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Complexation ability of modified Na-Humate and its application in removal of toxic metals from water

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ABSTRACT

Efficiency of an amine modified Na-Humate (Na-Hum), which was isolated from coal mine in Karaganda/Kazakhstan, was explored as a sorbent for removal of toxic metal ions from water. Na-Hum was immobilized with ethylene diamine to get a suitable adsorbent called modified humate (Mod-Hum). Pseudo-first-order and pseudo-second-order kinetic models gave the best correlation at the suitable pH. The experimental results were calculated according to the related adsorption formulas, which were then depicted in tables and graphics. The amount of toxic metal ions remained in the solution after treating with Mod-Hum was measured by atomic absorption spectroscopy. The process parameters such as mixing time, temperature, and pH during the adsorption were investigated to find optimum sorption capacity. The results after adsorption were compared to determine the differences between natural (Na-Hum) and the modified matter (Mod-Hum). The complexation ability of compounds by exchange of Na-Hum and Mod-Hum with several metal ions such as $Cu(CH_3COO)_2{\cdot}H_2O$, $Co(CH_3COO)_2{\cdot}4H_2O$, $Ni(CH_3COO)_2{\cdot}4H_2O$, and $Cd(CH_3COO)_2{\cdot}2H_2O$ was also investigated. All obtained compounds were characterized by several techniques such as FTIR, TGA/DTA, and SEM-EDAX, elemental analysis and XRD. The adsorption studies with both Na-Hum and Mod-Hum clearly demonstrated that Na-Humate treated with amine is a more efficient adsorbent than the natural form. In addition, Mod-Hum fitted better with pseudo-first-order model and removed water contaminants such as Cu, Co, Ni, and Cd more effectively, which was attributed to higher reactivity of N and O donor sites of the adsorbent toward toxic metals.

Keywords: Na-Humate; Adsorption; Complexation; Modification

1. Introduction

Humic acid is a well-known substance, which contains many carboxylic and phenolic groups [1]. Thus, it can be an appropriate substrate to bind metal atoms with its aliphatic and aromatic moieties, making it more surface active and hydrophobic.

Humic substance, which is mostly known as humic acid, is a heterogeneous aggregate consisting of the biodegradation of dead organic matters such as

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organic carbon in soil, sediments, and water. It contains a large number of functional groups such as phenolic and carboxylic derivatives. Humic substance is one of the most preferred materials due to the enclosing mineral particles to produce aggregates for considerable adsorption or complexation, which are also called as chemically and physically organic heterogeneous complexants because of their polyfunctional nature and conformational features [2,3].

Significant aspects of humic substances are their various affinities for heavy metal cations. The adsorption mechanism occurs by the deprotonation of functional groups such as as carboxylic and phenolic groups. Humic acid becomes negatively charged in weakly acidic and basic conditions, which enhances adsorption of cations through electrostatic interactions. The complexation of toxic metals with humic substances can be increased by making modifications onto the humic functionalization [4–7].

The humic substances are employed for removal of heavy metals because of their acid–base properties in a wide range of pKa values. They are also preferred due to their ability to mix with cross-linked polymers possessing various molecular weights and having a charge density enabling them to gain high affinities for both organic and inorganic surfaces. Furthermore, they are the representatives of environmental chemical systems which exhibit experimental and conceptual challenge to environmental chemist researchers [8–11].

Environmental protection studies, especially for water sources against harmful and toxic contaminants, are the most significant research interests under current conditions in human life [12]. Heavy metal compounds which we usually encounter in industrial life generally cause pollution of water and soil. This kind of wastewater emerges due to the nonferrous metals, mechanical engineering, galvanic, radio technical industries, etc., which are known as most widespread substances [1,4,6,13]. However, these contaminants may cause to poisons of cumulative, additive, cancerogenic, and mutagenic activity. Therefore, drainage waters containing heavy metals must be processed with fine purification.

Enormous number of analyzed or proven methods has been applied for drainage water purification in the last decade. Water purification from heavy metal ions by sorption processes using humic substances will be rather up-and-coming method of the above.

Na-Hum and its amine modified composition (Mod-Hum) have shown different sorption properties. Adsorption of heavy metals from water was achieved with expected results. Thus, natural sorbents together with the upgrading technologies have been attracted increasing demand for natural sources due to their effective and cheaper water purification from heavy metals ions. In this context, the complexation ability of humic substances was investigated by suitable methods. The obtained compounds were characterized with various techniques instrumentally. The data also supported the metal–adsorbent interactions via binding of metals to the donor sites to form an inorganic complex [14–17].

2. Experimental

2.1. Materials and methods

2.1.1. Materials

All chemicals and solvents were supplied from Merck or Fluka Chemical Corporations. The required purification and disinfection were performed routinely in laboratory conditions.

2.1.2. Instrumentation

The stock solutions of Cu, Ni, Cd, and Co acetate salts for adsorption experiments were prepared and employed in a flame atomic absorption spectrophotometer whose model is Perkin Elmer Analyst 400. The samples were centrifuged to precipitate the retained solid particles to get exact solution after adsorption. The pH values were set with a Hanna pH 211. The surface images were collected with a scanning electron microscope (SEM) (model QUANTA 250 FEG) which also works as EDAX apparatus simultaneously. The local elemental analysis of compounds was proved by mapping process of EDAX. The stretching and bending vibrations were analyzed with a Fourier transform infrared spectrophotometer FTIR (model; Perkin Elmer Spectrum 100) in the spectral region of 225–4,000 cm^{-1}. X-ray powder diffraction analysis was conducted by an X-ray powder diffractometer Bruker, D8 Discovery using Cu Kα radiation at 40 kV and 40 mA. Elemental analysis of carbon, hydrogen, and nitrogen was carried out on a Costech Combustion System CHNS-O instrument. Thermo gravimetric measurements were obtained with a Shimadzu DTG-60 thermo gravimeter.

2.1.3. Isolation of humic substances

Humic substances were obtained from brown coal of Shubarkul coal mine in Karaganda, Kazakhstan. Samples of pulverized coal can pass through a sieve of 0.25 mm. The process of extracting humic substances from the coal was performed in 2% NaOH (1:8 wt/vol.) for 1 h at 25˚C with vigorous stirring. The suspension was centrifuged and the filtrate obtained as sodium humate (Na-Hum) was dried in a vacuum oven at 105˚C.

