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SORPTION CHARACTERISTICS OF TRANSITION METAL IONS (Co, Ni) ON SODIUM HUMATE SORBENTS

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ABSTRACT

The main objective of this work was to study the possibility of using sodium humate as a sorbent for water purification of water from heavy metal ions (Co & Ni). Studied was complexing and sorption properties of sodium humate. Metal-humate complexes were also obtained by ion-exchange procedure with sodium humate by employing the metal salts such $Co(CH_3COO)_2{\cdot}4H_2O$, $NiSO_4{\cdot}6H_2O$. Maximum sorption percentages of humate achieved for 5 ppm 91.5%, 50 ppm 90.4%, 500 ppm 68.6% for Co(II) and 90% of 5 ppm, for 50 ppm 93.25%, 500 ppm 87.43% for Ni (II). Humate and metal ion interaction was investigated with special emphasis on the effects of pH, metal ions concentration and humate concentration. It has been found that the interaction of humate with metal ions in solution decreases with increases metal ion concentration and also increases with increases humate concentration. The pH experiment was investigated in the range for cobalt sorption was performed at a constant pH of 4, pH of the nickel ratio of 5, metal concentration was selected (5 mg/L, 50 mg/L, 500 mg/L), the sorbent was determined with the amount of 0.05 g, 0.1 g, 0.25 g, 0.5 g, 1 g, and 2 g. It is stated that sorption degree increases from 15 minutes to 2 hrs. The adsorption of toxic metal ions with sodium humate was measured by atomic absorption spectroscopy (AAS). All the obtained complex compounds were analyzed and characterized by FT infrared spectroscopy (FTIR), scanning electron microscopy (SEM).

Key words: Sorption, Transition metal ions, Sodium humate.

INTRODUCTION

Humic substances are a group of complex, high molecular weight compounds containing aromatic structures and related functional groups (carboxyl, phenolic, amide, carbonyl, quinone)[1]. The presence of these groups provides the ability of humic substances are capable to form complex compounds with some metal cations. There are numerous

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*Author for correspondence; E-mail: aliya_00188@mail.ru methods of cleaning pollutants from aqueous media, but effective method is sorption method with the use of natural sorbents such as humic substances. Humic substances act as natural detoxifiers. Binding of metals leads to decrease of concentration of the free form and to decrease toxicity. In this regard, a study of the sorption properties of humic substances with heavy metals is great interest[2].

It has been investigated that the sodium humate showed distinguished properties for the goal of our research. The purpose of adsorption of heavy metals from water was achieved in expected results. Thus, natural sorbents as well as upgrading of existing technologies by way of sorption processes prove capable of providing increase of the effect of natural and industrial waters purification from heavy metals ions is of great current interest. By the way, the complexation ability of humic substances was evaluated and the obtained compounds were enlightened with detailed instrumentation techniques. The data also supported the metal-adsorbent interactions via binding metals to donor sites to make an inorganic complex[3].

EXPERIMENTAL

Reagent and materials

Humic acid was obtained from brown coal of Shubarkul coal mine in Karaganda, Kazakhstan. The extraction process of humic acids from coal was carried out with 2% NaOH (1:8 m/v) during 1 hr at 25°C with intensive mixing. The suspension was centrifuged and the filtrate that was obtained as sodium humate dried in a vacuum oven at 105°C. Chemically pure of metals salts (Co, Ni) were purchased from Merck and Fluka Chemical Corporations (Diyarbakir, Turkey).

Measurements

Determination of cobalt (II), nickel (II) was carried out on atomic-absorption spectrophotometer (ICE 3000 Series). 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. The stretching and bending vibrations were analyzed with Fourier transform infrared spectrophotometer FTIR (Model; Perkin-Elmer Spectrum 100) in the spectral region of 225-4000 cm^{-1}.

