Removal of Cu^{2+} by Adsorption-Flocculation

Güldem GÜNEY [1], Saadet YAPAR [2♠]

[1] *Ege University, Engineering Faculty, Chemical Engineeering Department*
Bornova-İzmir, TURKEY

[2] *Ege University, Engineering Faculty, Chemical Engineeering Department*
Bornova-İzmir, TURKEY

ABSTRACT

In this work, removal of Cu^{2+}cations by adsorption-flocculation method was studied. In contrary of conventional adsorption processes, the method proposed supplies the removal of Cu^{2+} loaded adsorbent through the precipitation and thus the filtration step is skipped out. The precipitation of adsorbent is carried out by adding of a cationic surfactant in a certain amount so as to results in flocs and than the flocs are removed in a small retention time. The results of studies showed that copper was removed by adsorption and also precipitation on the clay surface. The Cu2+ loaded adsorbent was removed in amounts exceeding 90%. Besides, the amount of clay precipitated from the dispersion was high even in low copper concentrations in contrary of the cases at which only clay was used as adsorbent and it was not affected by solution's pH.

Key words: Adsorption, Copper, Montmorillonite, Flocculation, Adsorption-flocculation

1. INTRODUCTION

In parallel with the increasing contamination of surface and sub-surface waters by toxic metal ions, the research on the development of technologies targetting the removal of these cations becomes more and more important. The main criteria in the development of such systems are the effectiveness and costs. Besides, being practical and inexpensive, the process should include the accumulation of these toxic substances in a small volume and a safe recovery. As one of the methods used in the removal of toxic materials, adsorption seems to be appropriate in view of its effectiveness and low operational costs. Activated carbon, metal oxides, chelating ligands, nonspecific and specific adsorbents such as resins and carrier matrixes are commonly used in the removal of heavy metal ions.

Although clay minerals and their modified forms have relatively low adsorption capacities compare to synthetic adsorbents, they are commonly used in the adsorption processes due to their low costs. High specific surface area and especially the existence of a net permanent negative charge on the interlayer surfaces make the mineral attractive to the cation adsorption. Additionally, surface and structural properties such as surface area and porosity could be changed through the modification to obtain a more convenient structure for a special adsorbate. Acid activation is a good and commonly used method when the increase in surface area and porosity is targeted. When increase in the adsorbate-adsorbent interactions is targeted, surface properties are changed by applying different modification methods including the intercalation of inorganic and organic cations. In order to sorption of anions, the surface must possess positively charged

♠Corresponding author, e-mail: saadet.yapar@ege.edu.tr

exchange sites, therefore the charge on the surface is reversed through the forming a bilayer or patchy bilayer. Malakul et al. [1], used a two step modification procedure, ion exchange and hydrophobic anchoring to form such layer. They reported that the metal adsorption is mainly through the chemical complexetion rather than ion exchange. Atia [2] was used cetylpyridium in the modification and he determined that chromate and molybdate are adsorbed through the ion exchange with counter ions of the surfactant ion-pairs.

In contrary of anions, adsorption of cations requires a negative charge on the surface, therefore pristine clay seems advantageous due to the existence of permanent negative charge but the binding strength between metal ions and clay surface is very weak [3]. Therefore, the research on the adsorption of heavy metal cations on modified clays is also common. Eren [4] was studied adsorption of copper on manganese oxide coated bentonite he determined that modified clay has higher adsorption capacity than pristine clay. Lin and Juang [3] were used sodium dodecyl sulfate in the modification of clay and they reported that the modified clay has a higher affinity for Cu^{2+} and Zn^{2+} cations than the pristine clay. Özdemir and Yapar [5] were studied the effects of an anionic biosurfactant rhamnolipid (RL), and pH on the adsorption and desorption of copper on Na-montmorillonite. They carried out the experiments in three set. In the first set, they used pristine clay as adsorbent. In the second set, pristine clay was added to solutions containing copper and RL at certain concentrations. Last step was carried out using clay modified with RL before. They reported that modification of clay with RL causes in increase in the rate of adsorption.

In contrary of the works mentioned above, in this study the cationic surfactant was used as flocculent and thus the filtration step was skipped out through the precipitation of loaded adsorbent. To our knowledge, the same method was also used in the removal of phenol [6] and 90% phenol removal and nearly 100% bentonite recovery was reported. Different from Shen's work, cetylpridinium chloride was used in the study and clay was removed in the amounts exceeding 90%.