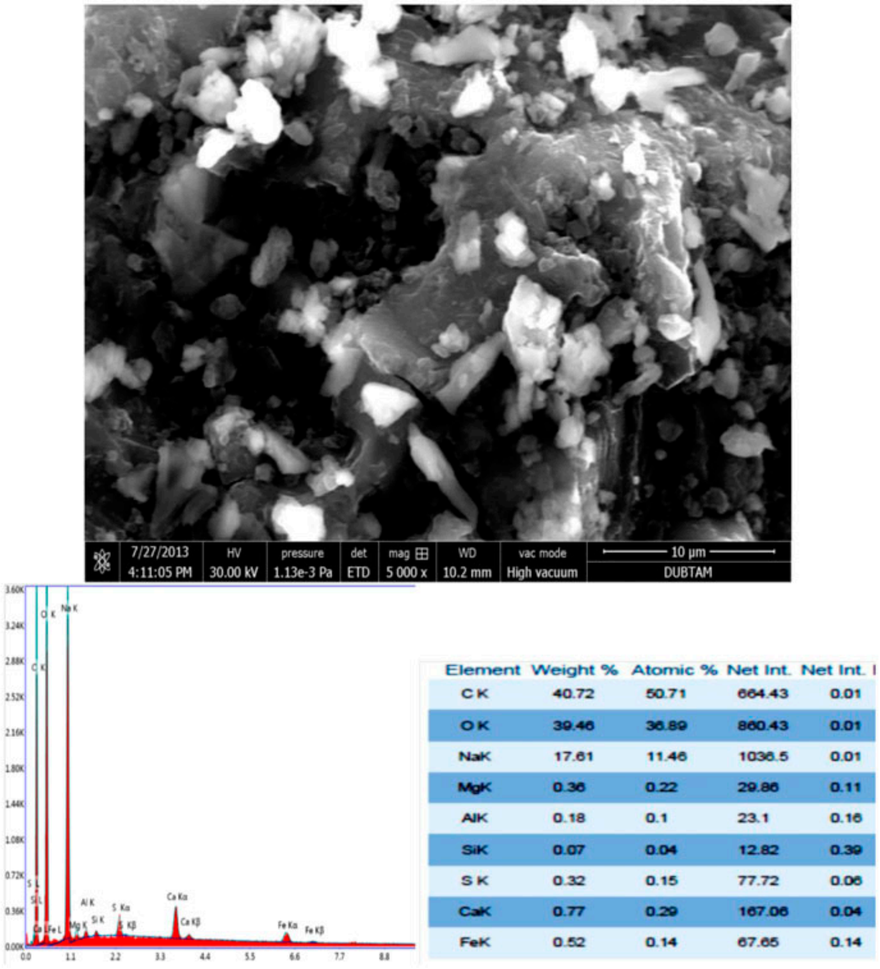
Eighty percent of organic matter in humic substance can be extracted from the soil with the aid of NaOH as extractant. This method is widely used for the recovering the organic structures in humic acid. Removing calcium and the other polyvalent cations facilitates extraction of organic matter with alkaline reagents. On the other hand, there are also some disadvantages of extraction with alkali solutions since they cause dissolving of protoplasmic and structural components from fresh organic tissues. Also, different chemical alterations can occur in alkaline solution. But even with these handicaps, Na-Hum as an extracting humic substance is a universally applicable process due to lack of inorganic contaminants such as clay and polyvalent cations.

2.1.4. Preparation of amine modified ethylenediamine humate composite

The stock solution of 1,000 μmol L^{-1} was prepared by dissolving 1.675 g humate sodium in 1 L of distilled water [7]. Five hundred milliliter of sodium humate solution was poured into a 1,000-mL two-necked reaction flask. The pH value of 3 g ethylene diamine was adjusted to 2 using 37% HCl to provide the cation exchange with Na^+. Then, this solution was added to the reaction flask and kept it stirring with a magnetic stirrer at 30˚C for 2 d. The precipitate was filtered, washed with distilled water, and dried at 60˚C for 24 h.

2.1.5. Synthesis of complexes

Transition metal complexes were prepared by ion exchange of sodium humate metal (Na-Hum) ions with $Cu(CH_3COO)_2{\cdot}H_2O$, $Co(CH_3COO)_2{\cdot}4H_2O$,



Element	Weight %	Atomic %	Net Int.	Net Int.
C K	40.72	50.71	664.43	0.01
O K	39.46	36.89	860.43	0.01
NaK	17.61	11.46	1036.5	0.01
MgK	0.36	0.22	29.86	0.11
AlK	0.18	0.1	23.1	0.16
SiK	0.07	0.04	12.82	0.39
S K	0.32	0.15	77.72	0.06
CaK	0.77	0.29	167.06	0.04
FeK	0.52	0.14	67.65	0.14

Fig. 1. The SEM image and EDAX results of Na-Humate.

$Ni(CH_3COO)_2{\cdot}4H_2O$, or Cd $(CH_3COO)_2{\cdot}2H_2O$. 0.25 g of sodium humate was dissolved in 25 mL of ethanol:water (1:1) solution for 15 min. Then, the metal salts of approximately 1 g in 40 mL ethanol were prepared and added dropwise for 30 min. The solution was refluxed for 24 h at 130˚C [14,18–20]. After the reaction completed, the precipitate was filtered off, washed with ethanol, and dried at 60˚C for 6 h. The complexes were first characterized by FTIR spectroscopy, and the expected stretching peaks were obtained. Further characterization was carried out later.

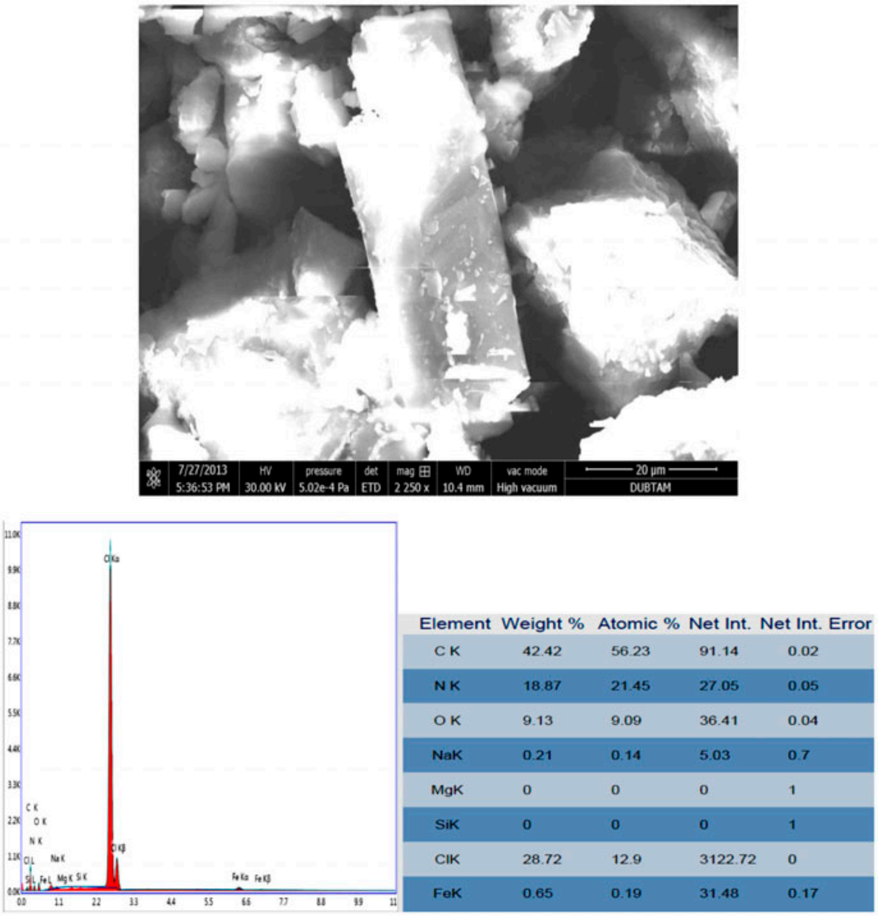
2.1.6. Adsorption process

The efficiency adsorption of Na-Hum and Mod-Hum was explored with each heavy metal ions about 50 mg L^{-1} which correspond to 50 ppm. The adsorbent and the standard metal solutions were poured into Erlenmeyer flasks to shake them in a water bath under various conditions. Experiments were conducted at room temperature adjusting pH values to 2, 4, 5, 6, and 8. The exact adjustment was also carried out with 0.1 M HCl/0.1NM NaOH when the desired value of pH was unstable. The solutions were stirred at 30˚C for various time scales ranging from 15 to 120 min [9]. The contents of the Erlenmeyer flasks were centrifuged to precipitate the adsorbent for 30 min at 6,000 rpm, and the stagnant solution was collected to analyze with atomic absorption spectroscopy.

