

Comparison of adsorption capacity of young brown coals and humic acids prepared from different coal mines in Anatolia

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Abstract

Binding of Zn^{2+} and Cd^{2+} cations to relatively young brown coals YBC (lignite), humic acids (HAs) and commercial humic acid (CHA) were studied in aqueous media at pH 2.7–6 by polarographic method. This study was conducted to evaluate the removal of heavy metals in an aquatic system without prior treatment. The general principles of cation binding to YBC and humic materials are discussed. Sorption of heavy metal ions (Zn^{2+} and Cd^{2+}) on samples of YBCs from three areas (Ilgin, Beysehir, and Ermenek) in the vicinity of the city of Konya in Anatolia (Turkey) were compared with sorption of these metal ions on HAs, prepared from these YBCs. The ability of both types of sorbent to remove metals from aqueous solutions was studied as a function of pH and concentration of initial metal solutions. Sorption depends strongly on pH, the origin of the YBC and on the nature of the metal ion. Whereas, for YBCs the main ligand groups seem to be carboxylate ions, this is not the case for the HA polymers, prepared from three YBCs, which differ substantially from properties of commercial samples of “HA”. The process is very efficient especially in the case of low concentrations of pollutants in water, where common methods are either economically unfavorable or technically complicated. Of the two metal ions examined, Cd^{2+} was found to form the most stable HA complexes, followed by Zn. Effective removal of metals was demonstrated at pH-values of 5–5.7. The adsorption isotherm was measured at 25 °C, using adsorptive solutions at the optimum pH-value to determine the adsorption capacity. An important aspect of the proposed method was that the removal was performed on several metals at a pH-range in which a given metal undergoes an adsorption process making the method useful for wastewater treatment.

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1. Introduction

Young brown coal (lignite) is an immature coal with large amounts of humic substances (humic and fulvic acids, with the former predominating). The primary use of YBC is as a fertilizer and soil conditioner in agriculture. YBC possesses a high content of oxygen, which is fixed in carboxyl and hydroxyl groups. These groups are active centre of the ion-exchange. So, the lignite-based materials can be used as an alternative cation-exchanger [1–3]. Carboxyl or hydroxyl groups are able to take part in the ion-exchange. Metal ion binding to natural YBC or HA is a subject of considerable importance since it can have a large impact on the total metal concentration in wastewaters. It is widely recognized that HA obtained from YBC have an ele-

vated cation-exchange capacity and form complexes with metal ions, and it is generally accepted that they contain several major functional groups: carboxyl (COOH), alcoholic (OH) and carbonyl (C=O). These properties enable YBC and HAs to be used as a wastewater treating medium to remove heavy metals. The low cost and the availability of this material make it a promising candidate for pollution remediation.

Heavy metals are ecologically significant because they are toxic and do not undergo biodegradation. In the case of insufficient wastewater treatment or if the polluted water is released to a watercourse, these metals can accumulate in the environment. Recovery of heavy metals present in wastewaters in relatively low concentrations is rather difficult. The binding of protons and metal ions by humic substances (fulvic and humic acids) is relevant to many environmental problems. The use of precipitation is limited by the effect of added reagent, which often results in increased pH of the water. The main obstacle in wide use of synthetic ion-exchangers is their cost and their need for peri-

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Table 1
Lignite reserves in the area in the vicinity of city Konya (Turkey)

Town/area	Reserves (tonnes)
Beysehir/Karadiken	107.000
Beysehir/Avdancik	132.000
Seydisehir/Akcalar	69.000
Ilgin/Haramikoy	10.987
Ilgin/Cavuslu	167.890
Ilgin/Kurugol	9.142
Ermenek/Boyalik	1.700
Ermenek/Tepebasi	4.821

odic washings. It would be preferable if the adsorbent material were a natural product, the use of which would not introduce foreign materials into the environment. Among such adsorbents belong to lignins [4–9], HAs [10], and more recently used certain types of coal have been used to remove metal. Preliminary experiments indicated that particularly relatively young types of brown coals are suitable as sorbents. The Anatolian region of Turkey offers several sources of such coals, called YBC, particularly in the vicinity of the city of Konya. In this contribution the sorptive properties of YBCs from three towns in the Konya vicinity, Ilgin, Beysehir, and Ermenek, which have considerable reserves of YBC (Table 1), will be compared. Of these three YBCs, the first two seem to be, based on a lower calorific value, younger than the YBC from Ermenek.

The common methods (conventional ion-exchange, electrolytic or liquid extraction, electro dialysis, precipitation, clarification and reverse osmosis) and others are not always effective in the removal of toxic metals [11–13]. Hydroxide precipitation is standard practice in the treatment of metal in wastewater. Both lime and caustic soda are used as the precipitating chemicals. The existence of a different pH for the precipitation of a given metal element limits its use when a varied number of metals coexist in the same waste solution. In order to meet more stringent effluent discharge standards, other techniques such as co-precipitation, ion-exchange and adsorption have been received closer attention. Sorption technology based on ion-exchange processes and physical and chemical sorption has found increasing application in various fields in recent years. The use of sorption processes for removal of heavy metals from wastewater is especially promising. Adsorption can occur during metal removal processes, making its application in wastewater treatment possible. In several previous reports, various authors have documented the use of treated activated carbons and coal-based sorbents [14–16]. The use of peat for the removal of transition metals from aqueous systems was extensively studied and had already been recommended in the past and they are also rich in hydrophobic sites that can bind organic complexes of transition metals [17–20]. The removal performance and the selectivity sequence of mixed metal ions in aqueous solution were investigated by adsorption process on pure and chamfered-edge zeolite 4A prepared from coal fly ash (CFA), commercial grade zeolite 4A and the residual products recycled from CFA [21].

