

Fe(II) Adsorption onto Natural Polymers Derived from Low-Grade Lignites

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ABSTRACT: In comparison with conventional chemical treatment methods for Fe(II) ions, adsorption and ion exchange are considered more easily applicable and economical, depending on the material used. Polymeric materials are the examples used in these commonly applied removal processes. In this study, the adsorption of Fe(II) ions from aqueous solutions onto two different natural polymers, insoluble humic acids (IHAs) extracted from low-grade lignites from Beysehir and Ermenek (in the central Anatolia region, Konya, Turkey), was investigated. The IHAs were synthesized through a series of acid–base reactions, and the obtained precipitates were chemically stable and had about 40% humic matter together with functional carboxyl and hydroxyl groups. The effects of the time and initial metal concentration on the effectiveness of the IHAs for Fe(II) adsorption were determined

through batch experiments; the adsorption isotherms and capacities were calculated. The IHAs were effective, with capacities of 59 mg/g for the Beysehir IHA and 57 mg/g for the Ermenek IHA, for Fe removal under neutral pH conditions. The adsorption followed mainly a Freundlich isotherm for both IHAs, and the calculated adsorption rates were 0.86 for the Beysehir IHA and 0.81 for the Ermenek IHA. This indicated that the effectiveness of the Beysehir IHA was slightly higher than that of the Ermenek IHA. The results confirmed the real possibility of the practical application of IHAs for the separation of Fe(II) in aqueous systems. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3146–3152, 2007

Key words: adsorption; FT-IR; metal-polymer complexes; synthesis; waste

INTRODUCTION

Humic substances with acidic properties are formed during the decomposition of vegetative matter through the condensation of breakdown products of terrestrial and aquatic plants. The acidic properties are derived from important functional groups, such as carboxyl (COOH) and hydroxyl (OH) groups. Humic acid (HA) is the soluble fraction in alkaline solutions, and insoluble humic acid (IHA) is the insoluble fraction in acidic solutions.^{1,2} Their elemental compositions and functional group contents vary with respect to their origins and preparation procedures.³ The average molecular weight of HAs varies between 1200 and 1500, and they have a complex polymeric structure. HAs occur not only in soils, natural waters, rivers, lakes, sea sediment plants, peat, and other chemically and biologically transformed materials but also in lignite and oxidized bituminous coal.⁴ The large number of diverse chemical functionalities contained in their molecules and their polymeric nature and relatively high chemical stability favor their practical exploitation.

HAs are formed from condensed aromatic systems having double bonds of the quinoid type inside their molecular structure (Fig. 1). It is possible to obtain IHA from lignites through a series of reactions. In the literature, HA extraction from natural deposits such as sediments has been well studied, but it is rare for IHA to be obtained from low-quality lignite.⁵

The interactions of humic substances with metals play an important role in metal mobility and bioavailability in the environment. Excessive amounts of any metal may present health hazards. Sources of metals in waters include dissolution from natural deposits and discharges of domestic, industrial, and agricultural wastewaters. The removal of heavy metals from wastewaters and natural waters has received much attention. The selective removal and recovery of metals from industrial effluents is an environmental problem and economic concern. Traditional treatment techniques used to remove dissolved metal ions, such as chemical treatments and ultrafiltration, do not always provide sufficient or economical removal. Ion exchange and adsorption are widely applied and suggested unit operations and processes for Fe removal because of their ability to remove higher concentrations of Fe with quite high efficiencies and easier applications. A great deal of interest has been observed with respect to the applicability of polymers for the removal, separation, and purification of metal ions from heavy-metal-conta-