2.1.7. Removal efficiency (%R) and pH effect

The percent removal of toxic metals from water was calculated as a function of time at different pHs. Eq. (1) was used for the expression of curve.

$$\%\ R = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$



Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	42.42	56.23	91.14	0.02
N K	18.87	21.45	27.05	0.05
O K	9.13	9.09	36.41	0.04
NaK	0.21	0.14	5.03	0.7
MgK	0	0	0	1
SiK	0	0	0	1
ClK	28.72	12.9	3122.72	0
FeK	0.65	0.19	31.48	0.17

Fig. 2. The SEM image and EDAX results of Mod-Humate.

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where C_0 is the initial concentration and C_e is the equilibrium concentration of metal ions (mg L^{-1}); V is the volume of the solution (L) and m is the mass of adsorbent (g).

3. Results and discussion

3.1. Characterization of Na-Hum and Mod-Hum

The natural and modified substances were characterized by different techniques such as SEM-EDAX, FTIR, TGA, and X-ray diffraction (XRD).

3.1.1. SEM-EDAX analysis

The surface morphology of the modified and natural form of humic compounds was obtained to see the distinguishable aspects. The images have no significant differences as expected. Nevertheless, the particle size was seen rather larger in Mod-Hum with a magnification of 2,250 even Na-Hum was examined at 5,000 magnification [21]. The EDAX apparatus that can work simultaneously to SEM, which combines elemental and structural analysis of compounds with mapping techniques, gives us the elemental mapping and percentage of the substances. The existence of nitrogen in Mod-Hum proved the binding of ethylene diamine to Na-Humate compound (Figs. 1 and 2). So, the results support the modification onto the Na-Humate allowing it to coordinate to and thus

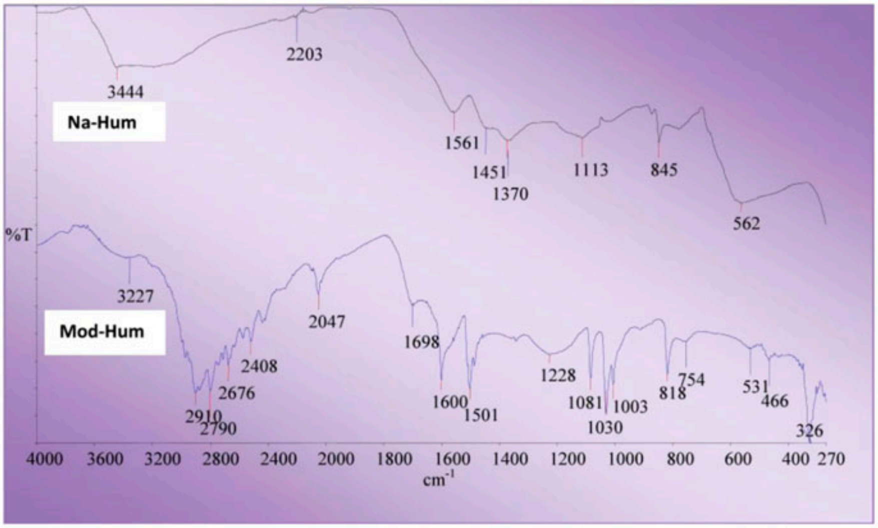


Fig. 3. FTIR spectra of Na-Hum and Mod-Hum.

Table 1
Elemental composition of Na-Hum and Mod-Hum complexes

	Elemental analysis				Atomic ratios		
Name	C [%]	H [%]	N [%]	O [%]	H/C	N/C	O/C
Na-Hum	53.90	9.56	1.02	35.52	0.177	0.018	0.658
Mod-Hum	70.42	18.89	10.22	0.47	0.268	0.145	0.006
Na-Hum Cu(II)	42.68	21.93	0.62	34.77	0.51	0.014	0.814
Na-Hum Co(II)	43.36	23.14	0.82	32.68	0.533	0.018	0.753
Na-Hum Ni(II)	48.28	18.68	1.00	32.04	0.386	0.020	0.663
Na-Hum Cd(II)	33.51	14.85	0.90	50.74	0.443	0.026	1.514
Mod-Hum Cu(II)	49.77	3.20	5.38	41.65	0.064	0.108	0.836
Mod-Hum Co(II)	36.31	3.49	6.72	46.52	0.096	0.185	1.281
Mod-Hum Ni(II)	43.05	3.87	5.16	47.92	0.089	0.119	1.113
Mod-Hum Cd(II)	51.89	2.89	5.16	40.06	0.055	0.099	0.772

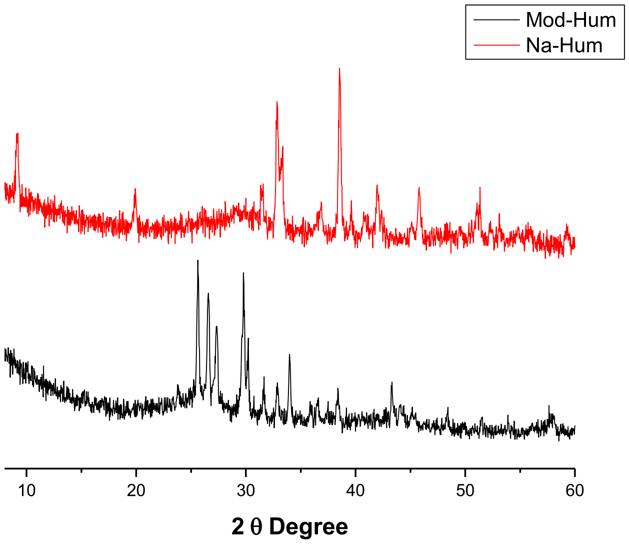


Fig. 4. X-ray powder diffraction patterns of Na-Hum and Mod-Hum.

