic parameters indicate spontaneous adsorption process of iron. Exothermic nature for adsorption of Fe3+ ions onto TUPUF/ZnO. ΔS values -0.108 KJ/mol K for Fe3+, which means decreasing in randomness as interface between adsorbent and adsorbate. In application at real sample, RSD% value is 2.9% for Fe3+ ions and that is a good accuracy for removal of different types of pollutants using TUPUF/ZnO.

Index Terms— adsorption, isotherm, kinetic, polyurethane, thermodynamic.

1. INTRODUCTION

The quality of water was untied rapidly in last few years due to environmental problems, civilization and manufacturing process [1]. Many pollutants change in chemical, physical and biological properties of water. These pollutants may be organic dyes or heavy metals ions pollutants [2]. According to UNISCO [3], there are about 1500 km3 of wastewater are generated world by emerging 2 million tons of sewage into drinking water. Consequently, removal of these types of pollutants is critical point, organic pollutants represent the main water pollution sources due to its applications in Leather, plastic, food, textile, cosmetics, etc. [4]. Heavy metals ions pollutants have risks on human health and organic dyes have toxic effects which can cause cancer for humans [5]. Remediation of pollutants occurs using different methods such as precipitation [6], ion exchange [7], membrane filtration [8], coagulation/flocculation [9], chemical oxidation [10] and physical adsorption [11] which they are depended on the containing system either organic dyes or metals ions. Most of these methods show high cost and high secondary toxic sludge with high cost to remove [12,13]. Adsorption is the most successful public and effective method due to its suitability for removal of different types of contaminants, low cost, simplicity, no secondary sludge and many available materials can be used [14]. The ideal adsorbent must have some features such as, costless, nontoxic material, can be used again and easy to remove pollutants [15]. Many adsorbent materials are applied for removal of heavy metals, including activated carbon [16], nanocomposite [17], graphene [18] and polymer [19]. Among nanocomposite, there is polymer nanocomposites which they based on polymer and nanoparticles, such as polyaniline (PANI) [20], polypyrrole (PPy) [21] and polythiophene (PTh) [22]. Polymer has an applications in removal of heavy metals ions, besides its porous structure, ability to regenerate and easy to synthesis [23]. Polymer nanocomposite is formed as combination between polyurethane foam (PUF) and zinc oxide nanoparticles (ZnO) which is used widely in batteries manufacturing [24], biomedical materials, [25] catalysts [26], nanocomposites [27] and adsorbents [28]. PUF is commercial available polymer which is characterized by chemical and thermal resistance, elasticity and porous structure with high adsorption capability [29]. Some studies indicate using of PUF as adsorbent for removal of different kinds of pollutants, Moawed, E.A et.al. [30] prepared Rosaniline-grafted polyurethane foam (Ros-PUF) for removal of Cd (II) and Hg (II) ions, El-Shahat et.al. [31] synthesized grafted polyurethane foam for separation of Fe, Zn, Hg and Cd metals from wastewater.

In this work, we focused on increase capacity for adsorbent to remove iron metal by using ZnO nanoparticles to form nanocomposite. PUF/ZnO was modified by adding thiourea and mixed with ZnO (1:1). We will know adsorption behavior of Fe metal on PUF/ZnO to reveal nature of adsorption process using batch adsorption technique.

2. Experimental

2.1 Materials and methods

Ferric chloride and ammonium thiocyanate were purchased from Sigma –Aldrich (USA). Adsorbent was synthesized using white sheets flexible PUF which was gotten from Egyptian company for foam production, urea and ZnO powder. Weigh about 2.89 gram of FeCl3 to dissolve in 20 ml HCl and stiller it very well with magnetic stirrer. The solution is completed to 1000 ml by distilled water, giving stock concentration [Fe3+] = 0.05 M. preparation 1 M NH4SCN is achieved by dissolving 38 in 500 ml distilled water. PUF was prepared before using by cutting sheet to small cubes, then soaked all night in 1 mol/L HCl.

Boehm titration was developed mainly to give quantity of
oxygen containing surface. A 25 ml of 0.1 M HCl, 0.1 M NaOH are added separately to 0.1 g TUPUF/ZnO. After 24 h shaking. The filtered solution is titrated with 0.1 M NaOH, 0.1M HCl.

2.2 Preparation of thioureido PUF/ZnO

TUPUF/ZnO was prepared by putting 5 g of ready-made PUF in a cold beaker containing 0.1 molar HCl, then drop wise addition of 25ml NaNO2 (2 molar) to the cold mixture with keep vigorous stirring until the pale yellow color appeared. A 0.3 ml CuCl was added directly to pale color PUF, reflux the green PUF with 50 g N2H4CS for 2 h using ethanol (C2H5OH). Equal amount of vanillin (C8H8O3) was added to dark brown PUF to reflux for 2 h.