Synthesis of complexes

Metal-humate complexes were obtained by ion exchange of sodium humate with metal ions $Co(CH_3COO)_2 \cdot 4H_2O$, $NiSO_4 \cdot 6H_2O$. 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 humate solution. The reaction mixture was heated to 100°C and mixed during 12 hrs. After the reaction was completed the precipitate was filtered, washed with water and dried at 60°C during 6 hrs[4]. Dry complexes were analyzed with the help of FTIR and SEM.

Sorption processes

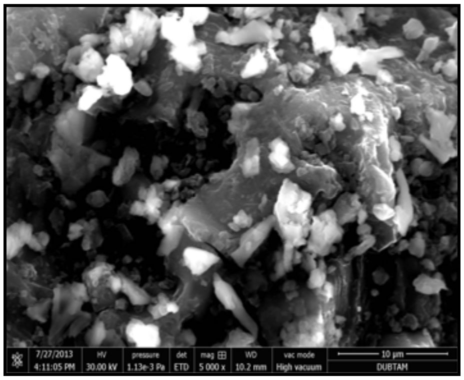
The sorbent in the amount of (0.05 g, 0.1 g, 0.25 g, 0.5 g, 1 g, and 2 g) was added to the pre-assigned volume of the metal salt solution with the concentration, which ranged from (5 mg/L, 50 mg/L, 500 mg/L) shaken up in an aqueous shaker at 25°C for 15 mins to 120 mins[5].

The pH experiment was investigated in the range for cobalt sorption was performed at a constant pH of 4, pH of the nickel ratio of 5. The content of bottles was subjected to centrifugation during 30 mins at 6000 r/m and then filtered out. The residual metal concentration in the solution was determined by AAS.

RESULTS AND DISCUSSION

Characterization of complexes

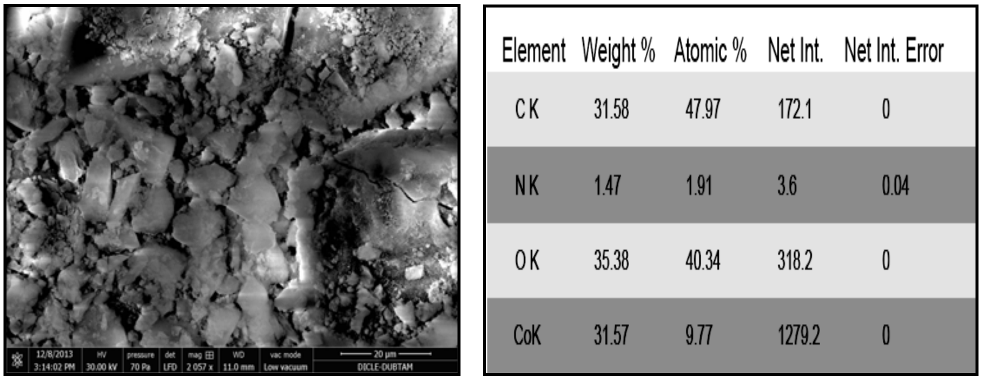
The surface morphology sodium humate was obtained to see the distinguishable aspects. The particle size is seen quite bigger sodium humate was examined at 5000 magnification (Fig. 1). The EDAX apparatus that can work simultaneously to SEM, which combines elemental analysis. It is seen that the particles aggregate to form larger particles, voids are present.



Element	Weight %	Atomic %	Net Int.	Net Int. Error
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
NK	0.52	0.14	67.65	0.14

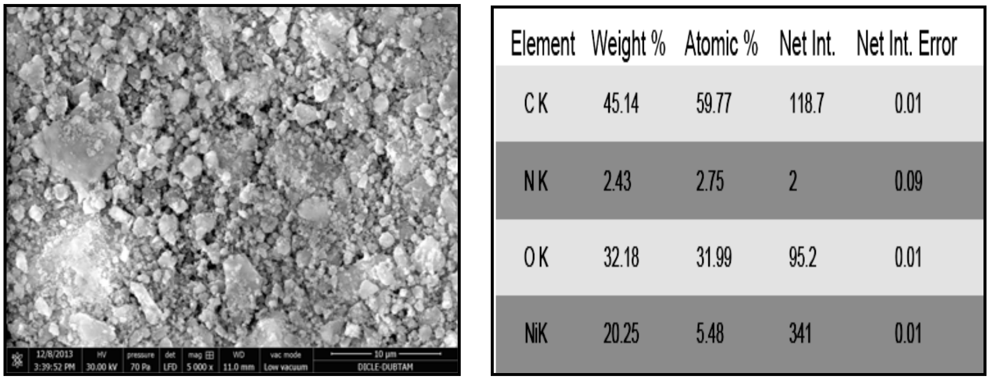
Fig. 1: The SEM image and EDAX results of sodium humate