2. EXPERIMENTAL

2.1. Materials Used

Bentonite obtained from Tokat, Resadiye region of Turkey was cleaned before use. The differential sedimentation technique was used to remove iron and silica. Cetylprydinium chloride (CPC) and copper (II) nitrate trihydrate (Cu (NO₃)₂ 3H₂O) were purchased from Merck and all the reagents used were of analytical grade.

2.2. Characterization

Pristine and used clay samples were subjected to XRD, SEM and FTIR analyses to determine the effect of Cu^{2+} and CPC adsorption on the surface. XRD analyses were carried out by using Rigaku Ultima-4 X-Ray diffraction spectrometer with Cu K radiation and FTIR analyses by using Perkin Elmer Spectrum Bx FT-IR System. SEM

images of the samples were taken in a JEOL, JFM-6060 scanning electron microscope at different resolutions; 1500x, 2500x, 5000x and 10000x.

2.3. Flocculation Studies

Experiments were conducted in three groups to see the effect of time, amount of solid and surfactant to the flocculation and settling. The same experimental procedure was followed in each case by changing the relevant parameter. The dispersions containing clay and/or clay+CPC were stirred at 800 rpm in a 250 ml beaker by using 4.5 cm diameter propeller, for 3 min. and then for a further 10 min at 200 rpm. The stirring period was followed by settling under the gravity. At the end of settling period, the amount of bentonite in the supernatant was estimated by absorbance measurements taken with a JASCO 7000 UV spectrophotometer at a wavelength of 650 nm. A calibration curve of absorbance versus bentonite concentration in the dispersion was determined by using pristine clay. Percentage of bentonite removed was calculated by using following equation.

$$\% \, Clay \, Removal = \frac{(m_1 - m_2)}{m_2} \times 100 \qquad (1)$$

where m_1 and m_2 are the initial and final amounts of clay in the dispersion.

In these groups, the time interval was 0-3 hours, amount of clay 0-1gr. In the determination of amount of surfactant, CPC was used in amounts equal to 25%, 50% and 100% of cation exchange capacity (CEC).

2.4. Adsorption-Flocculation Studies

Before the adsorption-flocculation experiments, kinetic studies were done to estimate the order of adsorption of those ions, since the clay was dispersed in a solution containing both surfactant and the copper ions during the adsorption-flocculation studies. The experiments were conducted by adding previously determined amount of clay to the solutions containing surfactant or copper ions at a certain concentrations and dispersions were shaken at 20°C for a time interval between 0-24 h. At the end of the shaking period, copper and CPC concentrations in the supernatants were determined through the AAS analyses for copper and UV analyses for CPC.

Adsorption – flocculation experiments were conducted by using surface active agents in amounts equal to various amounts of CEC of clay to see the effect of surface coverage to the adsorption. The same experimental procedure with the flocculation experiments was followed, the dispersions containing surfactant and copper at prescribed concentrations were stirred at 800 rpm in a 250 ml beaker by using 4.5 cm diameter propeller, for 3 min. and then for a further 10 min at 200 rpm. The stirring period was followed by settling under the gravity.

Adsorption-flocculation and a set of batch adsorption experiments were also conducted by using organoclay to compare the efficiency of the method proposed. Organoclay used in this group of experiments was prepared by using CPC in an amount equal to 25% of CEC according to the method described in an earlier work [7].

In all experiments, concentrations of copper solutions were in the range of 0-80 ppm and they were repeated by adjusting pH to 3, 4 and 5 to see the effect of pH.

3. RESULTS AND DISCUSSION

3.1.   Flocculation Studies

The results of the studies carried out to see the effect of settling time are given in Figure 1 for both clay and clay+CPC mixture. As shown in the Figure, percentage of solid removal increases with time of settlings for both cases, however the addition of CPC causes a considerable increase in the removal of solid.