The final step is nanocomposite making by adding 5 g from ZnO to PUF and reflux for 6 h. the cubes PUF was washed with distilled water, acetone and dried very well, then grinded to get fine powder from TUPUF/ZnO.

2.3 Adsorption experiments

UPUF/ZnO is a sorbent used to remove Fe³⁺ ions from water by batch adsorption technique. The adsorption process is made at temperature 30 °C by making sorbent attached iron solution and shaking the mixture. The filtrate is separated from mixture and measured by UV-vis spectrophotometer at maximum wavelength for iron. Taking different volume from stock solution and dilute to 25 ml distilled water to get definite concentrations at pH 7. Best condition for removal of Fe³⁺ can be determined using different pH, adsorption time and temperature. Concentration of pollutants is measured before and after time of shaking 0.1 g of sorbent with Fe³⁺ solutions to give C₀, Cₑ.

The quantity of pollutants adsorbed on the TUPUF/ZnO (qₑ) and percentage of elimination pollutants from solution (%E) can be calculated as follows

\[ qₑ = \frac{(C₀ - Cₑ)V}{m} \]  
\[ % E = \frac{(C₀ - Cₑ) \times 100}{C₀} \]

Where, V is volume attached to sorbent, m is weighted sorbent use and C₀ and Cₑ are initial and final pollutants concentration.

3. Results and discussion

3.1. Best conditions for removal of Fe³⁺ ions

(1) pH

The removal of Fe³⁺ ions from aqueous solution was studied in range pH 1-7. At acidic medium (1-3), the removal percentage increases from 62% to 96% as shown in fig. 1. At pH 5-7, the uptake percentage (%E) decreases to 89%.

(2) Contact time

A 0.1 g of TUPUF/ZnO was added to 25 ml iron solution in different flasks with concentration 9 mg/L at optimum pH for iron. Fig. 2 shows the high % removal starts from 99.4% in only three minutes. Increasing the contact time with TUPUF/ZnO keeps the % E increase little from 99.4% to 99.6 %. The drop occurs at time 30 min and that after saturation point. The best time for removal and detection of Fe³⁺ ions in aqueous solution at time 10 min.

(3) Concentration

Fig.3 indicates the relation between initial concentration of Fe³⁺ ions solutions (C₀, mg/L) and amount of ions adsorbed on the surface of TUPUF/ZnO. Raising the concentration leads to increase the capacity (qₑ, mg/g) until to get the point of saturation. The best capacity for removal and detection of metal ions is 420 mg/g.
A 25 ml of Fe^{3+} ions solutions are in contact with 0.1 g TUPUF/ZnO at definite pH with shaking at optimum times. Figure 4 indicates a high removal % (99 %) for iron at temperature 32°C. The higher temperature, the faster release of the metal ions from the removal of Fe^{3+} ions from surface (lower removal % ~ 96 %). The aqueous solution can be also achieved at higher temperature (92°C) and at room temperature.

3.2. Removal mechanism
3.2.1. Isotherm studies for Fe^{3+} ions
The removal of Fe^{3+} ions using adsorption process needs to study by Langmuir (3), Freundlich (4) and Dubinin-Radushkevich (5).

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_l} + \frac{1}{q_m} C_e \quad (3)
\]

\[
\log q_e = \frac{1}{n} \log C_e + \log k_f \quad (4)
\]

\[
\ln q_e = \ln q_s - K_{D-R} \epsilon^2 \quad (5)
\]

Isotherm models were applied on adsorption of Fe^{3+} ions onto TUPUF/ZnO at different concentrations. The correlation coefficient values (R^2) in table 2 show the higher values for Freundlich and Langmuir models. The domination of model other than one can be discovered by chi-square equation

\[
\chi^2 = \sum (q_{e, exp.} - q_{e, cal.})^2 / q_e \quad (6)
\]

where \(\chi^2\) is the calculated data by models and \(q_{e, exp.}\) is experimental data. The lower \(\chi^2\) value, the best fitted model for experimental data. The lower value of \(\chi^2\) and closely value of \(q_s\) value make D-R isotherm is dominated in removal of Fe^{3+} ions from water using TUPUF/ZnO.

In this work, the removal of Fe^{3+} ions by adsorption has much higher adsorption capacities than the reported literatures.

3.2.2. Thermodynamic studies for Fe^{3+} ions removal
The influence of temperature on adsorption process for Fe^{3+} ions can be evaluated by thermodynamic parameters including Gibbs free energy (\(\Delta G, \text{kJ/mol}\)), enthalpy change (\(\Delta H, \text{kJ/mol}\)) and entropy change (\(\Delta S, \text{kJ/mol K}\)), which they can be determined from (6-8)

\[
\Delta G = -RT \ln K_c \quad (6)
\]

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (7)
\]

\[
\ln K_c = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (8)
\]

where, \(K_c\) is equilibrium constant can be gotten in terms of \(Q_m\) and \(C_e\) (KC = \(q_s / C_0\)) at different T (°K) and R is gas constant. Plotting a relation between ln \(K_c\) and 1/T gives a straight line with intercept (\(\Delta S/R\)) and slope (-\(\Delta H/R\)) (fig. 6).