SEM images and EDAX results of complexes with metal ions are shown in (Figs. 2, 3). SEM images were taken with ×2000 magnification. The increase in the size of pores is observed on the surface of particles. 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 cobalt humate complexes sample (Fig. 2) show, interaction of cobalt ions made up 31.57% and for nickel humate complexes sample (Fig. 3) interaction of nickel ions made up 20.25%. As can be seen from the figure, nickel humate complexes distinctly different particles became smaller.



Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	31.58	47.97	172.1	0
N K	1.47	1.91	3.6	0.04
O K	35.38	40.34	318.2	0
CoK	31.57	9.77	1279.2	0

Fig. 2: SEM image of cobalt humate complexes sample and its chemical elemental composition



Element	Weight %	Atomic %	Net Int.	Net Int. Error
C K	45.14	59.77	118.7	0.01
N K	2.43	2.75	2	0.09
O K	32.18	31.99	95.2	0.01
NiK	20.25	5.48	341	0.01

Fig. 3: SEM image of nickel humate complexes sample and its chemical elemental composition

The stretching vibrations recorded at the range of 225 cm^{-1} and 4000 cm^{-1} of extracted humic compounds in the present work shows significant peaks correspond to the hydroxyl, carboxyl and the other substituents occupying on the compounds (Fig. 4). The broad peak around 3444, 3697, 3251, 3331 cm^{-1} is belonged to the hydroxyl groups and another peak which was covered by broadened OH vibrations also let us to predict aromatic structure of humic compounds. Participation of –COOH groups in the reaction with metals is indicated as characteristic band of cobalt humate at 1691 and 1700 cm^{-1}. Carboxylic groups exhibit short-wave band and they can also be seen as absorption at 1557 cm^{-1}.Vibrations in the region of 2322, 2119, 2051 cm^{-1} refer to stretching vibrations of $–CH_3$, $–CH_2$ and –CH groups of aliphatic structures. In the 526, 338.329 cm^{-1} band for cobalt humate and in 599, 369, 312 cm^{-1} absorption of nickel humate which confirm the formation of Me-O connection in the complexes[6].

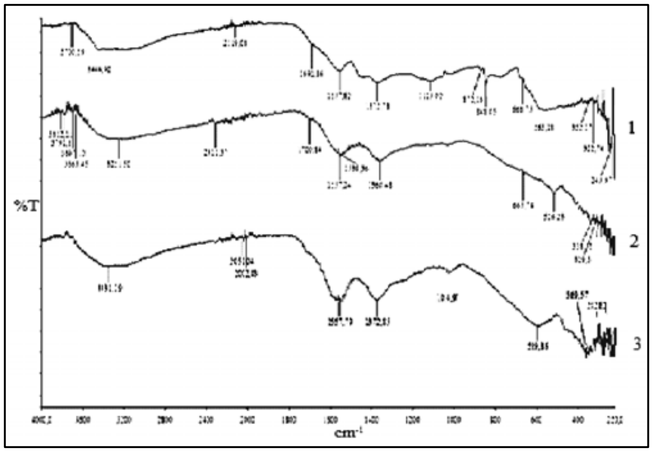


Fig. 4: FTIR-spectra of the samples: 1–sodium humate; 2– cobalt humate complexes; 3– nickel humate complexes

Sorption experiments

Removal efficiency (% R) and pH effect

The percentage of removability of toxic metals from water was calculated versus various times at changing grams. Equation (1) was used for the expression of graphic.

$$\% \text{ R} = \frac{C_o - C_e}{C_o} \cdot 100 \qquad \ldots(1)$$

where: C_0 is the initial concentration of metal ions in solution, mg/L; C_e is concentration of metal ions in solution after their interaction with the sorbent, mg/L.

