# Removability Efficiency of Heavy Metals with Modified Humate from Aqueous Media

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## Abstract

The main aim of this work was to study the possibility of using amine-modified humate as a sorbent for the purification of water from heavy metal ions (Cu&Co). One of the effective methods of creating new sorbents of humic acids is chemical modification based on the high reactivity of the functional groups in the composition of humic acids. The possibility of modification of humic acid with bis(3-aminopropyl) amine was illustrated. Modification was carried out with the aim of increasing its sorption capacity. Metal-humate complexes were also obtained by an ion-exchange procedure with modified humate (Mod-Hum) by employing metal salts such as $Cu(CH_3COO)_2 \cdot H_2O$, $Co(CH_3COO)_2 \cdot 4H_2O$. Maximum sorption percentages of Mod-Hum achieved were about 99.2% for Cu (II) and 90% for Co (II). The sorption degree depending on pH changes was studied in the range of 2 to 8, the sorption ability of the sorbents was stated to increase with the increase in pH. The degree of sorption of copper (II) on Mod-Hum in the studied range of pH 5 was higher and of cobalt (II) for which the sorption is optimal at higher values (pH 7-8). It is stated that sorption degree increases with the increase in time from 15 min to 2 h. The adsorption of toxic metal ions with Mod-Hum was measured by atomic absorption spectroscopy (AAS). The experimental results on determination of the adsorption isotherm were evaluated with the Langmuir equation. It is shown that the sorbent develops a high sorption capacity in regard to ions of Cu (18.42 mg/g) and Co (16.25 mg/g). All the obtained complex compounds were analyzed and characterized by FT infrared spectroscopy (FTIR), scanning electron microscopy (SEM).

## Introduction

Nowadays one of the most important problems is the protection of the environment against harmful industrial wastes. Heavy metal ions are amongst the most distributed and toxic substances [1]. Compounds of heavy metals must be subjected to nearly perfect purification. Purification of water from heavy metal ions with the help of sorption processes using humic substances is quite promising.

Humic substances are natural organic compounds making up from 50 to 90% of the composition of peat and coals. They are a mixture of high molecular substances of a complex structure substituted by different functional groups which, due to their chemical structure, can undergo chemical modification and provide the ability to form stable complexes with heavy metal cations [2].

Sorption properties of bivalent cations of $M^{2+}$ (Cu, Pb and Zn) and trivalent cations of $M^{3+}$ (Fe, Al) with humic acids from oxidized coals in aqueous solution were studied in [3]. The effect of pH, concentration of metal ions and humic acids on the process of interaction of metal with humic acids was studied. It is found that the sorption ability of humic acids increased with the increasing pH and concentration of humic acids and decreased with an increase in concentration of metal ions. Sorption of $Cu^{2+}$ and $Zn^{2+}$ cations from model solutions by humic acids was studied in [4]. Analysis of isotherms of $Cu^{2+}$ and $Zn^{2+}$ sorption showed that in the processes of removing bivalent cations from model solutions humic acids are more effective in comparison with active coals.

Thus, the search for and study of new natural sorbents as well as the improvement of the existing technologies by introduction of sorption processes that are able to provide a rise in the effect of purification of natural and technogenic waters from heavy metal ions are actual. Humic substances are promising adsorbents as they are easily available at a low price.

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## Experimental

### Reagents and Materials

Humic acid was extracted from brown coal of the Shubarkul deposit in the Karaganda region of Kazakhstan. The extraction process of humic acids from coal was carried out with 2% NaOH (1:8 m/v) during 1 h at 25 °C with intensive mixing. Modification of humate was carried out using bis (3-aminopropyl) amine. Chemically pure bis (3-aminopropyl) amine and acetates of metals (Cu, Co) were purchased from Merck and Fluka Chemical Corporations (Diyarbakir, Turkey).

### Measurements

Determination of copper (II), cobalt (II) was carried out on an atomic-absorption spectrophotometer «Perkin Elmer AAnalyst 400». The values of pH were controlled with the help of pH-meter «Hanna pH 211». The microstructure of the samples was studied using a scanning electron microscope «QUANTA 250 FEG», which also gives the elemental composition of the samples (EDAX). Stretching and deformation vibrations were analyzed with a FTIR-spectrophotometer «Perkin Elmer Spectrum 100» in the spectral region 225-4000 $cm^{-1}$.