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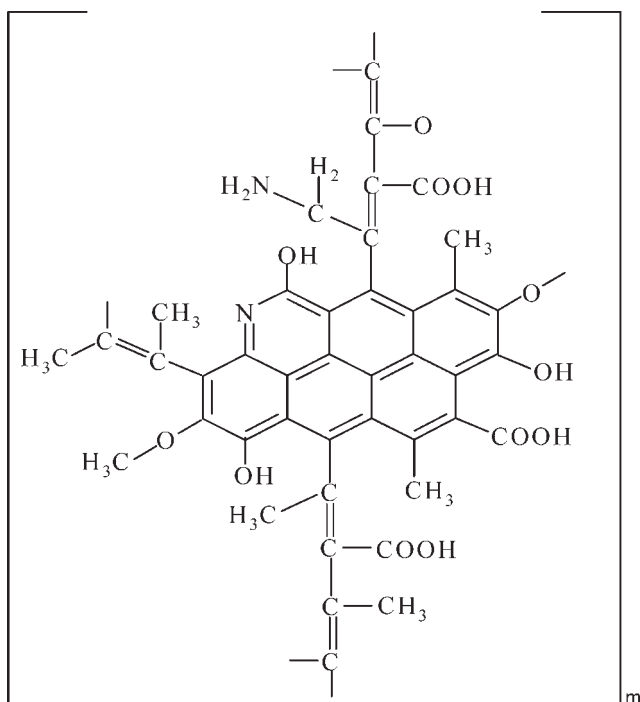


Figure 1 Molecular structure of HA.

minated water because of the ability of certain polymers to form polymer-metal complexes.

IHAs are highly functionalized carbon-rich biopolymers with a great capacity to bind metal cations. Their ability to sorb heavy metals has been demonstrated in a number of investigations.^{1,2,6-8} Madronova et al.⁶ investigated the metal-binding properties of IHAs obtained from North Bohemia coal. Ibarra et al.⁷ studied the adsorption of Sr(II), Pb(II), UO₂(II), and Th(IV) from solutions with several IHAs. IHA extracted from clay loam (Ontario, Canada) was used to adsorb heavy metals by Kerndorff and Schnitzer.⁸ These adsorption studies were performed under static equilibrium conditions, and all reported that the sorption capacity depended on the origin of the IHAs and their pretreatment. Seki and Suzuki² stated that it is difficult to use humic substances as adsorbents because of their high solubility in water. However, as mentioned by Ashley,¹ in a dissolved form, HAs have the ability to form complexes with metals, and when present as an organic solid phase, IHAs provide a surface for metal adsorption from aqueous systems.⁹ —COOH and/or —OH groups, present in HA samples, react with metal cations (Cu, Cd, Ba, Ni, Pb, Fe, and Al) to form complexes.^{4,7,8,10} Cezykova et al.³ determined the metal-binding capacity of IHAs. The value of the metal-binding capacity gives information about the ability of IHAs to react with metal ions present in water solutions. Eligwe and Okolue¹¹ studied the kinetics and mechanisms of adsorption of Fe(II) ions with brown coal, and they proved that the number of ions adsorbed increased in proportion to the increasing con-

centration of Fe ions, to the coal-to-solution contact time, and to the increasing pH value of the solution. Eligwe and Okolue also examined the adsorption and desorption of Cu, Zn, Ni, Co, and Fe ions on peat. They proved that ions having higher valence numbers, higher atomic masses, and lower ionization potentials have the highest ion-exchange capacities. In a reaction of Fe ions with HAs, Martyniuk and Wieckowska⁹ stated that some Fe ions are physically adsorbed, whereas the remaining ions take part in the exchange with one of their valence bonds only.

In one of the earliest studies, Baruah and Upreti¹² studied the interactions of HA, extracted from lignite, with cations. They showed that Mg(II), Co(II), Ni(II), Zn(II), Cu(II), Al(III), and Fe(III) form complexes with IHA. Of these cations, they found that Fe(III) has the greatest tendency to form complexes. The retention capacities were reported in the following order: Fe(III) > Al(III) > Cu(II) > Zn(II) > Ni(II) > Co(II) > Mg(II).

As shown in the aforementioned literature, there are very different opinions on the structures of metal-HA compounds. The differences may be attributed to distinct and complicated structures of HAs, to various conditions of adsorption, and to differences in the methods of examination of the metal-humic compounds obtained. Moreover, the literature indicates that Fe in an aqueous form, either in the Fe(II) state or in the Fe(III) state, can be removed through an adsorption and ion-exchange process; polymeric synthetic resins are available and are efficient for this process. Surely efficient and economical resins and natural materials in treatments are always preferred.