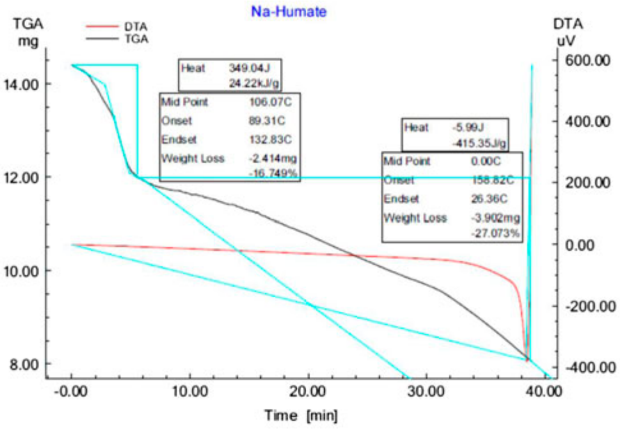


Fig. 5. TGA/DTA of Na-Hum.

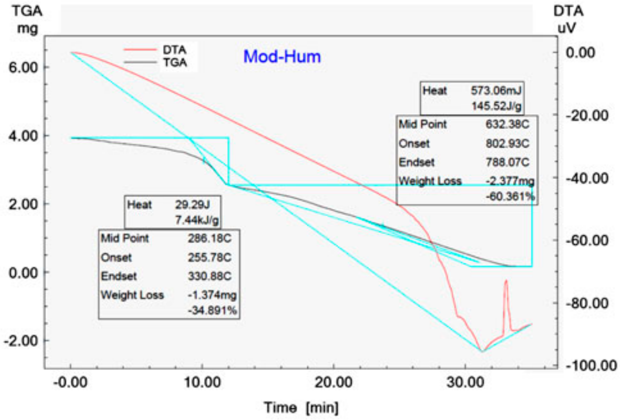


Fig. 6. TGA/DTA of Mod-Hum.

adsorb the heavy metals [22,23]. Investigation also enables us to determine percentage of nitrogen coming from the aliphatic amine source. This was compared with the used amount (as a gram) of Mod-Hum and then calculated in terms of whole weight.

3.1.2. FTIR analysis

IR spectrum was recorded in the range of 225–4,000 cm^{-1} for extracted humic acid called as Na-Hum. The present work shows significant peaks corresponding to the phenyl, hydroxyl, carboxyl, and the other substituents present on the compounds **(**Fig. 3**)**. The broad peak at 3,455 cm^{-1} can be attributed to the hydroxyl groups, and the peak at 3,050–3,090 cm^{-1} which is overlapped by broad OH vibrations may be assigned to the aromatic structure of the humic compounds. It is clearly seen that the new peaks appear in the spectrum of modified humate.

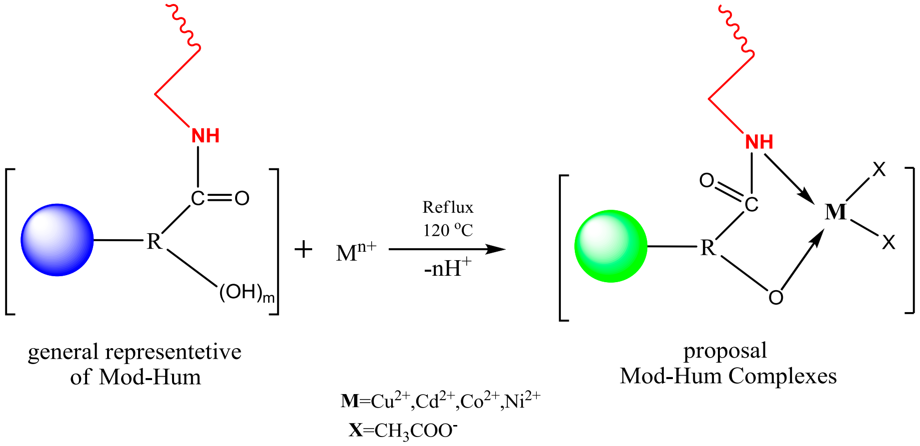


Fig. 7. The general description of synthesis of Mod-Hum complexes.

Furthermore, the aliphatic group from the amine structure can be seen at 2,910 cm^{-1}. The most considerable stretching peaks at 1,030 and 1,600 cm^{-1} are due to C–N stretching and N–H bonding, respectively, confirming the binding of ethylene diamine to Na-Hum compound. The new peak at 1,698 cm^{-1} in the spectrum can be assigned to C=O (amide) stretching vibration [7].

3.1.3. Elemental analysis

The elemental compositions of all compounds before and after modification were analyzed and the results were compared and listed in Table 1. As expected, percent of nitrogen in Mod-Hum is more than that of in natural one.

3.1.4. XRD experiment

XRD operation was utilized for the identification of diffraction patterns, crystalline, and amorphous features of the compounds to show the differences between natural and modified humate.

An X-ray powder diffractometer (Bruker, D8 Discovery EVA, Germany) was employed to collect XRD patterns using Cu Kα radiation at 40 kV and 40 mA in the range 8–60° (2θ) with an increment of 0.031 scan speed. Na-Hum and Mod-Hum were measured by the XRD and their crystallinity was found to be 68.6 and 63.0%, while the percentages of amorphness were 31.4 and 37.0%, respectively, revealing the rearrangement of structure after modification. Furthermore, as shown clearly in Fig. 4, the new peaks also support the structure of Mod-Hum [14,15,24–27].

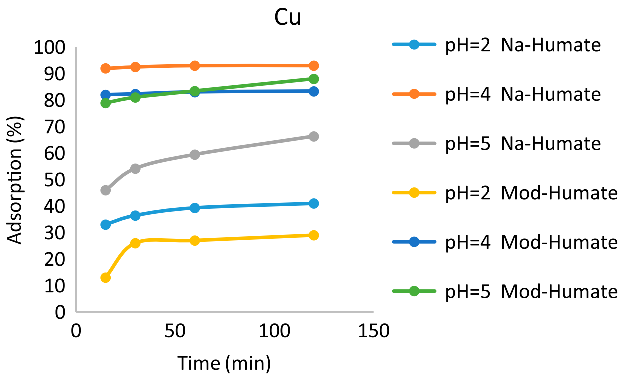


Fig. 8. Cu adsorption percentages of Na-Humate and Mod-Humate as a function of time at different pH values.

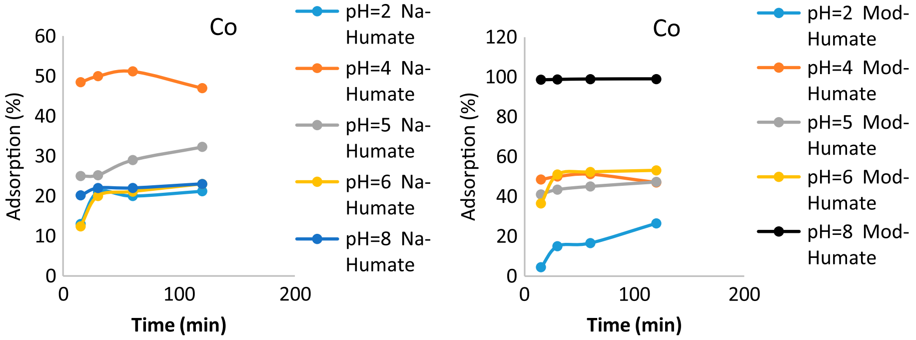


Fig. 9. Co adsorption percentages of Na-Humate and Mod-Humate as a function of time at different pH values.