The importance of humic substances is due to their high adsorptive capacity. These are capable of combining with metal

ions. The humic substances also influence the biological and physico-chemical properties of toxic ions acting as an accumulation phase for heavy metals following the formation of metal–humate complex or chelates with different degrees of stability [22]. Organic matter can have a dual role: it can reduce metal ion solubility through the binding of metal ions to solid organic sorbent or increase it through binding to dissolved organic matter.

The synthesis of HA in environment has been studied with by many workers and consequently many different theories for HA formation have been proposed. The constituent of HAs are believed to be macromolecules, with quinine and phenolic features, having a range of relative molecular masses from a few hundred to several million. Humic substances is a very complex organic material, the structure and reactions of which are not fully understood and possessing various functional groups (carboxylic, amino, phenolic groups, groups involving sulfur atoms) and moieties (aliphatic chains and aromatic rings) which characterizes its composition and properties [22,23]. The major binding sites in humic and fulvic acids are usually attributed to the carboxylic and phenolic groups present, although other less abundant functional groups (e.g. N- and S-containing groups) may also be important for metal ion binding. The oxygen containing functional groups in HA represent about a quarter of the total molecular weight of HAs. The carboxyl (COOH) group increases in abundance with humidification, reacts readily with metals, and gradually dissociates between pH 2.5 and 7 to form the carboxylate (COO⁻) group. The phenolic hydroxyl (OH) group is more abundant in the early stages of decomposition, is derived from lignin in woody plants, reacts less with metals, and dissociates between pH 8 and 13.5 [24–28]. The carbonyl (C=O) group increases in abundance with humidification, is the main functional group and transforms into the COOH group under oxidizing conditions. Wang et al. [29] suggested that carboxylic groups dominate the uptake of metal cations by the dissolved organic matter fraction of wastewater and sludge, and demonstrated the important role of carboxylic groups in the uptake of metal ion.

The infrared (IR) spectroscopic studies of metal–humic complexes suggested the participation of phenolic –OH and –COOH groups in binding of the metal ions followed –C=O and –NH– groups [30–36]. The reaction can be as follows:



This reaction leads to the acidification of the sorption solution. The pK (dissociation constant) values of carboxylic groups are generally between 4 and 6. Thus, the increase of H⁺ concentration in the solution due to Eq. (1) decreases –COOH ionization and, consequently, the ion-exchange capacity. So, the pH of aqueous solution has to be higher than 4.

The aim of the present work is to determine the adsorption capacity of YBC and HA from Anatolia (Turkey) with respect to aqueous solution of Zn²⁺ and Cd²⁺ and compare of them with CHA. This will permit the evaluation of YBC and HA for its utilization as an adsorbent in the elimination of this ion

from wastewater. To evaluate the sorptive properties of YBCs from these three areas, small samples of YBCs were equilibrated with a dilute solution of heavy metal ions in formate and acetate buffers. These buffers allowed studies of pH effects on the sorption between pH 2.7 and 5.7, and were chosen, as their anions form relatively weak complexes with studied metal ions (Zn^{2+} and Cd^{2+}). The sorption was followed by using polarographic methods of analysis, which enables determination of remaining free metal ions in suspension, containing small solid and colloidal particles eluted from YBC and HAs. The electroanalytical methodology, discussed in more detail elsewhere [4], is based on experience gained by using the polarographic method of investigation of sorption of organics and metal ions both on rot wood and Kraft lignins [5–10,37]. For comparison, HAs were prepared from the three types of YBC and their adsorption properties were compared with those of parent YBC and CHA.

2. Experimental

2.1. Preparation of solutions, coal and humic acid samples

Three samples of YBC used in this study from coalfield in the vicinity of Konya were denoted by the location of the mines, named Ilgin, Beysehir and Ermenek. The samples were ground using a ceramic mill and sieved to a particle size of 100-mesh. Materials for preparation of buffers (formic and acetic acid, ammonia and ammonium chloride) were reagent grade. The following salts cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) from Mallinckrodt, and zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) were used. A commercial sample of HA was obtained from Aldrich Chemical Company, Inc.

HA was also prepared from YBCs from the aforementioned three locations. For this purpose 1 g of the YBC sample was placed in 10 mL of distilled water and to the suspension 30 mL of 5% NaOH was added. The suspension was heated to boil for 3 min, cooled and centrifuged at 3200 rpm. The supernatant was decanted and 30 mL water was added. This suspension was again centrifuged, the supernatant decanted and the procedure was repeated until the supernatant was colorless. Supernatants from all centrifugations were collected and their pH was adjusted to 3 using a diluted solution of HCl. Resulting polymer, denoted HA, precipitated and was filtered off and dried at 105 °C.