The efficacy of adsorption of cobalt ions with the sodium humate concentration of 5 mg/L of Co^{2+} with different sorbent grams (0.05, 0.1, 0.25, 0.5, 1, 1.5, 2 g). It has been established that the increase of time of from 15 to 120 mins in a solution of cobalt content decreases. The pH experiment was investigated in the range for cobalt sorption was performed at a constant pH of 4. Fig. 5 shows that in grams sorbent 0.05 g to 1 g of the degree of sorption is in direct proportion to the increase in grams, that is, with its increase raises. So at 0.05 g sorbent 120 mins of sorption process purification rate is 50%, and at 1 g sorbent 120 mins of sorption degree reaches 91.5%.

With the increase in grams of sodium humate to 2.0 g degree of sorption is some what reduced. The degree of purification at 15 mins was 86%, and at 120 mins the degree of purification is 89%.

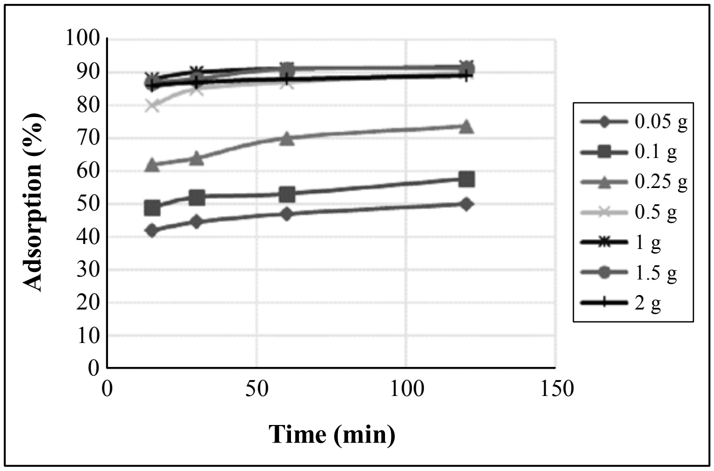


Fig. 5: Degree of the adsorption of Co (II) at a concentration of 5 mg/L depending on time for different sorbent grams

At cobalt concentrations of 50 mg/L 0.05 g sorbent 120 mins the degree (Fig. 6) of purification process is 32%. The greatest effect was with 15 mins of 1 g sorbent purification degree is 70%, and for 120 mins - 90.4%. When 1.5 g and 2 g of the sorbent is reduced to the extent of sorption of 76%. This is due to the fact that by increasing the grams to 2 grams of sodium humate can not fully interact with cobalt ions.

When the concentration of cobalt 500 mg/L with sodium humate from 0.05 to 2 g (Fig. 7), are linear straight and increases the process time and grams increase the degree of sorption of a sorbent increases. The degree of purification of cobalt sorbent 0.05 g at 15 mins is 2% at 120 mins - 10%, and at 2 g sorbent at 15 mins was 58%, 120 mins purification rate increased to 68.6%.

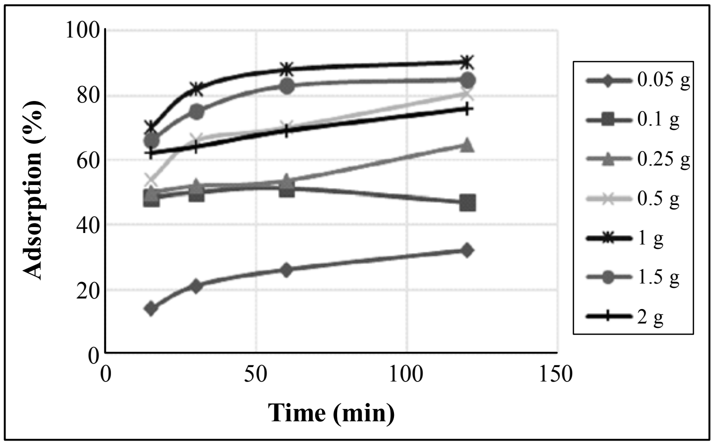


Fig. 6: Degree of the adsorption of Co (II) at a concentration of 50 mg/L depending on time for different sorbent grams