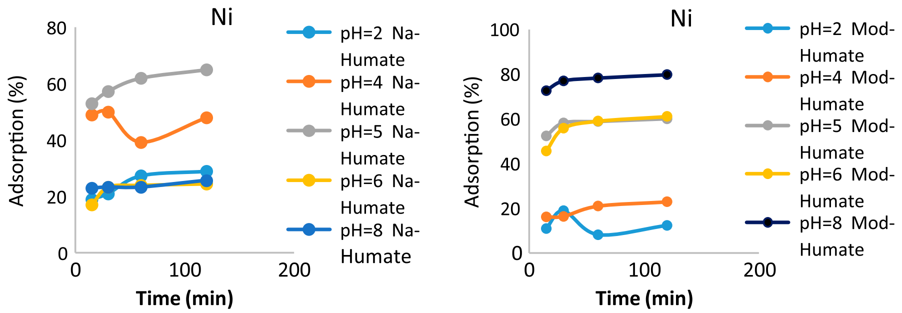


Fig. 10. Ni adsorption percentages of Na-Humate and Mod-Humate as a function of time at different pH values.

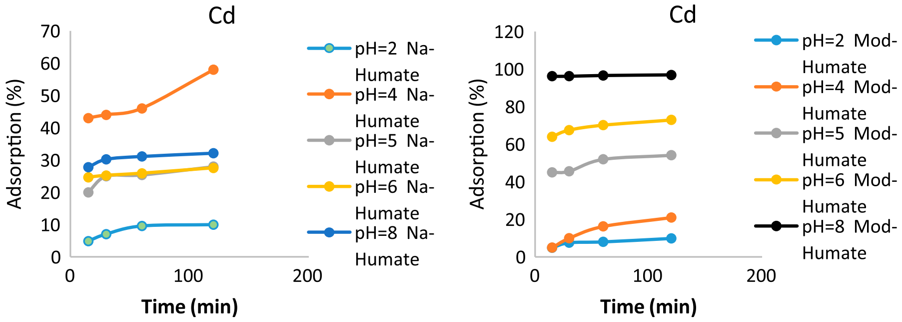


Fig. 11. Cd adsorption percentages of Na-Humate and Mod-Humate as a function of time at different pH values.

Table 2
Kinetic parameters of Na-Hum for adsorption of Cu(II), Ni(II), Cd(II), and Co(II) ions at different pHs

			First-order kinetic model			Second-order kinetic model		
Adsorbate	T (K)	pH	$q_{e,cal}$ (mg g^{-1})	$k_{ads,1}$ (1 min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	$k_{ads,2}$ (g(mg min)$^{-1}$)	R^2
Na-Hum Cu(II)	303	4	2.45	0.0396	0.9573	19.49	0.675	0.9999
Na-Hum Ni(II)	303	5	4.46	0.028	0.9998	17.95	0.0065	0.9963
Na-Hum Cd(II)	303	6	8.22	0.012	0.9957	24.75	0.0039	0.8793
Na-Hum Co(II)	303	4	3.32	0.022	0.9220	12.33	0.0355	0.9966

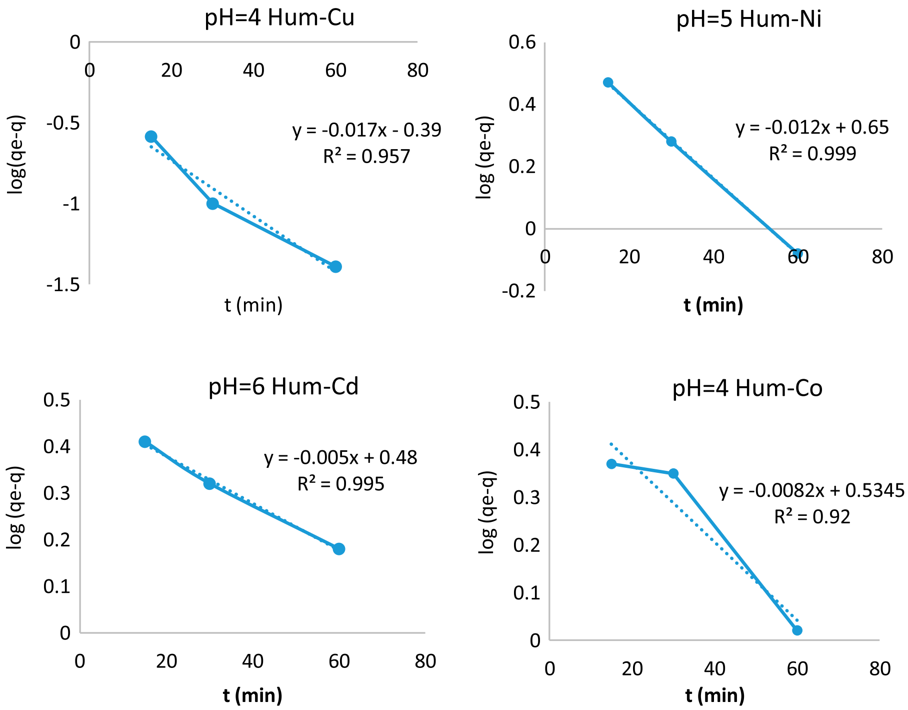


Fig. 12. Pseudo-first-order kinetic model of Na-Hum.

Table 3
Kinetic parameters of Mod-Hum for adsorption of Cu(II), Ni(II), Cd(II), and Co(II) ions at different pHs

			First-order kinetic model			Second-order kinetic model		
Adsorbate	T(K)	pH	$q_{e,cal}$ (mg g^{-1})	$k_{ads,1}$ (1 min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	$k_{ads,2}$ (g(mg min)$^{-1}$)	R^2
Mod-Hum Cu(II)	303	5	2.67	0.016	0.9997	21.09	0.0165	0.9995
Mod-Hum Ni(II)	303	6	6.45	0.043	0.9451	16.9	0.0116	0.9998
Mod-Hum Cd(II)	303	6	7.58	0.025	0.9877	44.64	0.0076	0.9998
Mod-Hum Co(II)	303	5	2.62	0.022	0.9697	14.62	0.0194	0.9997