Therefore, in this study, we obtained IHAs from low-grade lignites from Beysehir and Ermenek (in the central Anatolia region, Konya, Turkey) to determine their structures and to investigate their effectiveness for Fe adsorption. In many parts of the world, there are large deposits of low-grade lignites, which are the raw materials of IHAs, and these are not usable as fuel because of their potential for greenhouse-gas emissions. Their processing into HAs would enable their effective evaluation. Coal from certain localities contains more than high HAs, and IHA synthesis from these lignites is an easy process. Furthermore, adsorption, the widely preferred metal-removal technique in aqueous systems, requires cheap and available adsorbents with high metal-binding capacities and high stabilities after metal binding. IHAs are known to be sufficiently stable metal-binding materials, as stated in the aforementioned literature.¹⁻¹⁰

EXPERIMENTAL

Lignite samples

Lignite samples were taken from coal mine sites, around Beysehir and Ermenek, that had large depos-

its (ca. 200 million tons) of low-grade lignite. The HA contents of the lignite samples were determined by sequential fractionation in a Soxhlet extraction apparatus with benzene, water, 2% HCl, and 5% NaOH. First, lignite samples were extracted with benzene for 3 h at the boiling point to treat bitumen. After this first treatment, benzene was evaporated through the heating of the samples at 90°C, and a constant weight was obtained. In the second step, the samples were shaken with water for 1 h to treat pectin, centrifuged, and brought to a constant weight again. Third, the samples were extracted with 2% HCl, and in the last step, the samples were boiled with 5% NaOH. The HA that formed was precipitated with 5% HCl.

IHA preparation

Crushed and ground samples of the lignites were first sieved, and an 80-mesh portion was used in the IHA preparation after the determination of the HA content. The lignite (1 g) was mixed with 20 mL of 5% NaOH and 10 mL of distilled water; the mixture was heated on a bright flame, boiled for 3 min, and cooled immediately under tap water. The cooled mixture was centrifuged several times by the addition of distilled water until the supernatant became clear. The settled parts were collected into another beaker after each centrifugation. Distilled water (50 mL) was added to the rest of the solution, and the pH value was adjusted to pH 3.0 by the addition of 5% HCl. IHA that precipitated at the bottom of the flask was filtered and dried at 60°C in an open drier to prevent crumbling into powder. The chemical structures of the prepared IHAs were determined with IR.

Determination of the acid percentage in the IHA structures

The carboxylic acid contents of the prepared IHAs were determined titrimetrically. Twenty milliliters of 0.1N KOH was added to 1 g of HA. Then, the mixture was boiled under a reflux condenser in a water bath. After it was cooled, the surplus KOH was titrated with 0.1N HCl. The concentration of COOH groups bound to IHA was calculated with eq. (1) or (2):

$$\text{AN}_{\text{KOH}} = 56.1 \times (V_1N_1 - V_2N_2)/m \quad (1)$$

$$\text{AN}_{\text{COOH}} = (V_1 - V_2) \times 0.0045 \times 100/m \quad (2)$$

where AN_{KOH} represents the milligrams of KOH per gram of HA, AN_{COOH} is the percentage of COOH, V_1 is the volume of KOH added (mL), N_1 is the normality of KOH (0.1N), V_2 is the volume of HCl wasted, N_2 is the normality of HCl (0.1N), and m is the sample quantity (g).

Fe(II) adsorption onto IHA

Two prepared IHA samples were used as adsorbents for the removal of Fe(II) ions from aqueous Fe solutions freshly prepared with $\text{Fe}(\text{SO}_4)_2$.

The behaviors of Fe(II) adsorption onto IHA samples were studied as a function of the initial concentration of the adsorbate and the contact time in 300-mL flasks with a 200-mL liquid volume. Different initial Fe(II) concentrations were tried with 0.1 g of IHA added (the pH of the mixture was neutral). Flasks containing the Fe(II) solution and IHA adsorbent were placed in a shaker and shaken at a speed of 220 rpm and a constant temperature of 20°C, and the changes in the Fe(II) concentration were followed against time until an equilibrium was reached. In all flasks, 240 min was sufficient to reach an equilibrium.