2.2. Instrumentation

Fourier transform infrared (FTIR) spectrograms of YBC and HA samples embedded in KBr pellets were recorded with IR Perkin-Elmer 1600 series FTIR spectrometer. Some of the chemical characteristics and the FTIR spectra of the studied lignites and humic acids are given in Tables 2 and 3. The region corresponding to high wave numbers shows a broad band centered at 3300 cm^{-1} . This band is generally attributed to the (O–H) vibration of carboxylic and alcoholic groups. FTIR spectroscopy revealed the importance of carboxyl groups in the uptake. The content of carboxyl groups was determined by separation of the bands in the 1800–1500 cm^{-1} spectral region. The band at around 1420 cm^{-1} is assigned to symmetric COO^- stretching

motions and to the bending vibrations of aliphatic groups. Less intense band that appears in these spectra at around 1510 cm^{-1} can be attributed to (CH_2) and (CH_3) vibrations of aliphatic groups, another one at 1600 cm^{-1} to aromatic ring vibration. The band at 1615 cm^{-1} is assigned to aromatic carbonyl and carbonyl motion in carboxyl groups. The band appearing at approximately 1270 cm^{-1} can be attributed to the C–O stretching of phenolic groups. Accordingly, the effect of metal cations on loading on the FTIR spectra of the samples indicates that carboxyl functional groups play a major role in the uptake of them. Elemental analysis was carried out with a Perkin-Elmer Elemental Analyzer Model 240 instrument and was done at TUBITAK-Ankara Test and Analysis Laboratory. Inorganic and organic sulfur content was determined by Eschka Method. Pore volumes and average pore diameter greater than 20 Å, were determined by mercury porosimeter up to 2000 kg/cm using a Carlo Erba Model 200. The surface area of the coal sample was measured with a surface area apparatus (BET method). The specific surface area of the lignites is found to be 2.06, 2.96 and 2.20 m^2/g Beysehir, Ilgin and Ermenek, respectively, by BET method. It was seen that Beysehir and Ilgin lignites have more moisture, ash, volatile matter and oxygen content than Ermenek lignites but their calorific value is less than them.

The direct current (dc) polarographic current–voltage curves were recorded using a Sargent Model XVI polarography. The mercury electrode used had following characteristics: $m = 1.9 \text{ mg s}^{-1}$, drop-time $t = 3.3 \text{ s}$ at $h = 80 \text{ cm}$. Polarographic electrolyses were carried out in a Kalousek cell with a SCE separated by liquid as a reference.

For pH-measurements a bench top pH-meter (Denver instrument), for shaking the slurry containing the sample of YBC dispersed in a buffer solution with dissolved metal ion a shaker (Eberbach Corporation, Michigan) and for decantation of slurry a clinical centrifuge (International Company) were used.

2.3. Solution

The 0.1 M stock solutions of metal ions were prepared in water and the concentration of the metal ion verified by an EDTA titration. To minimize effects of buffer components as complexing agents, the concentration of the buffer anion was kept low and constant. All acetate buffers contained 0.05 M acetate ion and varied concentration of acetic acid: 0.005 M for pH 3.7, 0.05 M for pH 4.7 and 0.5 M for pH 5.7. All these buffers contained 0.1 M sodium perchlorate to increase conductivity. The formate buffer pH 2.7 contained 0.01 M formate and 0.09 M formic acid. 0.5% gelatin, used as a maximum suppressor was freshly prepared.

2.4. Procedures for binding of metal ions

Calibration curves for all metal ions were prepared for a concentration range from 0.1 to 2.0 mM in 0.1 M NH_3 , 0.1 M NH_4Cl buffer containing 0.005% gelatin. For the sorption studies 0.2 g of the sample of YBC (if not indicated otherwise) was dispersed 9 mL of a buffer and shaken for 1 h to ensure complete dispersion. Then an aliquot of stock solution of the metal ion was added

Table 2
Basic characteristic of the lignites in Konya

Chemical properties	Place of lignites		
	Ilgin	Beysehir	Ermenek
H ₂ O (%)	20.00	28.50	11.31
Ash (%)	11.00	25.00	23.00
Volatile matter (%) ^a	26.00	17.00	23.00
Heating value (kcal/kg) ^b	2.18	1.11	3.33
Humidity (%) ^b	50.00	48.00	27.00
C (%) ^a	62.50	60.50	65.50
H (%) ^a	5.75	5.60	5.50
N (%) ^a	1.88	1.87	1.80
O (%) ^a	28.80	31.40	26.50
S (%) ^a	1.98	1.55	2.10
–OH (%) ^a	8.20	10.30	6.80
–COOH (%) ^a	4.80	5.10	3.70
O/C (atomic %) ^a	0.35	0.39	0.30
mequiv. KOH/g (%) ^a	1.48	1.53	1.23
BET (m ² /g)	2.06	2.96	2.68
IR spectra (cm ⁻¹)	3388, 2362, 1615, 1507, 1419, 1269, 1029	3405, 2921, 1595, 1429, 1037	3751, 3649, 3419, 2363, 2343, 1616, 1558, 1507, 1457, 1030

^a Water- and ash-free (900 °C).

^b Water-free.

and volume adjusted. The initial concentration of the metal ion in the slurry varied between 0.2 and 20.0 mM. The slurry was shaken for 10 h to establish the equilibrium.

The suspension was centrifuged and 1 mL of the supernatant was added to 9 mL of 0.1 M NH₃, 0.1 M NH₄Cl buffer containing 0.005% gelatin. Concentration of the metal ion in this solution was obtained using a calibration curve. The ratio of the difference between the current before addition of YBC and the current after shaking to the initial current multiplied by 100 gives the percentage of the metal ion bound onto the given amount of YBC. To obtain the adsorption isotherms the amount of metal ion adsorbed on 1 g of YBC was plotted as a function of the equilibrium concentration of the metal ion. For adsorptions on HA, 0.2 g samples of HA were used and the same procedure was followed as for YBCs.

