Copper(II) Removal from Aqueous Solutions by Adsorption Method: Isothermal, Thermodynamic and Kinetic Studies

Bakır(II) İyonlarının Sulu Ortamdan Adsorpsiyon Yöntemiyle Uzaklaştırılması: İzotermal, Termodinamik ve Kinetik Çalışmalar

ABSTRACT

Study presents the utility of magnetic poly(ethyleneglycoldimethacrylate-N-vinil-2-pyrrolidon) [m-p(EG-VPN)] microspheres as an adsorbent for copper(II) ion removal from aqueous solutions. The magnetic polymer microspheres were characterized by elemental analysis, N₂ adsorption-desorption isotherm tests, swelling studies, scanning electron microscope (SEM) and vibrating sample magnetometer (VSM). Adsorption studies revealed that the maximum adsorption capacity of m-p(EG-VPN) microspheres was 270.3 mg/g. Besides, kinetic, isothermal and thermodynamic properties of the adsorption were also investigated.

Key Words
Cu(II) removal, adsorption kinetics, adsorption thermodynamics, Cu(II) ions.

ÖZ

Çalışmada, manyetik poli(etiilenlikoldimetakrilat-N-vinil-2-pyrrolidon) [m-p(EG-VPN)] mikrokürelerinin bakır (II) iyonlarının sulu ortamdan uzaklaştırılmasında adsorbent olarak kullanılabilirliği incelenmiştir. Manyetik polimer mikroküreler, elementel analiz, N₂ adsorpsiyon-desorpsiyon izoterm testleri, şişme testleri, taramalı elektron mikroskobu (SEM), titreşimli örnek manyetometresi (VSM) ile karakterize edilmiştir. Adsorpsiyon çalışmaları sonucunda m-p(EG-VPN) mikrokürelerinin maksimum adsorpsiyon kapasitesi 270.3 mg/g olarak belirlenmiştir. Ayrıca adsorpsiyon işlemlerinin kinetik, izotermal ve termodinamik özellikleri araştırılmıştır.

Anahtar Kelimeler
Bakır(II) uzaklaştırma, adsorpsiyon kinetiği, adsorpsiyon termodinamiği, Cu(II) iyonu.
INTRODUCTION

Environmental pollution is one of the main problems of expanding industrialization. Water contamination from industrial waste is an increasing case with each passing day. Since heavy metals can accumulate in human body, heavy metal content of water may have a great potential to be very hazardous to human health and natural life [1-3]. Copper(II) is an essential nutritional source such as zinc, manganese, iron, boron, molybdenum, chlorine. Nevertheless, it should be limited at between 5-20 ppm since it’s inadequate under 5 ppm and toxic at concentrations higher than 20 ppm. High copper(II) levels in aqueous media in nature may cause copper(II) poisoning which may end up with coma and death. So that, World Health Organization (WHO) reported that maximum levels of copper(II) concentration should be 1.5 ppm [4-5]. Adsorption is the most common selection among all methods for heavy metal removal. Adsorbent is the key factor which identifies the adsorption capacity. Future applications of adsorption are limited by generation of new and better adsorbents to improve the performance of current commercial processes as the adsorbent should be designed for the needs of specific applications [6]. In order to design an adsorbent for heavy metal removal, stability for the selective removal of metal ions, specific and fast complexation is of great importance [7]. Using chelating polymers to having features as mentioned above for heavy metal removal is widespread in environmental applications [8]. Number of chelating polymers have been produced by chelating monomers, such as acrylic acid, allythiourea, vinyl imidazole and vinyl pyrrolidone [9]. Magnetic material attachment to the chelating polymers enhance the properties of an adsorbent by means of diffusion resistance, adsorption capacity, fast separation for large volumes [10,11]. Determination of physicochemical parameters of adsorption allows of understanding the adsorption mechanism, surface properties, degree of affinity of the adsorbents and provide applicable practice of adsorption systems [12]. This paper presents kinetic, thermodynamic and isothermal investigation of Cu(II) adsorption onto magnetic(ethylene glycol dimethacrylate-N-vinyl-2-pyrrolidone) microspheres.