The standard spectrophotometric iron determination method was applied in the studies.¹³

Adsorption model

To quantify the adsorption capacities of IHAs for the removal of Fe(II) from water, the main two-parameter adsorption models, Langmuir and Freundlich isotherms, were used.

The Langmuir isotherm theory assumes monolayer coverage of the adsorbate over a homogeneous surface.¹⁴ The basic assumption is that sorption takes place at specific homogenous sites within the adsorbent. The Langmuir equation is as follows:

$$q = \frac{b \times q_m \times C_e}{1 + b \times C_e} \quad (3)$$

where q is the amount adsorbed per specified amount of the adsorbent (mg/g), b is the equilibrium constant related to the heat of adsorption, q_m is the maximum amount of the adsorbate that can be adsorbed when full monolayer surface coverage is achieved, and C_e is the liquid phase equilibrium metal concentration (mg/L). Hence, a plot of C_e/q versus C_e should give a straight line with a slope of $1/q_m$ and an intercept of $1/b \times q_m$.

The Freundlich isotherm is an indication of surface heterogeneity and deals with multilayer adsorption.¹⁵ The Freundlich equation is generally applicable to low concentrations of the adsorbate in the medium and assumes that the number of sites associated with a particular free energy of adsorption decreases exponentially as the free energy level increases:¹⁶

$$q = K \times C_e^{1/n} \quad (4)$$

where K is the measure of the sorption capacity and $1/n$ is the sorption intensity. The natural logarithm of the equation is in a linearized form, and a plot of $\ln q$ versus $\ln C_e$ should give a straight line with a slope of $1/n$ and an intercept of $\ln K$.

TABLE I
Results for Fractionation Materials for Lignite Samples by the Extraction Method

Fractionation and resultant materials	Lignite sample	
	Beysehir (3.2 g)	Ermenek (5.2 g)
Extraction in benzene		
Bitumen (%)	5.0	1.7
Sediment I (g)	3.0484	5.1927
Extraction of sediment I with water		
Pectin material (%)	13.24	5.56
Sediment II (g)	2.7770	4.9042
Extraction of sediment II with 2% HCl		
Hemicellulose %	6.55	1.67
Sediment III (g)	2.6589	4.7542
Extraction of sediment III with 5% NaOH		
HA (%)	42	30

The thermodynamic parameter ΔG , which is the free energy change, was computed as follows:

$$\Delta G = -R \times T \times \ln K \quad (5)$$

where R is the gas constant and T is the temperature (K). The adsorption kinetics were followed according to the intraparticle transport phenomenon:

$$x = K_t \times t^m \quad (6)$$

where x is the adsorption percentage, t is the time (h), m is a constant, and K_t is the constant coefficient indicating whether or not intraparticle transport is the only rate-limiting step.¹⁷

RESULTS AND DISCUSSION

HA contents of the lignites and IHA structures

The results of the sequential fractionation process are presented in Table I. The initial masses of the fractionated samples were different, but to be comparable, the extracted fractions were presented as percentages. A higher HA content (average = 42%) was determined for the Beysehir lignite sample than for the Ermenek lignite sample (average = 30%), as shown in Table I.

The carboxylic acid ($-\text{COOH}$) concentrations of the prepared IHAs, determined titrimetrically, were 13.55% for Beysehir IHA and 11.58% for Ermenek IHA. Beysehir IHA had more $-\text{COOH}$, promising higher adsorption with higher functional group contents.

The chemical structures of the prepared HAs, determined via IR spectra of the Beysehir and Ermenek lignites, are presented in Figure 2(a,b), respectively. There are one or two peaks at $1600\text{--}1700\text{ cm}^{-1}$, which indicate the presence of aromatic and COOH groups. OH bonds can be observed between 3400 and 3600 cm^{-1} in the IR spectra. Strong peaks can be

observed in both areas of the spectra. This shows that Konya lignite is rich in HAs.