3. Results and discussion

3.1. Binding of metal ions on YBCs and HAs

A suspension, containing a known amount of YBC from the three sources in buffers ranging from pH 2.7 to 5.7 was equilibrated and the main mass of YBC was separated by centrifugation. In the supernatant, containing small and colloidal particles of YBC (as indicated by the Tyndall effect) concentration of the free metal ion was determined by polarography, using a calibration curve. In suspensions, containing 10 mL of a buffer, the concentration of metal ions was varied from 2 to 20 mM. It was possible from the known initial concentration of the metal ions and determined concentration in the presence of the YBC to obtain the amount of metal ions bound on the sample

Table 3
Basic characteristic of the humic acids

Properties	Humic acids		
	Ilgin	Beysehir	Ermenek
H ₂ O (%)	50.00	48.50	27.31
Ash (%)	11.00	25.18	23.11
Volatile matter (%) ^a	36.71	17.00	27.78
C (%) ^a	42.40	41.50	45.8
H (%) ^a	5.70	5.60	5.3
N (%) ^a	1.63	1.28	1.61
O (%) ^a	18.38	22.42	12.25
S (%) ^a	1.00	1.01	5.12
–OH (%) ^a	5.10	4.50	4.40
–COOH (%) ^a	11.77	13.55	11.58
O/C (atomic %) ^a	0.16	0.18	0.11
mequiv. KOH/g (%) ^a	3.01	3.41	2.97
IR spectra (cm ⁻¹)	3420, 2364, 1617, 1541, 1368, 1078, 1038	3420, 2361, 1717, 1655, 1616, 1505, 1213, 1032	3420, 2362, 1639, 1616, 1567, 1383, 1335, 1003

^a Water- and ash-free (900 °C).

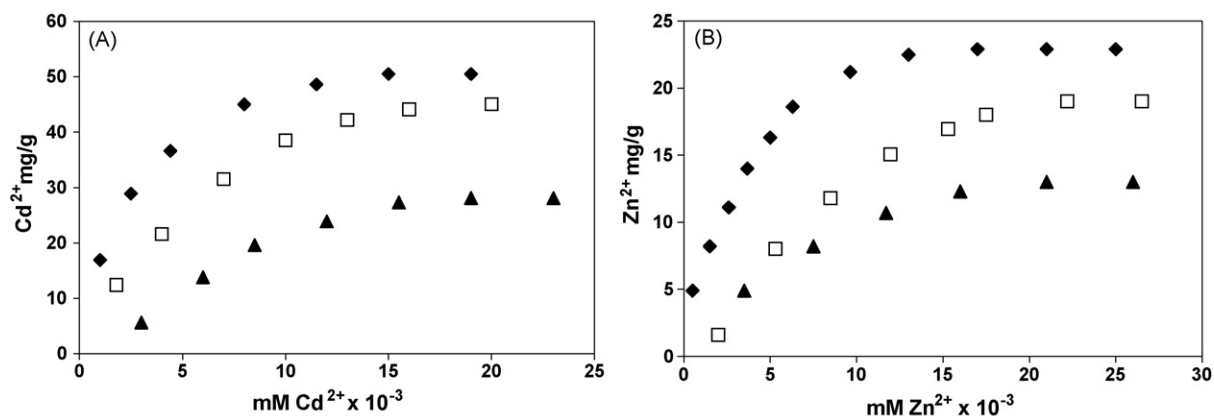


Fig. 1. Dependence of the amount of metal (in mg/g of Ilgin YBC) on equilibrium concentration of metal ion. In each experiment, 0.2 g of YBC was dispersed in 10 mL of an acetate buffer: pH 3.7 (▲), 4.7 (□), and 5.7 (◆). Metal ions used: Cd²⁺, Zn²⁺.

of YBC. Plots of the dependence of the amount of metal ions bound on the sample of YBC on concentration of the metal ion in equilibrated solutions have shapes resembling those of Langmuir type isotherms (Fig. 1). To minimize the effect of buffer components on formation of complexes, only acetate and formate buffers were used. Buffers were prepared at a constant, low concentration of the anion (which could act as a ligand) and varying concentration of the weak acid. Such buffers have also a constant ionic strength. Inspection of Fig. 1 indicates that in most curves largest fraction of the metal ion is bound in the presence of 0.2 g of YBC when the initial concentration of the metal ion was 20 mM. These maximum fractions of bound metal, obtained under such conditions, were summarized in Table 4.

Under similar conditions, data were obtained for maximum binding on samples of HAs and maximum fractions of bound metal, expressed in percent bound, obtained in the hence composition of YBC or HA and on the nature of the metal ion. Presence of 0.5 g of HA in a buffer containing 20 mM metal ion, are given in Table 5. Comparison of data in Tables 4 and 5 indicates a strong dependence of metal binding, both by YBC and HA (polymers prepared from these YBCs) and on pH, on the origins, and in general, the adsorption capacity of YBCs is in some instances comparable, in other smaller than that of the corresponding HA.