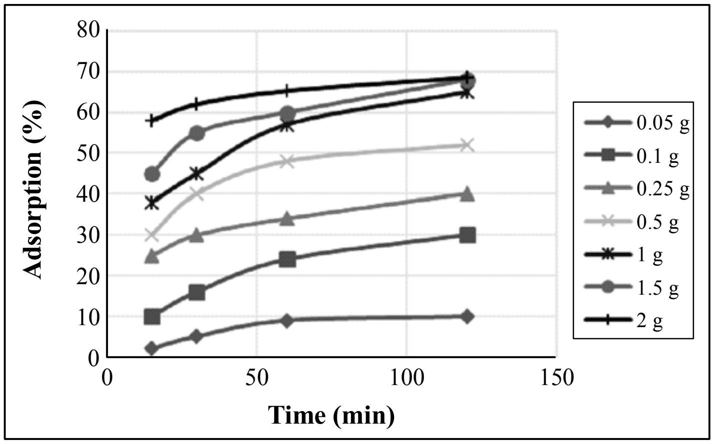


Fig. 7: Degree of the adsorption of Co (II) at a concentration of 500 mg/L depending on time for different sorbent grams

Apparently, for the sorption cobalt of the best cleaning results have in solutions with 5 mg/L a low concentration of cobalt and reaches 91.5%. Kinetic curves of sorption of nickel are shown in Fig. 8-10. Analysis of Fig. 8 shows that when the nickel concentration of 5 mg/L 0.05 g sorbent removal of nickel ions is 21%. By using 1 g of the sorbent already in the first 15 mins the concentration of nickel ions is reduced, the percentage adsorption of 64%. In further purification rate is increased to 120 mins to 75%. And by increasing the grams of 2 g of sorbent at 15 mins reaches a value of 81.8% and at 120 mins the degree of purification was 90%. The pH experiment was investigated in the range for nickel sorption was performed at a constant pH of 5.

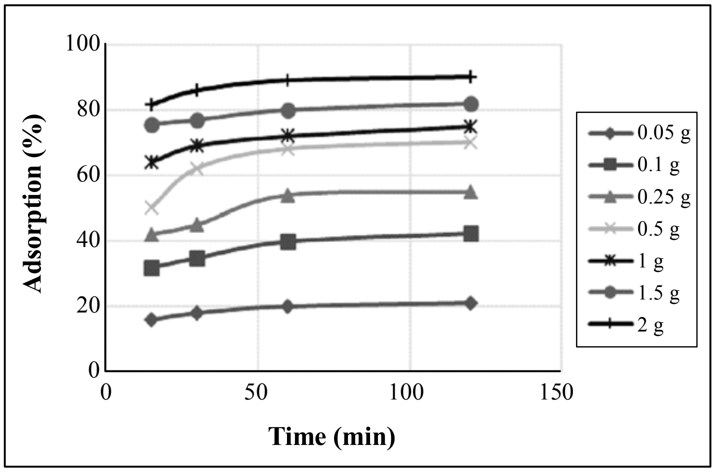


Fig. 8: Degree of the adsorption of Ni (II) at a concentration of 5 mg/L depending on time for different sorbent grams

Depending on the degree of extraction study (R,%) nickel ions in a concentration of 50 mg/L of from 15 mins to 2 hrs (Fig. 9), it was found that by increasing the grams to 1 gram sample increased degree of sorption. So when hitching 0.05 g was 32%, with an increase to 1 g sample increased the degree of sorption of nickel to 93.25%. When 1.5 grams of the sorbent and 2 g is reduced to the extent of sorption of 78.25%. This is due to the fact that by increasing the grams to 2 grams of sodium humate can not fully interact with the nickel ions.