Fe(II) removal from a solution via IHA

The adsorption behavior of Fe(II) onto IHA as a function of the shaking time and concentration of the adsorbate was studied. The results indicated that both IHA samples were effective for Fe(II) adsorption.

The effects of the shaking time and initial concentration of the adsorbate on adsorption are shown in Figure 3. In batch studies performed under different conditions for Fe(II), an equilibrium was attained approximately in the first hour. The graphs indicate that for all initial Fe(II) concentrations, a similar reduction pattern was followed. The quantity of the adsorbent was effective for higher initial Fe(II) concentrations, so the Fe(II) removal efficiency increased with an increasing initial Fe(II) concentration, reached an approximate maximum value at an initial Fe(II)

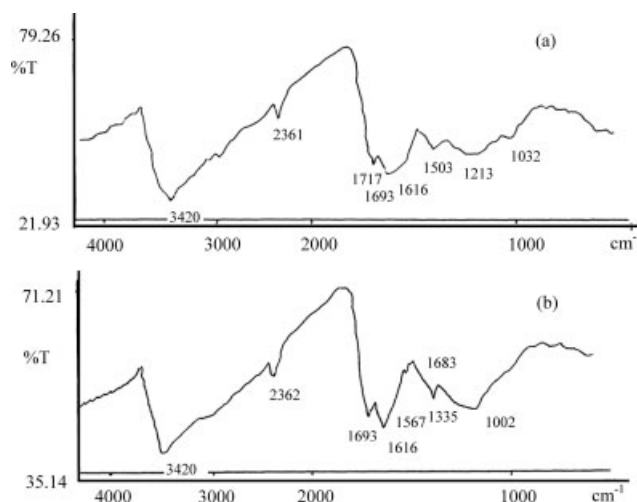


Figure 2 IR spectra of IHAs obtained from (a) Beysehir and (b) Ermenek lignites.

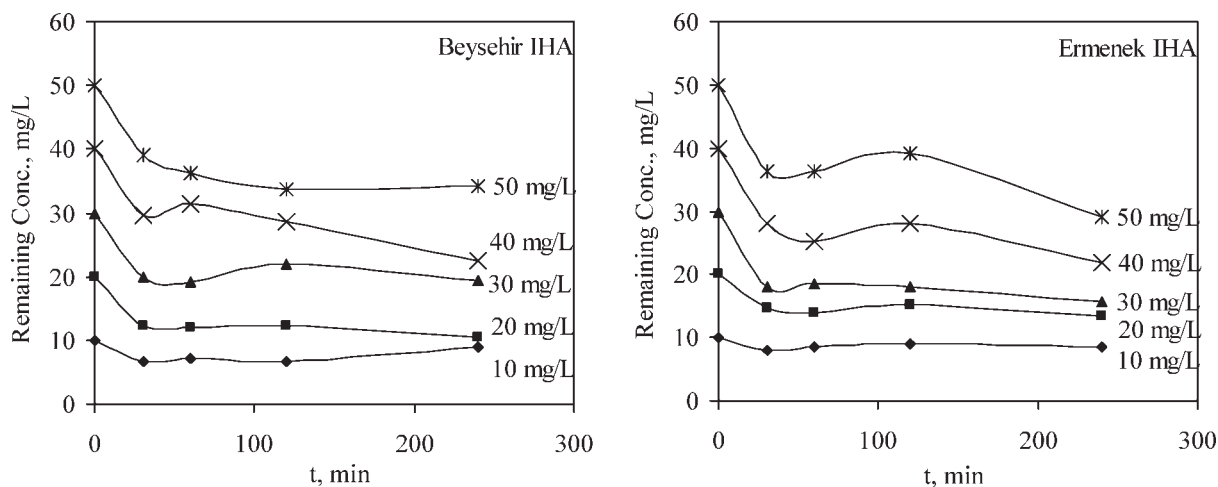


Figure 3 Time-concentration profiles for Fe(II) adsorption onto IHA samples.

concentration of about 40–50 mg/L, and remained constant after that (Fig. 4).