Although the percentage removal increases depending on settlings time, the rate of removal decreases for the prolonged settling times, therefore the settling time was fixed as 60 minutes.
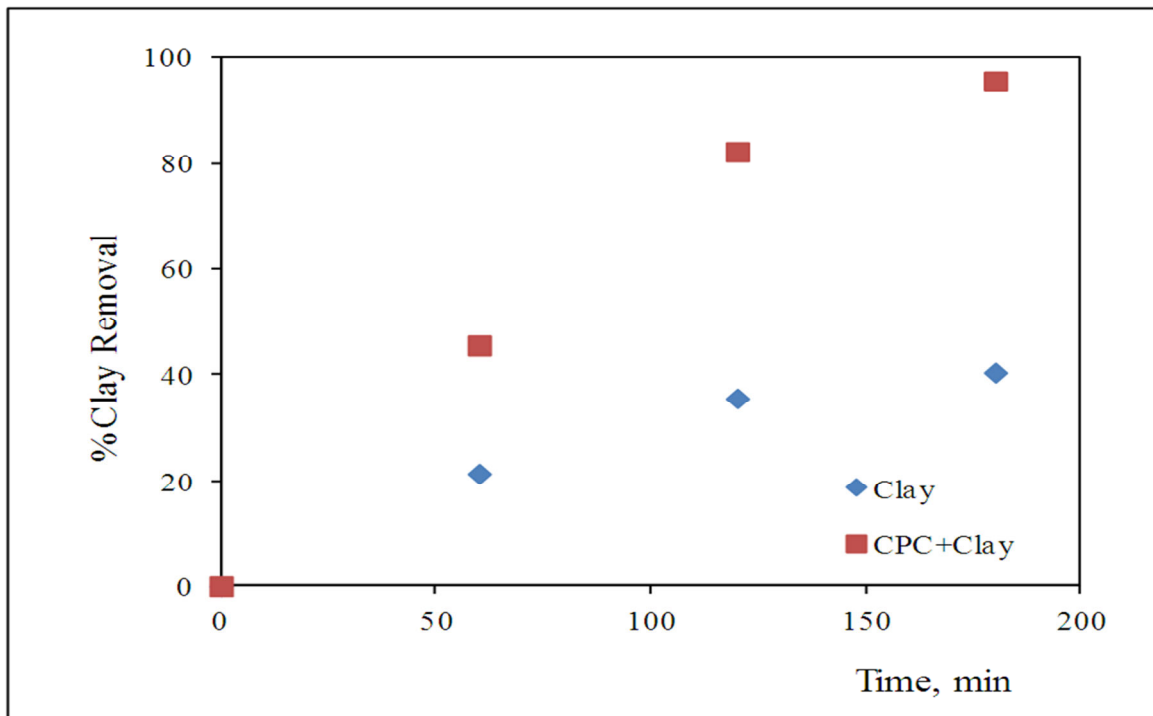

Figure 1. Effect of Time

In the second group of experiments conducted to see the effect of amount of CPC, a sharp increase is observed when CPC is added in an amount which is equal to 25% of CEC. As given in Figure 2, approximately 90% of clay is removed at this concentration but further increase in CPC concentration does not cause any considerable change in the percentage of clay removed. Besides, a small decrease is observed when the amount of CPC exceeds 100% of CEC. Therefore, adsorption-flocculation experiments were conducted by using CPC in amounts equivalent to 25, 50 and 100% of CEC.
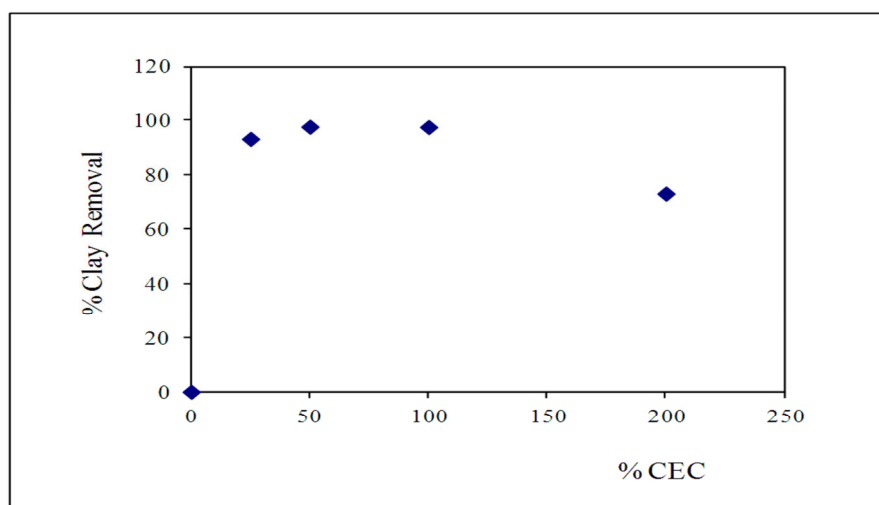
Figure 2. Effect of CPC addition