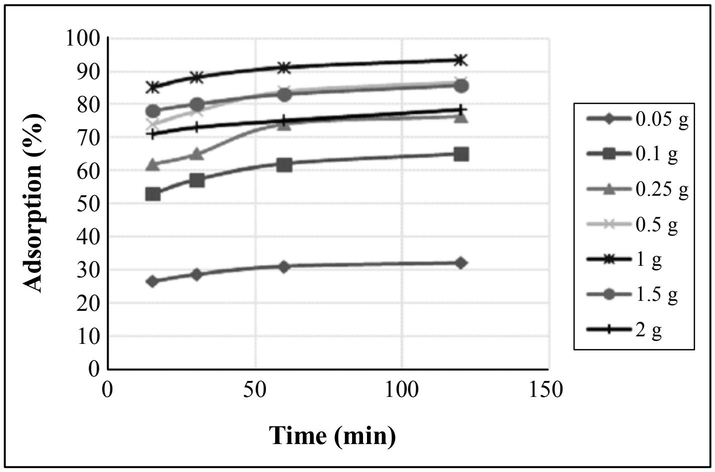


Fig. 9: Degree of the adsorption of Ni (II) at a concentration of 50 mg/L depending on time for different sorbent grams

Increasing the concentration of nickel to 500 mg when 0.05 grams sorbent nickel concentration decreased to 20% as in the previous experiments observed increase in sorption at 1 g sorbent at 120 mins to 87.43% (Fig. 10). Grams at 2 g sorbent degree of sorption is significantly reduced to 82.19%.

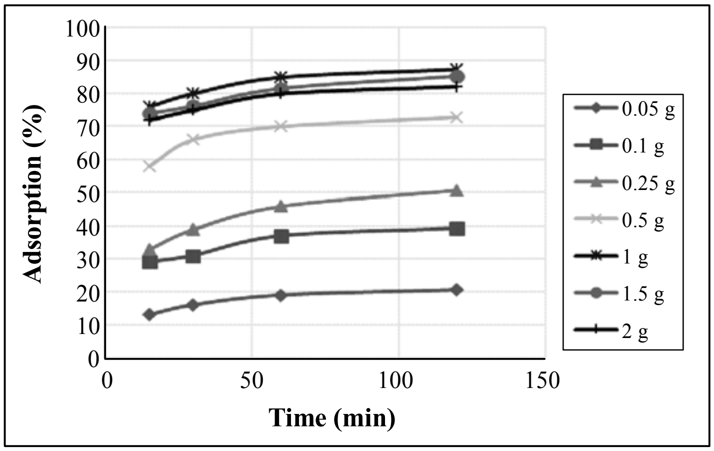


Fig. 10: Degree of the adsorption of Ni (II) at a concentration of 500 mg/L depending on time for different sorbent grams

CONCLUSION

The investigations showed that sodium humate can be used as a sorbent for purification of water from heavy metal ions. Maximum sorption degree of humate achieved for 5 ppm 91.5%, 50 ppm 90.4%, 500 ppm 68.6% for Co(II) and 90 % of 5 ppm, for 50 ppm 93.25%, 500 ppm 87.43% for Ni (II). Humate and metal ion interaction was investigated with special emphasis on the effects of pH, metal ions concentration and humate concentration. It has been found that the interaction of humate with metal ions in solution decreases with increases metal ion concentration and also increases with increases humate concentration. The pH experiment was investigated in the range for cobalt sorption was performed at a constant pH of 4, pH of the nickel ratio of 5. Furthermore, the complex reactions were done with sodium humate that revealed reasonable results after characterization with FTIR, SEM-EDAX. Sodium humate shows a great relevance to binding heavy metal atoms to remove them from the ecological environment.

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