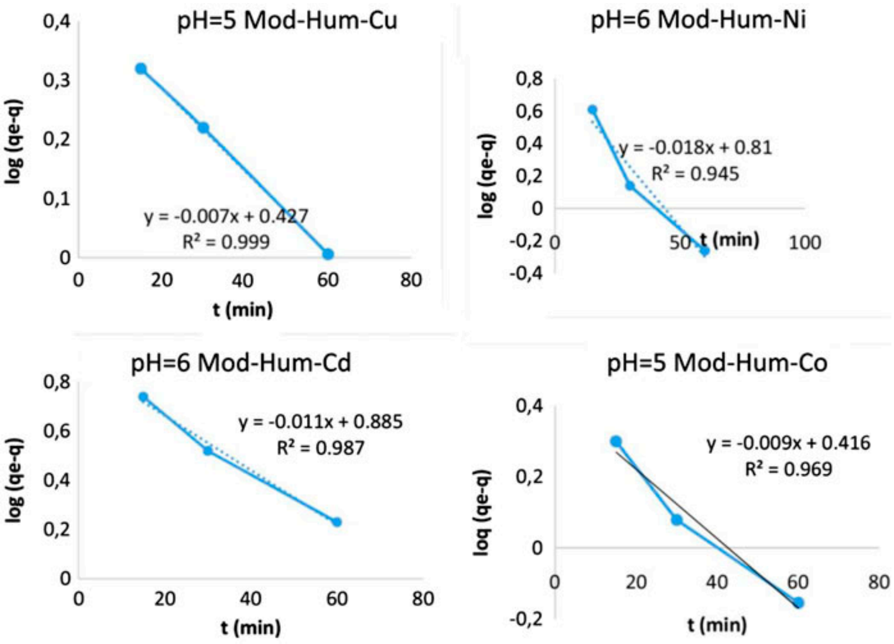


Fig. 13. Pseudo-first-order kinetic model of Mod-Hum.

Table 4
Important FTIR bands of Mod-Hum complexes

Compounds	ν(Ar–C=C)	ν(Alip-C–C)	ν(OH)	ν(COOH)	ν(M–N)	ν(M–O)
Mod-Hum Cu	3,075	2,940	3,239	1,564–1,370	526	431
Mod-Hum Cd	3,025	2,920	3,200	1,703–1,550	–	383
Mod-Hum Co	3,000–3,070	2,918	3,000–3,300	1,341–1,213	543	442–353
Mod-Hum Ni	3,074	2,910–2,980	3,200–3,400	1,703–1,532	608	363

3.1.5. Thermal Analysis

The stability of compounds at high temperatures was analyzed. The weight loss and heat were calculated with TA60 software. A weight loss of about 16.74% in the thermogram showed an endothermic behavior for the first step in the range of 25–770°C, while the loss of 27.07% in the second step was exothermic (Fig. 5).

For Mod-Hum, the weight loss is slightly more in the first curve at a higher temperature, which may be due to the structure of modified adsorbent bearing more organic groups, which make it to be rigid that can stay stable till higher temperatures. A loss of about 34.8% was obtained in the first step and 60.3% in the second step. The sudden weight loss and the quick exothermic peak can be attributed to the burning of organic groups (Fig. 6). The peaks corresponding to the weight loss are shown in Fig. 6 [3,15,28–31].

3.2. Sorption experiments

3.2.1. Removal efficiency (%R) and pH effect

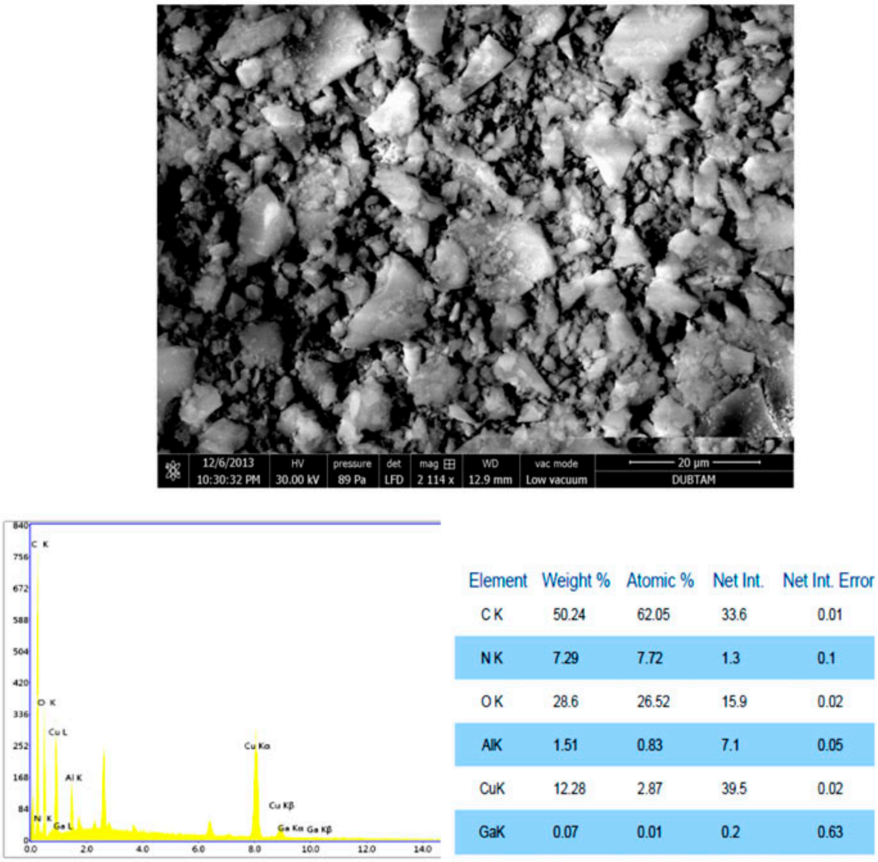
The proposed adsorption mechanism is shown in Fig. 7. The functional groups of humate and modified humate such as hydroxyl, carboxylate anions, and amines or amides are expected to bind metal atoms. Fig. 7 describes the coordinate covalent bond of N, O typed donor atoms on the modified humate substance to the heavy metals. The functional groups introduced by modification affects the adsorption. There is a correlation between the functional groups and adsorption of toxic metals, which also explains the metal affinities of the Mod-Hum for purification of the wastewater contaminant.

The adsorption of desired heavy metals by organic or inorganic materials usually depends on pH, which controls the sorption at water–adsorbent interfaces [7]. As it was with Na-Hum metal sorption, the sorption amount of Cu(II), Co(II), Ni(II), and Cd(II) increased at lower pHs (about 4–5). The best uptake happened due to the cation exchange with counter ions on the adsorbent surface. The protonated surfaces in the lower pH ranges could accelerate cation exchange between Na^+ and M^{n+} [32].

On the other hand, sorption of Mod-Hum was found rather good at higher pHs such as 8, which may be due to the basic effect of surface caused by the OH^- deprotonation from the amine-modified groups. The electrostatic repulsion in more concentrated media (pH 2–4) may prevent the metal binding to the amine-modified surfaces [5–7]. These results are displayed in Figs. 8–11.

Mod-Hum adsorbs Cu highest only at pH 5, which shows that the metal affinity of adsorbents depends on pH. On the other hand, Cu was adsorbed higher by Na-Hum than the modified one at pH 2 (Fig. 8).

Removal of Co from the solution by Mod-Hum reached a maximum at pH 8, while Na-Hum removed only small percentages of Co about 20 to 30%. Both of the adsorbents are reluctant to complexation with metals at lower pHs (Fig. 9).



Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	50.24	62.05	33.6	0.01
N K	7.29	7.72	1.3	0.1
O K	28.6	26.52	15.9	0.02
AlK	1.51	0.83	7.1	0.05
CuK	12.28	2.87	39.5	0.02
GaK	0.07	0.01	0.2	0.63

Fig. 14. The SEM image and EDAX results of Mod-Humate Cu(II) complex.