Based on the behavior of heavy metal adsorption on YBC, ion-exchange and hydrogen bonding may be the principal mech-

Table 4
Binding of metal ions

Metal ion	pH ^a	Maximum binding (%)		
		Ilgin ^a	Beyşehir ^a	Ermenek ^a
Cd ²⁺	2.7	18.0	31.0	16.8
	3.7	24.4	32.6	19.8
	4.7	33.6	50.0	20.9
	5.7	44.3	50.2	25.8
Zn ²⁺	2.7	15.3	27.9	9.4
	3.7	23.0	28.2	15.8
	4.7	23.3	28.9	16.0
	5.7	31.2	35.6	20.8

^a Origin of lignite.

Table 5
Adsorption of metal ions on HAs

Metal ion	pH ^a	% Sorption HAs from lignite			Commercial HA (Aldrich)
		Ilgin ^a	Beyşehir ^a	Ermenek ^a	
Cd ²⁺	2.7	17.2	31.2	9.5	61.0
	3.7	29.9	48.4	23.1	54.1
	4.7	51.6	68.3	47.0	78.6
	5.7	59.3	73.8	55.6	^b
Zn ²⁺	2.7	13.4	24.3	9.4	56.6
	3.7	19.8	29.7	15.8	53.4
	4.7	32.7	43.6	28.7	72.5
	5.7	39.6	49.5	35.6	^b

^a Origin of lignite.

^b The sample of commercial HA dissolved at this pH.

anism for the removal of heavy metals from aqueous solution. It has long been recognized that heavy metal cations are readily form complexes with functional oxidized groups such as (hydroxyl, methoxyl, carboxyl, phenol, etc.) in coal structures [38,39]. These functional groups are responsible for binding of metal cations and, in particular, heavy metal cations. YBC can be regarded as a weak acid exchanger in which the affinity for hydrogen ion is much greater than the affinity for metal ions. Thus, monovalent metal ions, which do not form complexes easily, are only weakly bound to the HA in YBC and are easily displaced by divalent metal ions which, although not having as great an affinity as hydrogen ion, are capable of being bound to the YBC either by donation of a single lone pair from oxygen or nitrogen or by chelation. The interactions of metals with coals surface molecules are complex, probably simultaneously dominated by adsorption, ion-exchange and chelation. The pH-dependence of adsorption may suggest that metal ions are adsorbed according to the ion-exchange mechanism may indicate the chelating mechanism [40].

YBCs are low-rank coals and characterized by their low calorific value, as well as high oxygen and moisture contents. They remove cations from solution via ion-exchange with carboxylic acid and phenolic hydroxyl functional groups on the surface of coals. The observed trend in adsorption efficiency, where adsorption increases as the rank of the coal substrate

decreases, is related to the number of surface sites available for adsorption on the substrate surface. Lower-rank coals possess higher surface functionality, and hence a greater number of sites are available for interaction with aqueous heavy metal ions. The data presented in Fig. 2 show that this trend becomes less clear as the rank of the coal is increased [41]. The maximum percent of bound metal ion (Tables 4 and 5) depends both on the volume of the metal ion and on the origin of the coal. Hence for YBC and HAs from Ilgin the amount of bound metal ion decreased in the following sequence: $\text{Cd}^{2+} > \text{Zn}^{2+}$. For the YBC and HAs from the Beysehkir region the maximum bound amount decreased in the following sequence: $\text{Cd}^{2+} \geq \text{Zn}^{2+}$ and

for the YBC and HAs from Ermenek, it decreases in the following sequence: $\text{Zn}^{2+} > \text{Cd}^{2+}$.

The same sequences have been obtained for CHA. HA are polyfunctional substances containing carboxyl, hydroxyl and amino groups. The carboxyl and amino groups of HAs form chelates with heavy metal cations. The HA extracted from the YBC tends to exhibit complexation tendencies for metal ions in a manner essentially quite similar to that exhibited by the synthetic HA. In reactions of HAs with metal ions, the main part plays carboxylic groups. It has been found that binding of double-charged metals to HAs depends on particular metal. The difference in adsorption behavior of metals can be explained