### Synthesis of Complexes

Metal-humate complexes were obtained by ion exchange of Mod-Hum with metal ions $Cu(CH_3COO)_2 \cdot H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$. Humate in the amount of 0.25 g dissolved in 25 mL of water was placed into a two-neck flask fit with a reflux cooler, magnetic mixer, thermometer and dropping funnel. Metal ions in the amount of 1 g dissolved in 40 mL of ethanol were added into this humate solution. The reaction mixture was heated to 100 °C and mixed during 24 h. After the reaction was completed the precipitate was filtered, washed with water and dried at 60 °C during 6 h. Dry complexes were analyzed with the help of FTIR and SEM.

### Sorption Processes

To study the sorption properties of Mod-Hum, ions of metals $Cu(CH_3COO)_2 \cdot H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$ were chosen. The sorbent in the amount of 0.1 g was added to the pre-assigned volume of the salt solution with the known concentration (50 mg/L), shaken up in an aqueous shaker at 25 °C from 15 min to 2 h. The value of pH was increased from 2 to 8 with the help of 0.1 N HCl/0.1N NaOH [5]. The content of the bottles was subjected to centrifugation during 30 min at 6000 r/min and then filtered out. The residual metal concentration in the solution was determined by AAS.

## Results and Discussion

### Characterization of Complexes

The morphology of the sample surfaces was determined by SEM. The energy dispersive X-ray analysis (EDAX) apparatus that can work simultaneously to SEM which combines elemental and structural analysis of compounds with mapping techniques gave us the elemental map and percentage of substances. Net intensity (Net Int.) represents the exact intensity of the corresponding peaks for each element in the compound. Net intensity error (Net Int. Error) means the possible deviation from the net intensity of the peak. Figure 1 presents a picture of the microstructure of Mod-Hum surface with a magnification of ×1517. It is seen that particles aggregate forming larger and smaller particles.
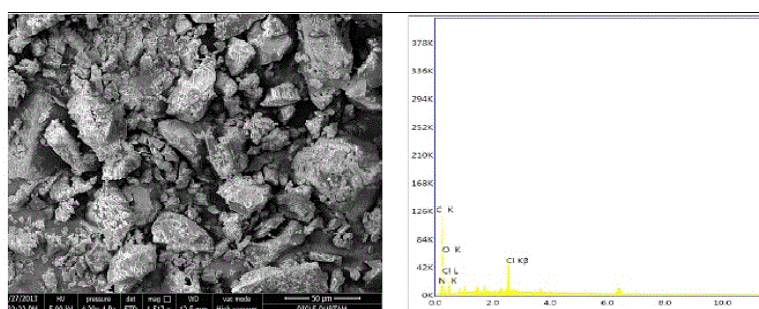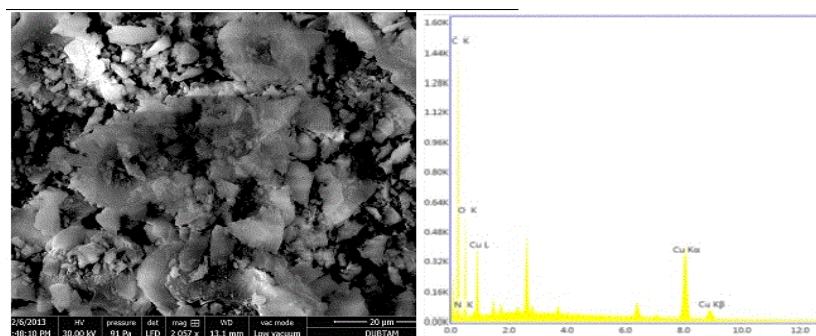


| Element | Weight % | Atomic % | Net Int. | Net Int. Error |
|---------|----------|----------|----------|----------------|
| CK | 55.72 | 65.55 | 539.3 | 0 |
| NK | 13.26 | 13.37 | 49.1 | 0.01 |
| OK | 17.97 | 15.87 | 200.4 | 0 |
| ClK | 13.05 | 5.2 | 3547.3 | 0 |

Fig. 1. SEM image of Mod-Hum sample and EDAX results.