The effect of amount of solid to the amount of clay removed is given in Figure 3 as a function of solid concentration in the dispersion. An increase in solid concentration causes an increase in both the amount of solid removed and also amount of solid remaining suspended in the dispersion. Because the aim of the study is both the removal of Cu^{2+} through the adsorption and Cu^{2+} loaded clay particles, the amount of solid to be used in adsorption- flocculation studies determined as the percentage of solid at which 80% removal is observed.
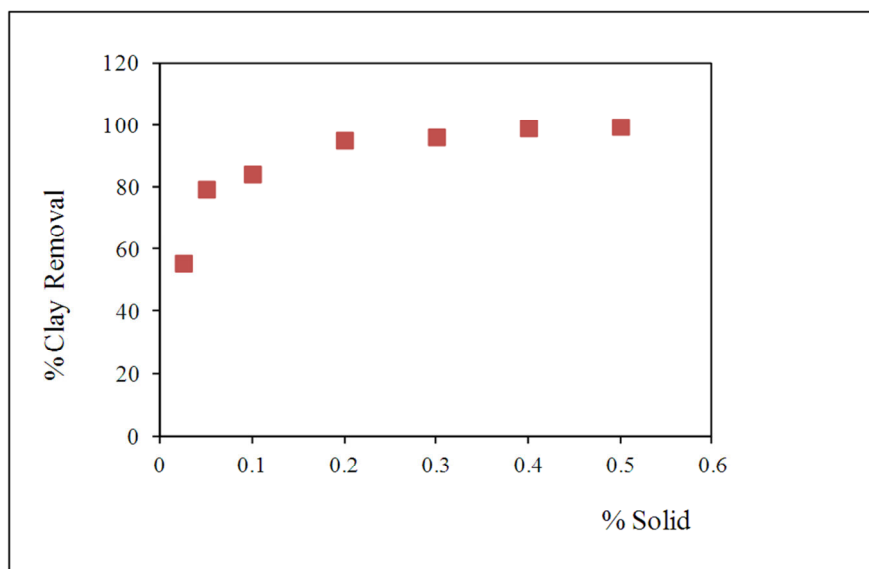
Figure 3. Effect of Solid Concentration

3.2. Characterization Studies

Clay mineral used in this study is a typical Na-smectic with 1.26 nm basal spacing [7]. Results of XRD analyses of organoclay samples prepared by using CPC in amounts equivalent to 25%, 50% and 100% of CEC and clay flocculated by using same amounts of CPC are given in Table 1. As shown in the Table both organo- and flocculated clays almost have the same d_{001} values indicating the existence of alkylammonium cations in the form of mono- mixed-, and bilayers [8].

Table 1. Results of XRD analyses

% CEC	d_{001}(nm)	
	Flocculated clay	Organoclay
0	1.26	1.26
25	1.31	1.35
50	1.38	1.45
100	1.92	1.83

FTIR spectra of organoclay and the clay used in the adsorption-flocculation experiments are given in the Figure 4. As shown in the Figure, FTIR spectrum of organoclay exhibits the typical bands of clay mineral and multiple bands which are assigned to C-H and C=C bonds [9-13]. These bands and their assignments are tabulated in Table 2.

Table 2. FTIR bands and their assignments

Wavenumber, cm^{-1}	Assignments
3626	OH stretching vibration of structural OH groups
3400	OH stretching vibration of hydrogen-bonded water
2925	Asymmetric stretching vibrations of C-H bonds
2853	Symmetric stretching vibrations of C-H bonds
1630	Bending vibration of water
1487	Bending vibration of C=C of aromatic ring ; CH_2 scissors