Adsorption isotherms

A successful representation of the dynamic adsorptive separation of a solute from a solution onto an adsorbent is dependent on a good description of the equilibrium separation between the two phases.¹⁸ An equilibrium is established when the amount of the solute being adsorbed onto the adsorbent is equal to the amount being desorbed. Plotting the solid-phase concentration against the liquid-phase concentration graphically depicts the equilibrium adsorption isotherm (Fig. 5). The resultant data from the batch studies gave the isotherm plots presented in Figure 5, which are characteristic isotherms for both IHAs. The Fe binding capacities of the Beysehir and Ermenek IHAs were 1.06 and 1.02 mmol/g (59 and 57 mg/g),

respectively, and were much higher than the estimated capacity for Fe in the literature for IHAs obtained from North Bohemia coal (0.4 mmol/g).³

In this study, the experimental data were analyzed according to two of the single-component isotherms: Langmuir and Freundlich. The data were subjected to a mathematical analysis for isotherm generation. The Freundlich and Langmuir isotherms were checked and are presented in Figure 6, in which the linearized forms of the isotherm equations have been plotted and a curve fitting has been applied via a linear regression analysis. The R^2 values presented with the equations representing the correlations of the data and system fit the isotherm whose R^2 value is high enough and closer to 1. The related parameters for the fitting of the Langmuir and Freundlich isotherms for both IHAs at a constant temperature (20°C) are summarized in Table II.

The adsorption of Fe(II) onto IHA followed the Freundlich isotherm in a correlation higher than 95%

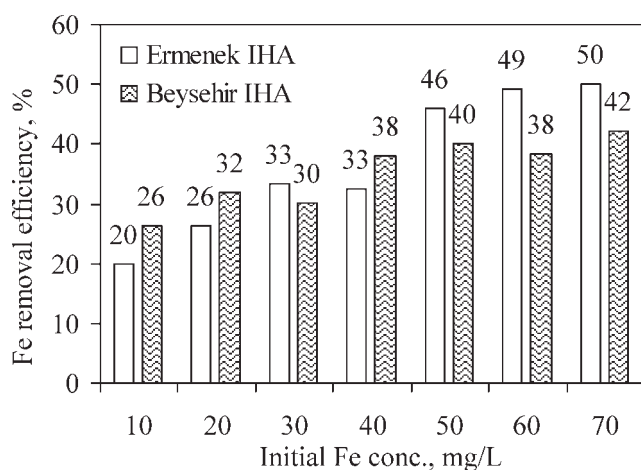


Figure 4 Comparison of the overall Fe(II) removal efficiencies of the IHA samples.

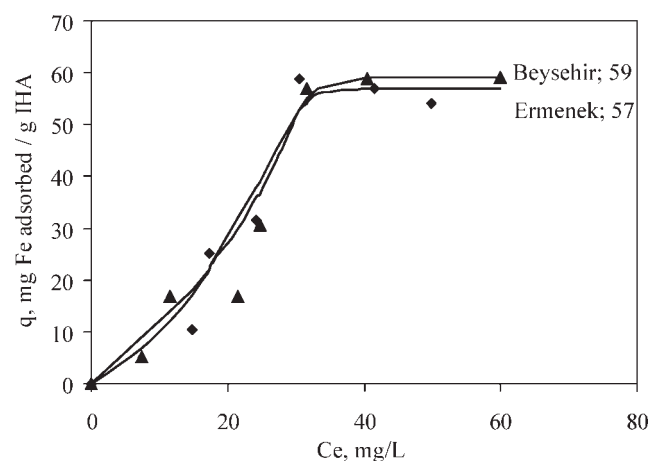


Figure 5 Adsorption isotherm plots of the IHA samples.