MATERIALS and METHODS

Materials

Ethylene glycol dimethacrylate (EGDMA), poly(vinyl alcohol) (Mw: 72,000, 98% hydrolyzed), 2,2’-azobisisobutyronitrile (AIBN), sodium hydroxide (NaOH) and nitric acid (HNO₃) (Merck, Darmstadt, Germany), 1,2-N-vinylpyrrolidone (VPN) (Aldrich, Steinheim, Germany), magnetite (Fe₃O₄; diameter 20-30 nm, Aldrich, USA), copper(II) nitrate trihydrate (Cu(NO₃)₂.3H₂O) (Carlo Erba Reagent). All other reagents were of analytical grade and were used without further purification.

Synthesis of the m-p(EG-VPN) Microspheres

M-p(EG-VPN) microspheres was prepared by suspension polymerization. Procedure is as follows: In order to obtain suspension aqueous and organic phases are set. Aqueous phase consists of 0.2 g PVA as a stabilizer and 50.0 mL distilled water. Organic phase contains 0.1 g AIBN as initiator, 10.0 mL toluene as a pore former, 5.0 mL EGDMA as a crosslinker and 3.4 mL VPN as a monomer. At first, PVA was dissolved in water and put into sealed-cylindrical pyrex polymerization reactor temperature stated at 65°C. Secondly, magnetite was added to the aqueous phase. Then, organic phase containing monomer, crosslinker, initiator and pore former was added to the reaction mixture by stirring it with magnetic stirrer for 4 h at stated temperature. Afterwards, polymerization temperature was set to 75°C and the reaction was proceeded for 2 h at 600 rpm stirring rate (Schema 1). Synthesised microspheres were kept waiting in ethanol/water mixture for a day. Then by decantation of liquid mixture, polymer microspheres washed with ethanol and water in order to remove unreacted monomer or diluent and dried in a vacuum oven at 70°C. Dried microspheres then sieved to 53-512 μm size range by using sieve set (AS200, Retsch Gmb & Co., KG, Haan, Germany).

Characterization of the m-p(EG-VPN) Microspheres

Morphological Properties of m-p(EG-VPN) Microspheres

Morphological properties of m-p(EG-VPN) microspheres, which were sieved and 53-212 μm size-ranged, were examined by scanning electron microscopy (SEM, Carl Zeiss Evo 40, Cambridge,
The porosity of the size-ranged microspheres was determined by N₂ gas adsorption/desorption isotherm technique (Quantachrome, Poremaster 60, USA). The specific surface area of microspheres in a dry state, was determined by a multipoint Brunauer-Emmett-Teller (BET) apparatus (Quantachrome, Autosorb-6, USA). BJH model (Barret, Joyner, Halenda) was applied in order to determine the pore volumes and average pore diameter of polymer microspheres.

Swelling Tests
1.023 g dry m-p(EG-VPN) microsphere sample was immersed in 50 mL of distilled water in 100 mL glass bottle placed in an isothermal water bath at 25°C and kept waiting for 2 h. Sample was filtrated and weighed. The percentage of swelling was determined by the following formula:

\[ \text{swelling ratio} = \frac{\text{weight of swollen sample} - \text{weight of dry sample}}{\text{weight of dry sample}} \times 100 \]

Elemental Analysis
Monomer incorporation to m-p(EG-VPN) microspheres were identified with elemental analysis (Leco Elemental Analyser, CHNS-932, USA).

Adsorption Experiments
Batch adsorption experiments carried out with m-p(EG-VPN) microspheres and aqueous Cu(II) solutions. Concentration of every solution was 1000 mg/L since the spectrophotometric analysis indicated that it was the most appropriate concentration as a stock solution. In order to obtain desired concentrations, every solution was prepared by diluting the solution. However, concentration studies were carried out with more concentrated solutions. pH was adjusted by using NaOH and HNO₃ solutions.

Adsorption processes were as follows: 50 mg m-p(EG-VPN) microspheres were added to 50 mL Cu(II) solutions in 100 mL erlenmayer flasks and kept waited for 2 h and filtered. The filtrate and the initial solution were analysed by using UV-vis spectrophotometer (Shimadzu-2100 UV-vis, Japan), was used as a complexing agent. The amount of adsorbed Cu(II) ions calculated from difference between initial and the filtrate concentration.