When the FTIR spectra of the clay minerals used in adsorption-flocculation experiments and organoclay given in Figure 4 are compared, it is observed that both spectra have C-H, C=C bands. Existence of these bands reveals that the adsorption kinetics of CPC is very rapid and approximately 80 minutes which is the clay-CPC total contact time is enough for the formation of organic layer on the surface.
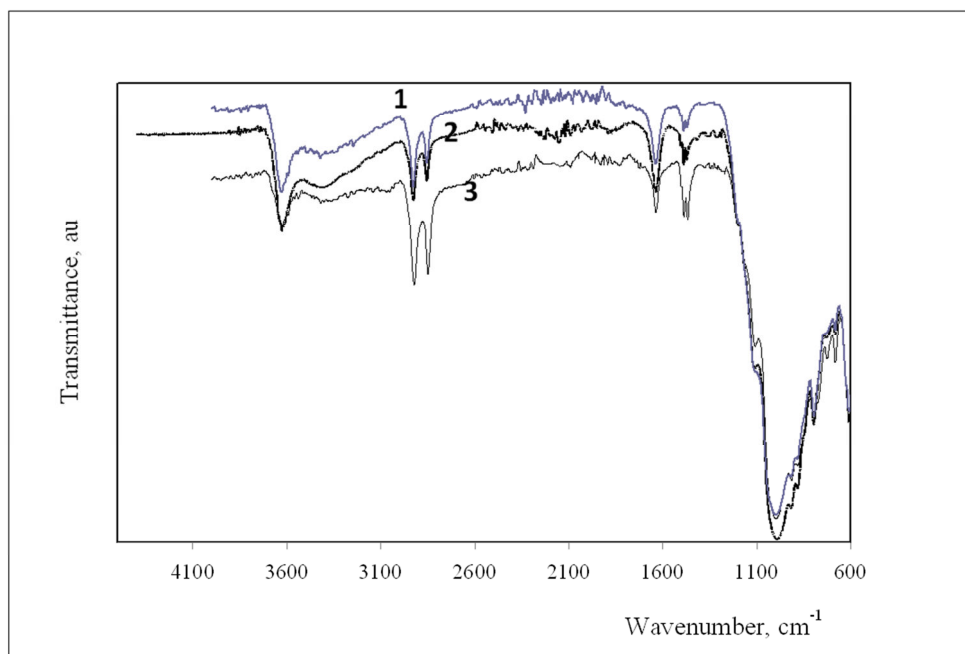
Figure 4. FTIR Spectra of organo and pristine clay used in flocculation Experiments (1: organoclay, 2: Pristine clay+CPC(25% CEC), 3: Pristine clay+CPC(100% CEC))

The FTIR spectra of Cu loaded organoclay samples given in the Figure 5 have almost same features except the appearance of two new bands at around 1417 cm^{-1} and 1340cm^{-1}. Abou –El-Sherbini and Hassanien [11] were also reported the occurence of new bands at 1447 and 1362 cm^{-1} in the FTIR spectrum of Cu loaded organomontmorillonite and they explained the occurrence of new band by the bonding of Cu (II) to organomontmorillonite in the enol form via O and N atoms. As seen in Figure 5, the region between 1500-1300 cm^{-1} also covers characteristic features for C-H, C=C bonds and no shift is observed in the bands.

Therefore the occurence of these bands indicates the existence of Cu(II), but the complexity of these region does not allow to estimate which interaction is really exists and/or dominant. On the other hand, there are no shifts in the bands assigned to fundamental vibrations of OH that are expected to be influenced by Cu (II) cations [14, 4]. This observation reveals that Cu (II) cations mainly interact with the organic cation on the surface.
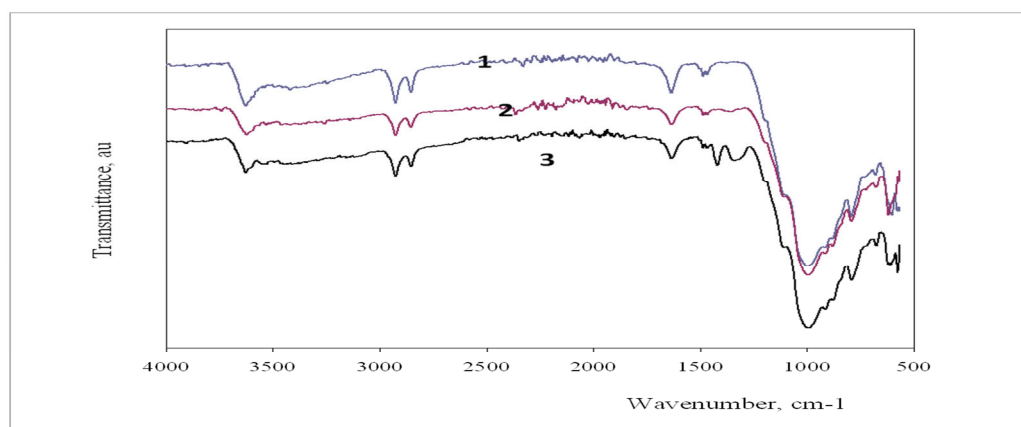

Figure 5. FTIR Spectra of Cu^{2+} loaded Organoclay (1: organoclay, 2: Organoclay+6 ppm Cu^{2+}, 3: Organoclay+79ppm Cu^{2+})