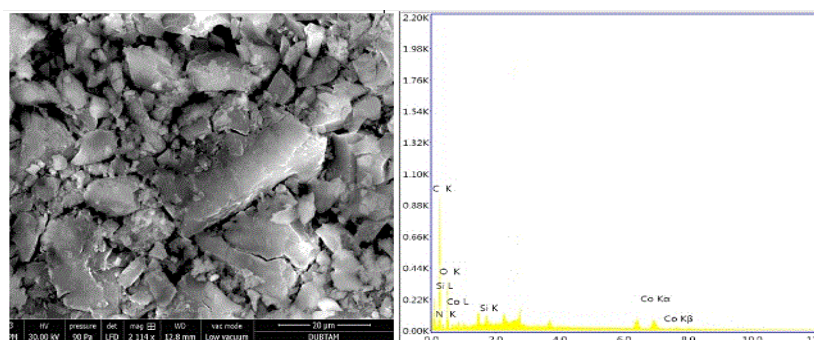SEM images and EDAX results of Mod-Hum complexes with metal ions are shown in Figs. 2 and 3. SEM images were taken with ×2000 magnification. The increase in the size of pores is observed on the surface of the particles [6, 7]. Heavy elements are sorbed mainly in pores; the change in the increase of the particle surface is likely to affect complex formation. As the EDAX results of Mod-Hum-Cu sample (Fig. 2) show, interaction of copper ions made up 11.09% and for Mod-Hum-Co sample (Fig. 3) interaction of cobalt ions made up 2.41%.



| Element | Weight % | Atomic % | Net Int. | Net Int. Error |
|---------|----------|----------|----------|----------------|
| CK | 53.07 | 64.08 | 31.2 | 0.01 |
| NK | 7.01 | 7.26 | 0.9 | 0.09 |
| OK | 28.83 | 26.13 | 12.3 | 0.02 |
| CuK | 11.09 | 2.53 | 28.1 | 0.02 |

Fig. 2. SEM image of Mod-Hum-Cu sample and EDAX results.



| Element | Weight % | Atomic % | Net Int. | Net Int. Error |
|---------|----------|----------|----------|----------------|
| CK | 50.79 | 58.14 | 22.8 | 0.01 |
| NK | 10.36 | 10.17 | 0.9 | 0.09 |
| OK | 35.95 | 30.89 | 10 | 0.02 |
| SiK | 0.5 | 0.24 | 2.1 | 0.16 |
| CoK | 2.41 | 0.56 | 5 | 0.11 |

Fig. 3. SEM image of Mod-Hum–Co sample and EDAX results.

Stretching vibrations are determined between the ranges of 225 to 4000 cm$^{-1}$. In the FT-IR spectrum (Fig. 4) of the samples there are intensive bands in the regions of 3683-3663 cm$^{-1}$ and 3238 cm$^{-1}$ due to stretching vibrations of hydroxyl groups –OH forming hydrogen bonds. Vibrations at 1027, 1032 and 1057 cm$^{-1}$ are attributed to the deformation and bending vibrations of C–OH groups. In Mod-Hum (Fig. 4. 1) the characteristic absorption band at 2921 to 2028 cm$^{-1}$ is due to the stretching vibrations of C-H bonds in aliphatic fragments in the humic compounds. The carboxyl group is characterized by a frequency bandwidth of 1700 cm$^{-1}$ and the absorption bands at 1573 cm$^{-1}$ and 1027