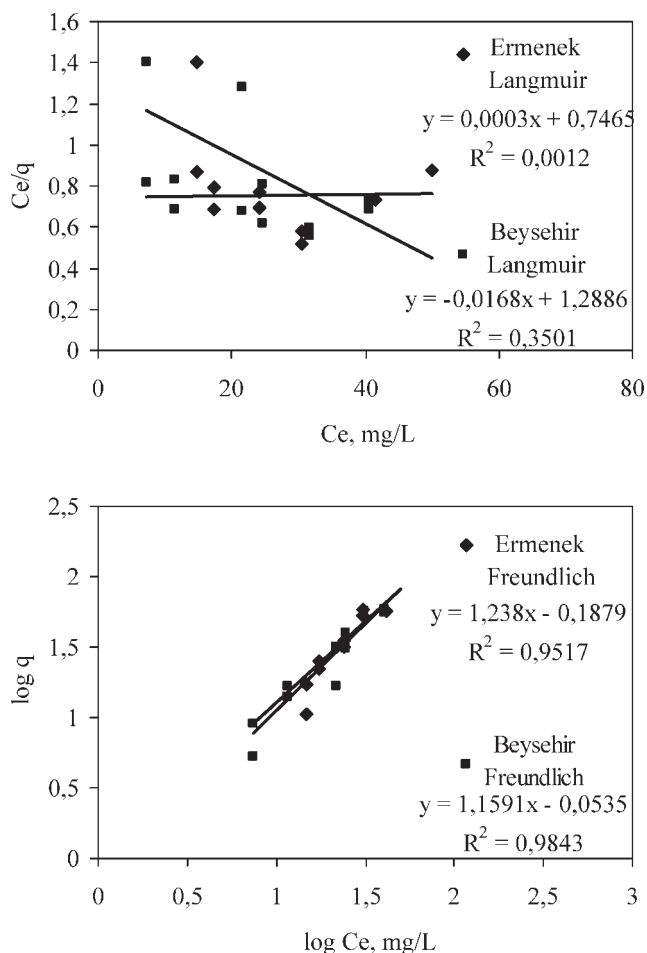


Figure 6 Linearized Langmuir and Freundlich isotherm check plots for the IHA samples.

(i.e., with $R^2 > 0.95$) for both IHA samples (Fig. 6 and Table II). Parallel to the close removal efficiency and capacity findings, the Freundlich isotherm constants were also very close to each other for both IHAs. The adsorption rates calculated from the Freundlich constants ($1/n$) were 0.86 and 0.81 for the Beysehir IHA and Ermenek IHA. The findings parallel the capacities: the higher the adsorption rate was, the higher the capacity was. The experimental data did not fit the Langmuir isotherm, and this indicated multilayer Fe(II) adsorption onto IHA surfaces with high heterogeneity. This can be explained by the chemical struc-

TABLE II Isotherm Constants and Coefficients of Least-Square Fittings to Straight Lines

IHA	Adsorption rate	Langmuir isotherm			Freundlich isotherm		
		b	q_m	R^2	K	$1/n$	R^2
Ermenek	0.81	0.0004	3333	0.0012	0.98	1.24	0.9517
Beysehir	0.86	-0.0013	-60	0.3501	0.95	1.16	0.9843

TABLE III Thermodynamic Parameters for Fe(II) Adsorption onto Both IHAs

IHA	Freundlich isotherm		
	$\ln K$	ΔG (kJ/mol)	R^2
Ermenek	-0.1879	8.17	0.9517
Beysehir	-0.0535	2.33	0.9843

ture of IHA, which is explained in the previous section: IHA contains $-\text{COOH}$ functional groups, and metal ions mainly bind to these. The higher the pH is of the solution, the higher the adsorption is of the ions. At $\text{pH} > 5$, the share of the COOH groups involved in ion exchange increased, and at $\text{pH} 6-7$, all the groups were engaged in the process. The solution pH was neutral, and the uptake of Fe(II) was mainly due to physisorption. The free energy and free energy changes are presented in Table III. The free energy of the process was negative and higher for Ermenek IHA, indicating that the process was spontaneous in