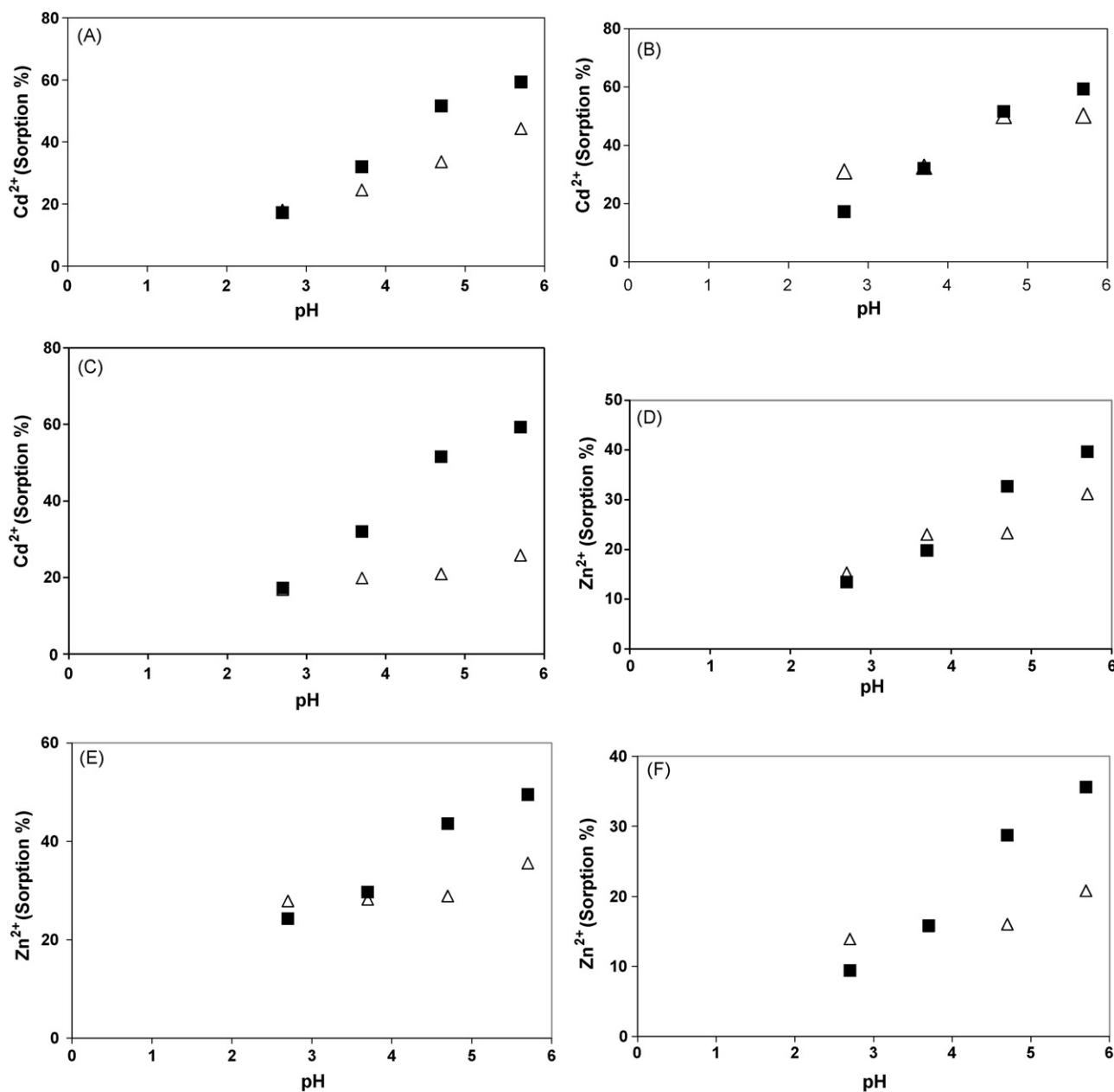


Fig. 2. Comparison of the dependence of the maximum amount of metal ion bound on 0.2 g of sorbent from the Ilgin (A, D), Beysehkir (B, E), and Ermenek (C, F) YBCs and HAs in 10 mL of an acetate buffer containing 20 mM Cd^{2+} and Zn^{2+} ion on pH. Metal ions used: Cd^{2+} , Zn^{2+} . In all cases, sorbent used: (△) YBCs and (■) HAs.

by the different affinity of metal ions for the donor atoms (i.e. oxygen, sulphur and nitrogen) in the HA structure. A difference in coordination behavior is most probably also the case for the complexing groups on the HA sample resulting in a relatively high adsorption of metal ions under non-competitive adsorption conditions.

3.2. Effect of pH of the aqueous media

An important influencing factor for heavy metal adsorption on YBC and HAs has been referred to as pH [42–44]. The effect of environmental pH on the sorption equilibrium is discussed and perhaps the most instructive is the comparison of the dependence of maximum binding on pH (Fig. 2). It is strongly indicated that values for YBC and HAs, the binding increase with increasing pH over the entire pH-range studied. For YBC, on the other hand, the binding in most instances reaches a limiting value at low pH-values, and another one at higher pH-values. Such behavior resembles that of dissociation curves of carboxylic acids. Thus, in YBCs, the predominant ligand seems to be carboxylate groups, whereas in HAs prepared from these YBCs it is not the case. The role of carboxylate groups was further supported by titration of samples of YBCs [4]. The equilibrium between solute and sorbent is quite dependent on pH of the aqueous solution. In a certain pH-range, most metal adsorption increases with increasing pH up to a certain value and then decreases with further pH increasing. Beyond pH 5.7, the determination could not be performed due to the low solubility of the metal ion in the solution phase. The metal ions are completely released under circumstances of extreme acidic conditions of the medium. It was observed that the removal percentage was maximum at pH-value 5.7 and the adsorption of metal ions on the YBC and HA was negligible at $\text{pH} < 2.5$. This is readily explained by the adsorption mechanism. At lower pH, the H^+ ions compete with metal cations for the exchange sites on the YBC and HA, thereby partially releasing the metal ion. The percentage of adsorption of metal ions increased with an increase in pH up to 5.7 as seen in Tables 4 and 5. At lower pH (< 2.5), the positive charged metal ion may compete with H^+ and be adsorbed at the surface of the YBC by ion-exchange mechanism. As the pH increases metal ions will replace hydrogen ions from the surface of the YBC and therefore the extent of the adsorption will increase. Similar results have been reported by many authors in studies of the removal of different metal ions on various adsorbents [21,40,44–46]. The experiments showed that maximum adsorption is attained at around pH 5.7. Adsorption capacities of all adsorbents were calculated from Tables 4 and 5. The adsorption capacities are 4.58, 5.22, 3.05 mg Zn^{2+}/g adsorbent for Ilgin, Beysehir and Ermenek YBC and 5.81, 7.26, 5.23 mg Zn^{2+}/g adsorbent for Ilgin, Beysehir and Ermenek HA, respectively. The adsorption capacities are 10.12, 11.46, 5.77 mg Cd^{2+}/g adsorbent for Ilgin, Beysehir and Ermenek YBC and 13.52, 16.83, 12.68 mg Cd^{2+}/g adsorbent for Ilgin, Beysehir and Ermenek HA, respectively. The adsorption capacity is 10.64 mg Zn^{2+}/g adsorbent and 17.92 mg Cd^{2+}/g adsorbent at pH 4.7 for CHA. CHA and HAs have bigger adsorption capacities than YBCs.