Desorption and Repeated Use Experiments
Cu(II) attached m-p(EG-VPN) microspheres desorbed in 0.2 M NaOH solution [7] in a shaking water bath at 300 rpm for 24 h at room temperature. The desorption ratio was calculated according to the following expression:

\[ \text{Desorption ratio} = \frac{\text{Amount of desorbed Cu(II) ions to the desorption medium}}{\text{Amount of Cu(II) ions adsorbed onto m-p(EG-VPN)}} \times 100 \]
Reusibility of m-poly(EGDMA-VPN) microspheres were investigated by repeating adsorption-desorption cycles for ten times by using the same magnetic polymer microspheres.

RESULTS and DISCUSSION

Morphological Properties of m-p(EG-VPN) Microspheres

Scaning electron microscope image of m-p(EG-VPN) microspheres can be seen in Figure 3. The image clearly demonstrated the spherical shape of m-p(EG-VPN) adsorbent. According to the calculations of N$_2$ adsorption/desorption isotherm tests, the BET surface area was 140.7 m$^2$/g, BJH pore size range was 1.650-9.464 nm, total pore volume range was 0.07124-0.6335 cm$^3$/g (Tables 1 and 2). These results indicated that the m-p(EG-VPN) microspheres were mainly mesopores. M-p(EG-VPN) microspheres have large pores that make the adsorbent have better diffusion properties. All these features may increase the binding capacity onto m-p(EG-VPN) microspheres and mass transfer rate of Cu(II) ions [18].

Magnetic Properties of m-p(EG-VPN) Microspheres

Magnetic properties of polymer microspheres was determined by using VSM technique. As it can be driven from VSM spectrum, Figure 3, saturation magnetization value, $M_s$, 9.08 emu/g, magnetic coercive field, $H_c$, 0.0118 T, magnetic remanence, $M_r$, 1.06 emu/g and polymer microspheres were soft magnetic material. Since magnetite was superparamagnetic material, synthesized microspheres being soft magnetic proved that magnetite particles were contributed the polymer structure.

Analysis of Adsorption Isotherms

Data of the effect of initial concentration of Cu(II) adsorption onto m-p(EG-VPN) microspheres investigation used to evaluate adsorption isotherms: Langmuir and Freundlich isotherm models.
The Langmuir isotherm expression is as follows [13]:

\[ \frac{C_e}{q_e} = \frac{1}{Q_L K_L} + \frac{C_e}{Q_L} \]  

(2)

where \( Q_L \) (mg/g) is the maximum amount of Cu(II) ion adsorbed onto per unit weight of m-p(EG-VPN) microspheres to form complete monolayer coverage on the surface and also represents a particle limiting adsorption capacity when the adsorbent surface is fully covered with Cu(II) ion, \( q_e \) is the amount of Cu(II) ion at equilibrium time (mg/g), \( C_e \) (mg/L) is equilibrium concentration, \( K_L \) (1/mg) is Langmuir constant related to affinity of binding sites. \( Q_L \) and \( K_L \) values of Cu(II) adsorption were calculated from the slopes and intercepts of plot of \( C_e/Q_e \) versus \( C_e \) and given in Table 3. The linearized form of Freundlich isotherm equation [14]:

\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \]  

(3)

In this equation, \( q_e \) and \( C_e \) have the same definitions with Langmuir isotherm model, \( K_f \) \( 1/n \) and \( n \) are isotherm constants indicates the capacity and intensity of adsorption, respectively. The values of \( K_f \) and \( n \) calculated from the slope and the intercept of the plot \( \ln Q_e \) versus \( \ln C_e \) Obtained values are demonstrated in Table 3.