Thermodynamic parameters for Fe^{3+} are shown in table 3, which indicate negative value of \(\Delta G, \Delta H\) and \(\Delta S\). The adsorption mechanism of Fe^{3+} is spontaneous, endothermic nature. Negative value of entropy \(\Delta S\) means decreasing in randomness as interface with TUPUF/ZnO.
Table 1
Langmuir, Freundlich and Dubinin-Radushkevich isotherms for the removal of Fe³⁺ ions using TUPUF/ZnO

<table>
<thead>
<tr>
<th>( q_{\text{exp}} ) (mg/g)</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Dubinin-Radushkevich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_m ) (mg/g)</td>
<td>( K_L ) (L/mg)</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>420</td>
<td>630</td>
<td>0.150</td>
<td>0.906</td>
</tr>
</tbody>
</table>

Fig. 5 the three isotherm models for the removal of Fe³⁺ ions using TUPUF/ZnO.

\( q_{\text{exp}} \): Experimental adsorption capacity; \( q_m \): Langmuir monolayer capacity; \( K_L \): Langmuir constant; \( K_F \): Freundlich constant; \( n \): Freundlich constant; \( q_{D,R} \): Dubinin-Radushkevich constant; \( K_{D,R} \): Dubinin-Radushkevich constant; \( R^2 \): Coefficient of determination.
3.2.3. Kinetic studies for Fe^{3+} ions removal

The rate transfer of metal ions into TUPUF/ZnO and interaction nature between adsorbate and adsorbent can be known by kinetic studies using pseudo first order (9) and pseudo second order (10) models.

\[
\log\left(\frac{Q_t}{Q_e}\right) = \log Q_e - \frac{K_1 t}{Q_e} \quad (9)
\]

\[
\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (10)
\]

where \(Q_e, Q_t\) are capacity at equilibrium and at time \(t\) (mmol/g), \(K_1\) is rate constant for pseudo first order (1/min) and \(K_2\) called pseudo second order rate constant (g/mmol min).

Table 2
Comparison of adsorption capacity for the removal of Fe^{3+} by many adsorbents

<table>
<thead>
<tr>
<th>adsorbent</th>
<th>(q_e) (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolitic tuff</td>
<td>20.7039</td>
<td>[32]</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>8.06</td>
<td>[33]</td>
</tr>
<tr>
<td>Wild jack</td>
<td>0.2570</td>
<td>[34]</td>
</tr>
<tr>
<td>Halo polyurethane</td>
<td>7.448</td>
<td>[35]</td>
</tr>
<tr>
<td>Commercial Activated carbon</td>
<td>38.57</td>
<td>[36]</td>
</tr>
<tr>
<td>Raw clinoptilolite</td>
<td>98.00</td>
<td>[37]</td>
</tr>
<tr>
<td>TUPUF/ZnO</td>
<td>620</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table 3
Thermodynamic parameters of Fe^{3+} ions removal using TUPUF/ZnO.

<table>
<thead>
<tr>
<th>(\Delta S^o) (KJ/mol K)</th>
<th>(\Delta H^o) (KJ/mol)</th>
<th>(\Delta G^o) (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.108</td>
<td>-52.24</td>
<td>-20.16</td>
</tr>
</tbody>
</table>

4. Application

Optimum conditions for removal of Fe^{3+} ions from water were applied on real samples (wastewater, Nile water). A 0.1 g of TUPUF/ZnO was added to 200 μg of pollutants and completed to 25 ml from real samples. In Fe^{3+} ions removal from wastewater has recovery percentage 99%. The RSD% value is 3.5 % for Fe^{3+} ions. Lowering RSD% than 10%, so the accuracy of the method is good for removal Fe^{3+} ions from real samples.

5. Conclusion

Thioureido polyurethane foam /zinc oxide nanocomposite is the new sorbent for removal and detection different types of metals ions. Batch technique was set to study effect of pH, temperature, and contact time to detect iron metals in water. Best pH for Fe^{3+} is at pH 3, best time is 10 min and lower temperature has a good removal percentage. Thermodynamic parameters prove that the removal process by adsorption of Fe^{3+} is spontaneous and easy to do (\(\Delta G^o = -ve\)) and exothermic in nature. The negative value of \(\Delta S\) means decreasing in randomness as interface with TUPUF/ZnO. Dubinin-Radushkevich isotherm model is fitted to adsorption process for Fe^{3+} ions and pseudo second order are best model to illustrate kinetic studies. For real samples, RSD% value is 2.9 %, which is lower than 10% with a good accuracy for removal of metal ions using TUPUF/ZnO.
References