cm$^{-1}$ (stretching vibrations of C=O and C–N) correspond to those of amide groups. In the IR spectrum of Mod-Hum-Cu (Fig. 4. 2) the carboxyl group band shifts slightly to 1701 cm$^{-1}$. The substitution of the proton carboxyl group with metal copper ions retains the COO-group and increases the band at 1555 cm$^{-1}$, attributed to the asymmetric stretching vibrations of the COO- groups. Also, an absorption band appears 1362 cm$^{-1}$, also associated with the -COOH group. The IR spectrum of Mod-Hum-Co (Fig. 4. 3) is characterized by the presence of vibrations in the region of 2899 to 2128 cm$^{-1}$, related to stretching vibrations of –CH$_3$, –CH$_2$ and –CH groups of aliphatic structures, the carboxyl group at 1695 cm$^{-1}$ and the peaks with frequencies of 1527 and 1360 cm$^{-1}$, the vibrations of atoms of the carboxyl group in the Mod-Hum-Co. The FTIR spectra of the obtained samples confirm the formation of metal-humate complexes by binding the metal to donor atoms with coordinated covalent bonds for Mod-Hum-Cu by the 669, 406, 340 and 326 cm$^{-1}$ peaks and for Mod-Hum-Co by the 606,469,419 and 341 cm$^{-1}$ peaks which confirm the formation of M-O connection in the complexes [8]. Thus, based on the experimental data it can be argued that the interaction of ions of copper and cobalt with humic substances is predominantly due to adsorption. The infrared spectrum of Mod-Mod-Cu and Hum-Hum-Co provides bands characteristic of the functional groups of humic substances. The interaction of copper and cobalt ions occurs mainly with -COOH groups. Carboxyl groups of humic substances are mainly associated with the carbon atoms of an aromatic structure and exhibit a strongly pronounced ability to form complexes with metal ions. Thus, sorption proceeds with the inclusion complexation mechanism.
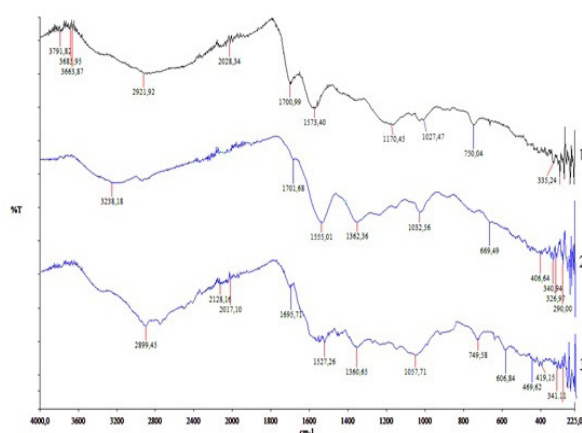


Fig. 4. FTIR-spectra of the samples: 1 – Mod-Hum; 2 – Mod-Hum-Cu; 3 – Mod-Hum-Co.

### Removal Efficiency (R, %) and pH Effect

Investigations on the degree of water purification with sorbents were carried out on a laboratory scales. The solutions were separated from the solid part by filtration and the residual concentration of metal ions in solution was determined by the AAS method. The obtained data allowed calculating the metal ion removal percentage (R, %) and the amount of sorption (qe, mg/g) was calculated by the difference in the initial and residual concentrations according to Eqs. 1 and 2:

$$\% R = \frac{Co - Ce}{Co} \cdot 100 \qquad (1)$$

$$qe = \frac{(Co - Ce) \cdot V}{g} \qquad (2)$$

where Co is the initial concentration of metal ions in solution, mg/L;
Ce is the concentration of metal ions in solution after their interaction with the sorbent, mg/L;
qe is the adsorption capacity, mg/g;
V is the volume of solution, mL;
g is the mass of sorbent, g.

The obtained results allowed to plot the dependency of the sorption degree of metal ions vs. time and then optimum values of pH for sorption were determined (Figs. 5 and 6).

Sorbent Mod-Hum in acid medium (pH 2-4) sorbs copper(II) ions from 18 to 81% and at pH 5 the degree of sorption increases up to 99.2% and reaches its maximum and then the degree of sorption sharply decreases to 60% at pH 6-7. After this jump the percentage of sorption degree slightly lowers till 59% at pH 8. This is explained by the fact that sorption of copper takes place in the neutral field of pH and decreases at low or high values of pH. The degree of sorption of copper (II) on Mod-Hum in the studied range of pH 5 was higher. It is stated that sorption degree increases with the increase in time from 15 min to 2 h.