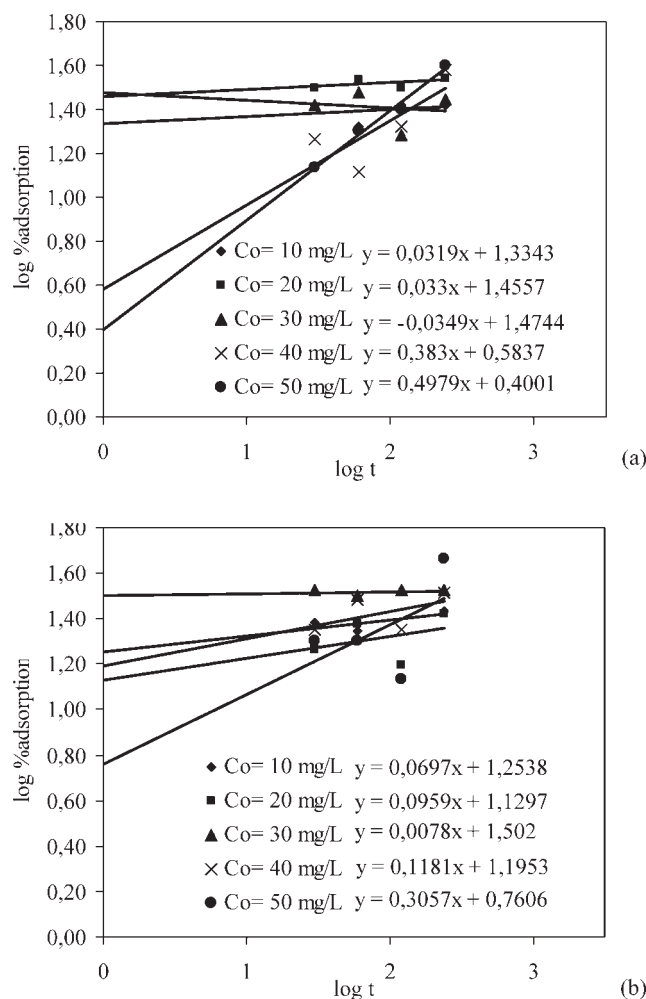


Figure 7 Kinetics of the adsorption of Fe(II) onto (a) Beysehir and (b) Ermenek IHAs.

nature. This also supports the idea that an endothermic system consumes sufficient energy for enhancing the rate of intraparticle diffusion of the adsorbate.

The adsorption kinetics were checked with a linearized plot of eq. (6) as the logarithm of time versus the logarithm of the adsorption percentage, and the results are given in Figure 7. The deviation of the straight line from the origin is characterized by an intercept and presented as least-square-fit equations on graphs for different initial Fe(II) concentrations for both IHAs. As shown in Figure 7, the $\log K_t$ values were smaller for higher initial Fe(II) concentrations; $\log K_t > 0$ indicates that besides intraparticle transport, Fe(II) ions transported from the solution through the particle solution interface into the pores of the particle and the adsorption on the available surfaces of IHAs were both responsible for the uptake.¹⁹

CONCLUSIONS

IHAs were prepared from two different low-grade lignites obtained from coal mine sites in Beysehir and Ermenek in the central Anatolia region in Turkey. The HA content of the Beysehir coal sample (42%) was higher than that of the Ermenek coal sample (30%). Moreover, the —COOH content of the prepared IHAs was 13.55% for the Beysehir IHA and 11.58% for the Ermenek IHA.

Fe(II) can be adsorbed by IHAs prepared from low-grade lignites. The adsorptive capacity of the IHA samples was calculated to be 59 mg/g (1.06 mmol/g) for the Beysehir IHA and 57 mg/g (1.02 mmol/g) for the Ermenek IHA from isotherm calculations. The adsorption pattern onto IHA followed the Freundlich isotherm, with R^2 higher than 0.95 for both IHAs.

The adsorption rates of the Beysehir IHA and Ermenek IHA were found to be 0.86 and 0.81, respec-

tively. These indicate that the effectiveness of the Beysehir IHA was slightly higher than that of the Ermenek IHA. The results confirm the real possibility of the practical application of IHAs for the separation of heavy metals (Fe in this study) from wastewaters.

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