The pH effect of adsorption on YBC and HA can be explained by the surface characteristics of the adsorbent. Hydrogen ions affect metal complexation because they have a great affinity for many complexing and ion-exchange sites. At very low pH (< 2) functional oxidized groups (hydroxyl, carboxyl, phenol, methoxyl, etc.) of HAs are protonated. With an increase in pH, metal ion species, mainly neutral, may be adsorbed by hydrogen bonding mechanism along with ion-exchange.

Due to the relatively low pH of the original solutions used for adsorption experiments, only a part of the COOH groups in the HA–Me preparations was bound with metal ions, but it should be noted that even at pH (3.5–5.7), the Cd^{2+} ions will react with carboxylic and phenolic groups as well. The higher pH solution, the higher is adsorption of the ions. At $\text{pH} < 3.7$, only a part of the total amount of the COOH groups reacts with metal ions, but at $\text{pH} > 3.7$, share of the carboxylic groups involved in ion-exchange increases and at pH 4.5–5.7 all the groups are engaged in the process. The Cd^{2+} ions are exceptional because even at low pH reaction of the solution (< 4.7), they are bounded with phenolic groups as well. The participation of the phenolic groups in the bonding of other metal ions is relatively small.

4. Conclusion

YBCs and HAs acids proved to be useful and inexpensive sorbents for Zn^{2+} and Cd^{2+} ions. When the sorption equilibrium is known precisely, it is possible to predict the optimum conditions for a pre-concentration or removal of metal ions from waste streams. The brown coals are readily available in Anatolia, so they can be used by small-scale industries having low concentrations of metal ions in wastewater.

The adsorption properties of the sorbents were strictly defined by the physico-chemical nature of their surface and their texture-pore volume, pore size distribution, surface area. The limited reversibility of the sorption indicates that an ion-exchange is not the main operating process. Based on the behavior of heavy metal adsorption on YBC, ion-exchange, hydrogen bonding and metal complexation may be the principal mechanism for the removal of heavy metals from aqueous solution. The working hypothesis is that the size and shape of the cavities within the three-dimensional structure of YBC and the presence and nature of functional groups inside these cavities play an important role in the binding ability of YBC. Both the pH-dependence of maximum binding and the IR results indicate a role of carboxylic groups in the interaction with studied metal ions.

At very low pH (< 2) functional oxidized groups (hydroxyl, carboxyl, phenol, methoxyl, etc.) of HAs are protonated. It was observed that the removal percentage was maximum at pH-value 5.7 and the adsorption of metal ions on the YBC and HA was negligible at $\text{pH} < 2.5$.

The experiments showed that maximum adsorption is attained at around pH 5.7. The adsorption capacities are 4.58, 5.22, 3.05 mg Zn^{2+}/g adsorbent for Ilgin, Beysehir and Ermenek YBC and 5.81, 7.26, 5.23 mg Zn^{2+}/g adsorbent for Ilgin, Beysehir and Ermenek HA, respectively. The adsorption capacities are 10.12, 11.46, 5.77 mg Cd^{2+}/g adsorbent for Ilgin, Beysehir

and Ermenek YBC and 13.52, 16.83, 12.68 mg Cd²⁺/g adsorbent for Ilgin, Beysehir and Ermenek HA, respectively. The adsorption capacity is 10.64 mg Zn²⁺/g adsorbent and 17.92 mg Cd²⁺/g adsorbent at pH 4.7 for CHA.

Both pulverized YBCs, HAs prepared from these and CHA adsorb strongly heavy metal ions. Bindings on both YBCs and HAs have been found strongest for the YBC from the Beysehir area. Selectivity of sorption does not show any clear pattern neither for YBC nor corresponding HAs. The pH-dependence of sorption indicates a role of carboxyl groups in the samples of YBCs, but not for their HAs.

The amount of toxic metals bound to YBC and HAs increased with the pH increasing from 2.7 to 5.7. It was found that Cd ion has the highest affinity to ion-exchange centers of HAs.