Ni bound nearly 80–90% to donor sites of Mod-Hum at pH 8. As seen in Fig. 10, the adsorption increases as pH increases.

Cd is also one of the best adsorbed heavy metals at pH 8. Efficiency of Mod-Hum for removal of the metal is obvious. Also, the adsorption of Cd reaches equilibrium in a shorter time. This aspect of the adsorbent provides good advantages for removal (Fig. 11).

3.2.2. Sorption kinetics

The kinetic models called as pseudo-first-order, pseudo-second-order, Bangham intra-particle diffusion are generally used to determine the amount of the adsorption, two of which were used for investigation of the adsorption kinetics of Na-Hum and Mod-Hum.

First, the kinetic data were fitted using pseudo-first-order models, whose linear form is given as:

$$\log(q_{\mathrm{e}} - q_t) = \log q_e - \frac{k_{\mathrm{ads},1}}{2.303} t \quad (3)$$

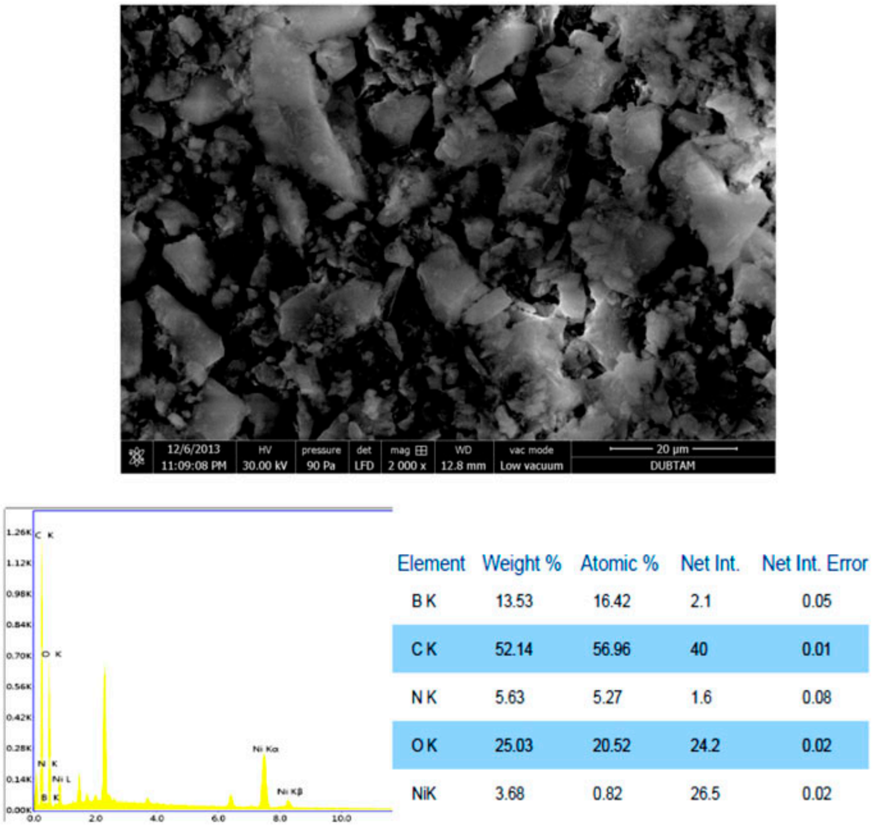
where q_{e} (mg g^{-1}) is the amount of adsorbed heavy metals by adsorbent at equilibrium, q_{t} (mg g^{-1}) is the amount of adsorbate adsorbed at time t, and $K_{\mathrm{ads},1}$ (min^{-1}) is the rate constant of pseudo-first-order adsorption.

The pseudo-second-order rate model was also applied:

$$\frac{t}{q_t} = \frac{1}{k_{\mathrm{ads},2q_{\mathrm{e}_2}}} + \frac{1}{q_{\mathrm{e}}} \quad (4)$$

where $k_{\mathrm{ads},2}$ (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order adsorption.

Kinetic parameters with correlation coefficients of the kinetic models for the Na-Hum are shown in Table 2, which also summarizes the ideal pHs for each Na-Hum adsorption of metals. Generally, a pH between 4 and 6 is the best adsorption condition for these types of experiments. The calculated correlation coefficients of pseudo-second-order rate model were also found better than those of second-order-kinetic model (Fig. 12) [32,33].



Element	Weight %	Atomic %	Net Int.	Net Int. Error
B K	13.53	16.42	2.1	0.05
C K	52.14	56.96	40	0.01
N K	5.63	5.27	1.6	0.08
O K	25.03	20.52	24.2	0.02
NiK	3.68	0.82	26.5	0.02

Fig. 15. The SEM image and EDAX results of Mod-Humate Ni(II) complex.

Mod-Hum was also studied using parameters of the kinetic models, and it was found that sorption fitted better to pseudo-first-order model. Both the k_{ads} and R^2 have reasonable values (Table 3, and Fig. 13) [31,34,35]. Although the correlation coefficients are higher in pseudo-second-order-kinetic model, the amounts of adsorption are considerably lower. That is, adsorption constants are also larger in the pseudo-first-order kinetic model (Table 3).

3.3. Characterization of Mod-Hum complexes

Transition metal complexes of the modified humate were characterized by several instrumental techniques as follows:

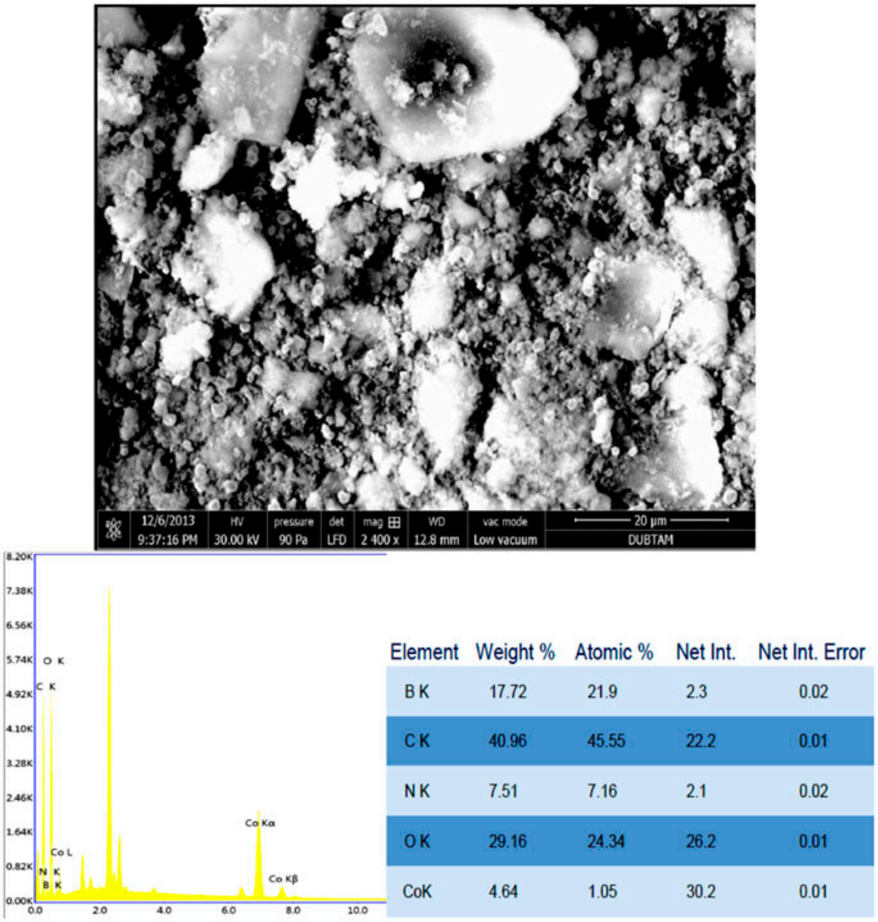
3.3.1. FTIR analysis of Mod-Hum complexes