At low values of pH (2-4) sorbent Mod-Hum sorbs Co(II) ions with a quite low degree up to 16 %, at pH 5 up to 27% and with the increase of pH to 7-8 the sorption degree a sharp increases up to 81.5-90%. At low values of pH, H$^+$ ions get adsorbed on the surface so that the total charge becomes positive. This inhibits adsorption of the positively charged Co ions. As pH increases, the OH$^-$ concentration increases on the surface and Co adsorption increases dramatically.
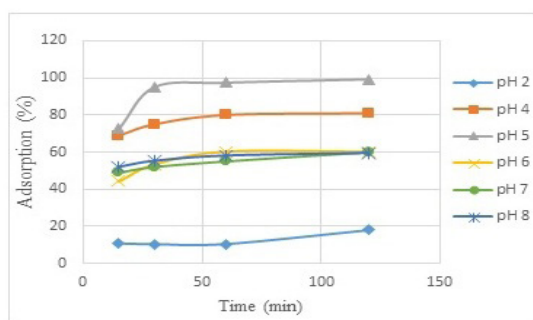
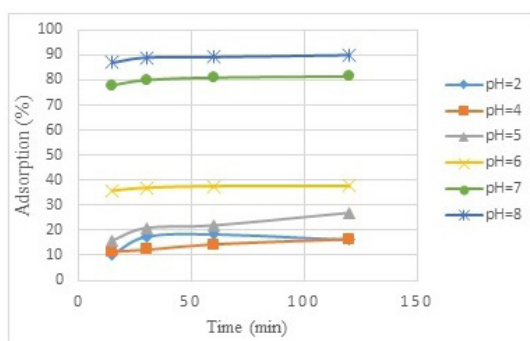Fig. 5. The degree of sorption of Cu(II) with sorbent Mod-Hum depending on time at different values of pH.



Fig. 6. Dependency of the degree of sorption of Co (II) with sorbent Mod-Hum depending on time at different values of pH.

### *Sorption Isotherm*

The experimental data on the sorption of Cu (II) and Co (II) ions with Mod-Hum were processed using the Langmuir equation. To treat the experimental data on the subsequent parts of the isotherms, we used the linear form of this Eq. (3) [9]:

$$\frac{Ce}{qe} = \frac{1}{q_m \cdot b} + \frac{Ce}{q_m} \qquad (3)$$

where $q_m$ is the theoretical maximum adsorption capacity, mg/g; $b$ is the Langmuir isotherm constant related to the energy of adsorption, mg/l.

The initial parts of the isotherms ($qe$ vs. $Ce$) have a linear character (Henry's Law region), that allows calculating the values of the distribution coefficient (4):

$$K_d = \frac{qe}{Ce} \qquad (4)$$

where $K_d$ is the distribution coefficient, mL/g.

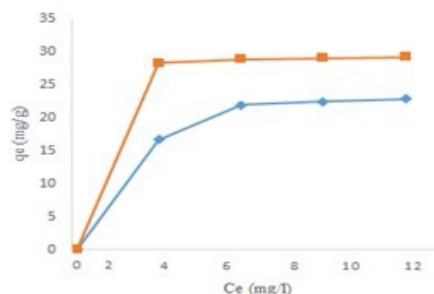Figure 7 presents an isotherm of sorption of Cu(II) and Co(II) ions with Mod-Hum.



Fig. 7. Isotherms of sorption of Cu (II) and Co (II) ions with Mod-Hum: 1 – Mod-Hum-Cu (pH 5); 2 – Mod-Hum-Co (pH 8).

The calculated values of $q_m$, $K_d$, and the correlation coefficient $R^2$ of Mod-Hum samples appeared to be most informative (Table 1).

**Table 1**
Adsorption parameters

| Name | $q_m$, mg/g | $b$, mg/L | $K_d$, mL/g | $R^2$ |
|---|---|---|---|---|
| Mod-Hum-Cu | 18.42 | 4.865 | 5625 | 0.9999 |
| Mod-Hum-Co | 16.25 | 2.663 | 4317 | 0.9998 |

It follows from the table that Mod-Hum samples most effectively sorb Cu (II) and Co (II) ions. The value $K_d$ increases indicating the increase in affinity of the sorbents for metal ions. The value $b$ is used to estimate the strength of the bond between the adsorbent and the adsorbate. Consequently, under the conditions of solution of the Langmuir isotherm equation, sorption of metal ions increases with the increase in pH of the medium. Correspondingly, the maximum sorption capacity $q_m$ increases.

### Conclusions

The investigations showed that modified humate having an amine functionality can be used as a sorbent for the purification of water from heavy metal ions. Evaluation the adsorption degree's dependency to pH showed that modified humate possesses the best sorption properties in regard to Cu (II) and Co (II) ions at higher values of pH. The maximum sorption degree of copper is equal to 99.2% and that of cobalt to 90%. It is stated that the sorption degree increases with an increase in time from 15 min

to 2 h. It is also shown that the sorbent develops a high sorption capacity in regard to ions of Cu (18.42 mg/g) and Co (16.25 mg/g). The process of adsorption can be adequately described by the Langmuir equation.

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