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References

- [1] C. Lafferty, M. Hobday, *Fuel* 69 (1990) 78.
- [2] K. Murakami, T. Yamada, K. Fuda, T. Matsunaga, *Fuel* 80 (2001) 599.
- [3] M. Jochova, M. Puncochar, J. Horacek, K. Stamberg, D. Vopalka, *Fuel* 83 (2004) 1197.
- [4] E. Pehlivan, A. Richardson, P. Zuman, *Electroanalysis* 16 (2004) 1292.
- [5] F. Kulik, J. Wieber, B. Pethica, P. Zuman, *J. Electroanal. Chem.* 214 (1986) 331.
- [6] F. Kulik, J. Wieber, B. Pethica, P. Zuman, *Colloids Surf.* 33 (1988) 141.
- [7] M.A. Rubio, B.A. Pethica, P. Zuman, S.I. Falkenhag, in: G.E. Inglett, S.I. Falkenhag (Eds.), *Dietary Fibers and Nutrition*, Academic Press, New York, 1979, p. 251.
- [8] C.A. Paden, A.S. Frank, J.M. Wieber, B.A. Pethica, P. Zuman, L. Jurasek, *Properties of wood lignin*, ACS Symp. Ser. 214 (1983) 241.
- [9] P. Zuman, S. Ainsow, C. Paden, B.A. Pethica, *Colloids Surf.* 33 (1988) 121.
- [10] S. Ainsow, C. Paden, B.A. Pethica, P. Zuman, *Colloids Surf.* 33 (1988) 133.
- [11] G. Holmes, B.R. Singh, L. Theodore, *Handbook of Environmental Management and Technology*, Wiley, New York, 1993, p. 229.
- [12] M. Josef, S. Yabe, E. Oliveira, *Adv. Environ. Res.* 7 (2003) 263.
- [13] F. Gode, E. Pehlivan, *J. Hazard. Mater. B* 100 (2003) 231.
- [14] P.W. Lankford, Removal of Metals to Nontoxic Levels, in: P.W. Lankford, W.W. Eckenfelder (Eds.), *Toxicity Reduction in Industrial Effluents*, Van Nostrand Reinhold, New York, 1990, p. 98.
- [15] M.A. Ferro-Garcia, J. Rivera-Utrilla, J. Rodriguez-Gordillo, I. Bautista-Toledo, *Carbon* 26 (1998) 363.
- [16] S.B. Lalvani, T. Wiltowski, A. Hiibner, A. Weston, N. Mandich, *Carbon* 36 (1998) 1219.
- [17] P.A. Brown, S.A. Gill, S.J. Allen, *Water Res.* 34 (2000) 3907.
- [18] Y.S. Ho, G. McKay, *Water Res.* 34 (2000) 735.
- [19] F.J. Stevenson, *Humus Chemistry*, 2nd ed., Wiley and Sons, New York, 1994, p. 446.
- [20] L. Ringqvist, I. Oborn, *Water Res.* 36 (2002) 2233.
- [21] K.S. Hui, C.Y.H. Chao, S.C. Kot, *J. Hazard. Mater. B* 127 (2005) 89.
- [22] J.E. Boily, J.B. Fein, *Chem. Geol.* 168 (2000) 239.
- [23] M.J. Angove, B.B. Johnson, J.D. Wells, *J. Colloid Inter. Sci.* 204 (1998) 93.
- [24] M.A. Rashid, *Geochemistry of Marine Humic Compounds*, Springer-Verlag, New York, 1985, p. 300.
- [25] K.M. Spark, J.D. Wells, B.B. Johnson, *Aust. J. Soil Res.* 35 (1997) 89.
- [26] R.N. Yong, D. Mourato, *Can. Geotech. J.* 25 (1988) 599.
- [27] D.L. Lavti, K.V. Paliwal, *J. Indian Soc. Soil Sci.* 29 (1981) 30.
- [28] P. Pillon, J.M. Portal, B. Gerard, P. Jeanson, L. Jocteur-Monrozier, *Org. Geochem.* 9 (1986) 313.
- [29] J. Wang, C.P. Huang, H.E. Allen, L.R. Takiyama, I. Poesponegoro, H. Poesponegoro, D. Pirestani, *Water Environ. Res.* 70 (1998) 1041.
- [30] B. Manunza, S. Deiana, V. Maddan, C. Gessa, R. Seeber, *Soil Sci. Soc. Am. J.* 59 (1995) 1570.
- [31] F. Khalili, *Soil Sci.* 150 (1990) 565.
- [32] C.R. Evanko, D.A. Dzombak, *J. Colloid Interf. Sci.* 214 (1999) 189.
- [33] J.E. Boily, J.B. Fein, *Geochim. Cosmochim. Acta* 60 (1996) 2929.
- [34] S.A. Wasay, S. Barrinton, S. Tokunaga, *Water Air Soil Pollut.* 116 (1999) 449.
- [35] C. Namasivayam, K. Kadirvelu, *Carbon* 37 (1999) 79.
- [36] J.S. Allen, J.L. Whitten, M. Murray, O. Duggan, *Technol. Biotechnol.* 68 (1997) 442.
- [37] E. Rupp, Q. Zhong, P. Zuman, *Electroanalysis* 4 (1992) 11.
- [38] K. Gao, J. Pearce, J. Jones, C. Taylor, *Environ. Geochem. Health* 21 (1999) 13.
- [39] J. Lakatos, S.D. Brown, C.E. Snape, *Fuel* 81 (2002) 691.
- [40] L.J. Yu, S.S. Shukla, K.L. Dorris, A. Shukla, J.L. Margrave, *J. Hazard. Mater. B* 100 (2003) 53.
- [41] C.A. Burns, P.J. Cass, I.H. Harding, R.J. Crawford, *Colloids Surf. A* 155 (1999) 63.
- [42] C. Raji, T.S. Anirudhan, *Indian J. Chem. Technol.* 3 (6) (1996) 345.
- [43] C. Raji, T.S. Anirudhan, *Indian J. Chem. Technol.* 4 (5) (1997) 228.
- [44] L.M. Yates, R.V. Wandruszka, *Environ. Sci. Technol.* 33 (1999) 2076.
- [45] C.K. Jain, R. Daya, *Water Res.* 31 (1997) 154.
- [46] N. Petrov, T. Budinova, I. Khavesov, *Carbon* 30 (1992) 79.