IR spectra of Na-Hum and Mod-Hum were discussed before (Section 3.1.2). Existence of specific bands of such metal–oxygen (M–O) and metal–nitrogen (M–N) bindings confirms coordination of Cu(II), Co(II), Ni(II), and Cd(II) to Na-Hum. The proposed coordination mechanism is depicted in Fig. 7.

The shift in peak values also supports formation of the obtained structure compared to those of Na-Hum [27]. Several important peaks are given in Table 4.

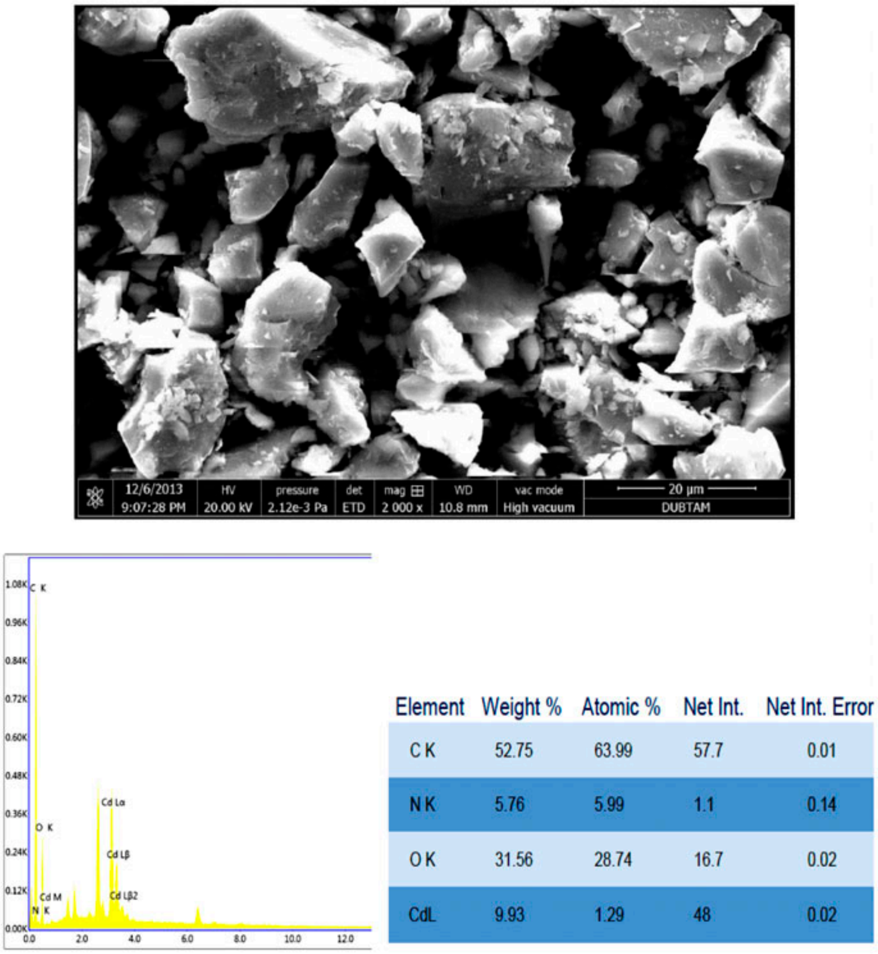
3.3.2. SEM-EDAX analysis of Mod-Hum complexes

The SEM images and the EDAX results of the modified humate complexes are shown in Figs. 14–17 for Cu(II), Ni(II), Co(II), and Cd(II), respectively. SEM images were obtained just about 2,000 magnification under low vacuum. EDAX experiments introduce the local elemental analysis with mapping technique by X-ray dispersion. The difference in particle sizes and surface of compounds indicate formation of the anticipated structure compared to the unmodified form which has larger particle size. Percentages of



Element	Weight %	Atomic %	Net Int.	Net Int. Error
B K	17.72	21.9	2.3	0.02
C K	40.96	45.55	22.2	0.01
N K	7.51	7.16	2.1	0.02
O K	29.16	24.34	26.2	0.01
CoK	4.64	1.05	30.2	0.01

Fig. 16. The SEM image and EDAX results of Mod-Humate Co(II) complex.



Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	52.75	63.99	57.7	0.01
N K	5.76	5.99	1.1	0.14
O K	31.56	28.74	16.7	0.02
CdL	9.93	1.29	48	0.02

Fig. 17. The SEM image and EDAX results of Mod-Humate Cd(II) complex.

metal for Mod-Hum complexes were obtained as 12.28, 3.68, 4.64, and 9.93% for Cu(II), Ni(II), Co(II), and Cd(II), respectively.

4. Conclusion

Competition for complexation and removal of several heavy metals (Cu(II), Co(II), Ni(II), and Cd(II)) was studied by Na-Hum and Mod-Hum adsorbents, which was extracted from a coal mine in Karaganda/Kazakhstan. The adsorption efficiency of Na-Hum and Mod-Hum was investigated with these heavy metal ions at room temperature at different pH values such as 2, 4, 5, 6, and 8. It was found that metal sorption of Na-Hum increased at lower pHs such as 4 and 5.

Amount of adsorption for each metal ion was calculated and depicted in Figs. 8–10. The best sorption of metal was obtained at lower pHs. However, sorption of Mod-Hum was good at higher pH such as 8, which may be attributed to the basic effect of surface caused by the OH^- deprotonation from the amine-modified groups. The kinetic models were also applied to natural and modified humic substance whose sorption fitted better to pseudo-first-order model.

Adsorption experiments with both Na-Hum and Mod-Hum revealed that the modification of the natural humate is quite favorable for removal of the heavy metals. Kinetic data of Mod-Hum were applied to pseudo-first-order model and pseudo-second-order model and fitted best to pseudo-first-order model to clarify adsorption of heavy metals from water contaminants. Moreover, the percent removal increased after the modification of Na-Hum with amine.

Furthermore, several transition metal complexes were prepared by different techniques such as FTIR, SEM-EDAX, XRD, and TGA/DTA. In conclusion, one can say that Mod-Hum removes the heavy metals from the ecological environment by binding them.

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