In addition to Langmuir and Freundlich isotherm models, in order to have a detailed information about adsorption mechanism, Dubinin Radushkhevich isotherm (D-R isotherm) model was prefered as this model predicts the nature of adsorbate sorption onto the adsorbent and also it is possible to calculate the mean free energy of adsorption. The non-linear D-R isotherm expression:

\[ Q_e = Q_{D-R} \exp(-K_{D-R} \varepsilon^2) \]  

(4)

And the linearized form of this equation is:

\[ \ln Q_e = \ln Q_{D-R} - K_{D-R} \varepsilon^2 \]  

(5)
where $Q_e$ has the same definition with Langmuir isotherm model, $Q_{D-R}$ is the maximum adsorption capacity (mg/g), $K_{D-R}$ is the D-R constant (mol$^2$/J$^2$), $\varepsilon$ is Polanyi potential (J/mol). This potential can be calculated from the following equation:

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right)$$

(6)

$R$ is the gas constant (J/mol K), $T$ is the absolute temperature (K) and $C_e$ has the same definition with the Langmuir isotherm model. The mean free energy of adsorption ($E_{fe}$) was calculated from the following equation [15,16]:

$$E_{fe} = \frac{1}{\sqrt{-2K_{D-R}}}$$

(7)

All the calculated parameters of all adsorption isotherm models are shown in Table 1.

Table 3. Parameters of Langmuir, Freundlich and Dubinin Raduskhevich isotherm models for Cu(II) adsorption onto m-p(EG-VPN) microspheres.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Langmuir isotherm constants</th>
<th>Freundlich isotherm constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_L \times 10^3$ (L/mg)</td>
<td>$Q_L$ (mg/g)</td>
</tr>
<tr>
<td>277</td>
<td>1.089</td>
<td>204.1</td>
</tr>
<tr>
<td>298</td>
<td>1.394</td>
<td>270.3</td>
</tr>
<tr>
<td>318</td>
<td>1.461</td>
<td>277.8</td>
</tr>
<tr>
<td>338</td>
<td>1.501</td>
<td>285.7</td>
</tr>
</tbody>
</table>

Dubinin-Raduskhevich isotherm constants

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$K_{D-R} \times 10^9$ (mol$^2$/J$^2$)</th>
<th>$E$ (kJ/mol)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>277</td>
<td>-12.72</td>
<td>6.269</td>
<td>0.9890</td>
</tr>
<tr>
<td>298</td>
<td>-9.516</td>
<td>7.662</td>
<td>0.9904</td>
</tr>
<tr>
<td>318</td>
<td>-8.407</td>
<td>7.712</td>
<td>0.9866</td>
</tr>
<tr>
<td>338</td>
<td>-6.645</td>
<td>8.874</td>
<td>0.9860</td>
</tr>
</tbody>
</table>

Table 4. Parameters that indicate the adsorption is favorable.

<table>
<thead>
<tr>
<th>$R_L$ Values</th>
<th>Isotherm Type</th>
<th>Unfavorable</th>
<th>Linear</th>
<th>Favorable</th>
<th>Irreversible</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_L &gt; 1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_L = 1$</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>$0 &lt; R_L &lt; 1$</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>$R_L = 0$</td>
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</tbody>
</table>

Langmuir isotherm fits better with the experimental data correlation coefficient and calculated maximum adsorption capacities are close to maximum capacities obtained at equilibrium compare to other isotherm models. This case can be explained as there is homogeneous distribution of active sites on the surface of m-p(EG-VPN) microspheres since the Langmuir equation assumes that the surface is homogeneous.

 Besides, the characteristic of the Langmuir isotherm can be expressed by a dimensionless separation factor ($R_L$) [17]:

$$R_L = \frac{1}{1 + K_L C_e}$$

(8)

Based on Table 4, we may say $R_L$ values indicates Cu(II) adsorption onto m-p(EG-VPN) microspheres is favorable.
The $E_a$ value of adsorption ascertains the type of adsorption process. If the value is between 8-16 kJ/mol, it's said that the adsorption type is chemical adsorption. Values lower than 8 kJ/mol indicate that adsorption type is physical adsorption [18-20]. In this case, we can assume that the adsorption process is physical in nature at 277 and 298 K.

**Thermodynamic Analysis of Adsorption**

By using the van’t Hoff equation, thermodynamic parameters of adsorption can be evaluated. The integrated form of the equation is as follows:

$$
\ln K_e = \frac{\Delta S^o}{R} \cdot \frac{1}{T} (9)
$$

The standard enthalpy and entropy changes of an adsorption process can be determined from the slope and intercept of the line obtained by plotting $\ln K_e$ versus $1/T$. Gibbs free energy of the adsorption process was determined by the following equation:

$$
\Delta G^o = \Delta H^o - T \Delta S^o (10)
$$

| Table 5. Thermodynamic parameters of Cu(II) adsorption onto m-p(EG-VPN). |
|-----------------------------|-----------------------------|
| $\Delta G^o$ (kJ/mol) at 298 K | $\Delta H^o$ (kJ/mol) | $\Delta S^o$ (J/mol K) |
| -11.11 | 3.992 | 50.06 |

Negative value of Gibbs free energy change indicated that the adsorption process was thermodynamically feasible and spontaneous (Table 5). The standard enthalpy change of the adsorption was related to process being endothermic in nature. Since standard entropy change value is low, we may say there was no remarkable entropy change [21].

**Analysis of Adsorption Kinetics**

In order to determine the mechanism of adsorption, Pseudo-first order kinetic model, Pseudo-second order kinetic model, Ritchie's second order kinetic model and intraparticle diffusion model were investigated at 400 mg/g initial concentration, pH: 6.5, at four different temperatures (277, 298, 318 and 338 K).

The pseudo-first order kinetic model, Lagergren equation is as follows [22]:

$$
\log\left( q_e - q_t \right) = \log q_e - \frac{k_1}{2.303} t (11)
$$

Where $Q_e$ (mg/g) is the amount of adsorbed Hg(II) ions onto m-p(EG-VPN) microspheres at equilibrium, $q_t$ (mg/g) is the amount of adsorbed Hg(II) ions onto m-p(EG-VPN) microspheres at time (min) and $k_1$ (1/min) is the rate constant of Pseudo-first order adsorption.

The pseudo-second order kinetic model, Ho equation is as follows [23]:

$$
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} (12)
$$

Where $Q_e$ and $q_t$ have the same definitions with the pseudo-first order kinetic model and $k_2$ (g/mg.min) is the rate constant of Pseudo-second order adsorption.

The initial adsorbent rate ($h$, mg/g.min) equation is given below:

$$
h = k_3q_e^2 (13)
$$

Ritchie's second order kinetic model expression is [24]:

$$
\frac{1}{q_t} = \frac{1}{k_4q_e} + \frac{1}{q_e} (14)
$$

Where $Q_e$ and $q_t$ have the same definitions with the Pseudo-first order kinetic model and $k_4$ (1/min) is the rate constant.

The intraparticle diffusion model expression is [25]:

$$
q_t = k_i t^{1/2} (15)
$$

Where $q_t$ (mg/g) have the same definitions with the Pseudo-first order kinetic model and $k_i$ (mg/min1/2) is the intraparticle diffusion rate.

In order to determine the mechanism of adsorption, pseudo-first order kinetic model, pseudo-second order kinetic model at four different temperatures (277, 298, 318 and 338 K) and results were given in Table 6.
The correlation coefficients for the linear plots of kinetic models demonstrates poor correlation of the pseudo-first kinetic model and intraparticle diffusion models compare to pseudo-second order kinetic model for m-p(EG-VPN) microspheres. Consequently, Cu(II) adsorption onto produced adsorbents followed pseudo-second order kinetic model. Several studies have also been stated in the literature that Cu(II) adsorption onto polymeric or magnetic adsorbents followed pseudo-second order kinetic model. [26-36]

**CONCLUSION**

In this present study, adsorption properties of a new magnetic chelating polymer adsorbent m-p(EG-VPN) microspheres were investigated in order to use Cu(II) ion removal from aqueous media. According to kinetic studies, the adsorption process could be best described by the pseudo-second order kinetic model. Isothermal studies demonstrated that all the isotherm data can be fitted with Langmuir isotherm model. The total adsorption capacity of m-p(EG-VPN)
microspheres was 270.3 mg per gram adsorbent. If the magnetic features, adsorption capacity and their reusability were taken into consideration, m-p(EG-VPN) microspheres have a potential applicability for Cu(II) removal in industrial waste water treatment.

References