The spectra of clay used in the adsorption-flocculation experiments are given in Figure 6. These spectra are almost identical to the spectra given in Figure 5 and the existence of the bands around 2900 cm^{-1} and

1490 cm-1 and also the bands at 1447 and 1362 cm^{-1} indicating the simultaneous adsorption of Cu(II) and CPC on the surface.
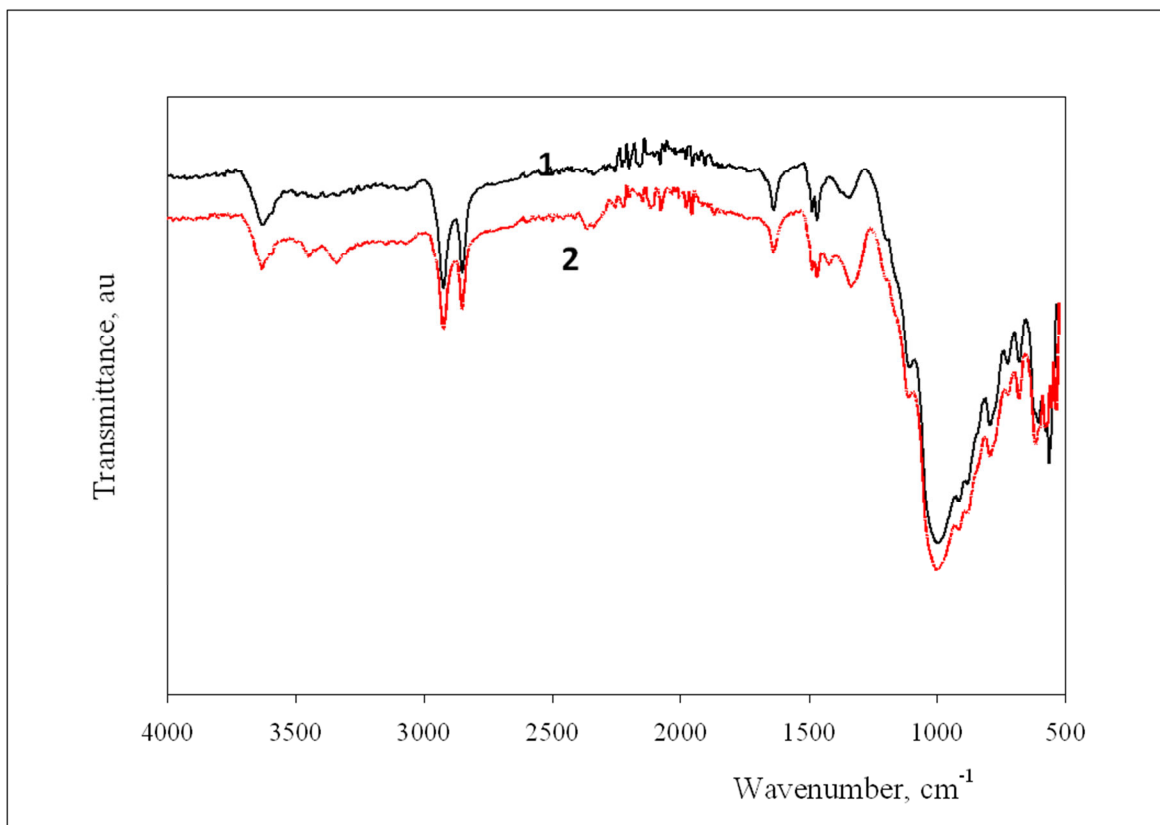

Figure 6. FTIR Spectra of pristine clay used adsorption-flocculation (1: Clay+ 13 ppm Cu^{2+}, 2: Clay+79 ppm Cu^{2+})

The results of SEM analyses are given in Figures 7, 8 and 9. As shown in Figure 7, pristine clay has typical smectite surface features with curly margins. Addition of alkylammonium cations will cause some changes in the surface morphology and also these changes depend on the amount of alkylammonium cations. In figure 8, the surface morphologies of the clay used in flocculation experiments are compared with those of

pristine and organoclays. A close examination of the figure reveals that the clay used in the flocculation experiments has a similar morphology with organoclays. This result conforms the XRD, FTIR analyses showing the existence of CP cations on the surface and also kinetic results indicating that the CPC molecules have very rapid adsorption kinetics.
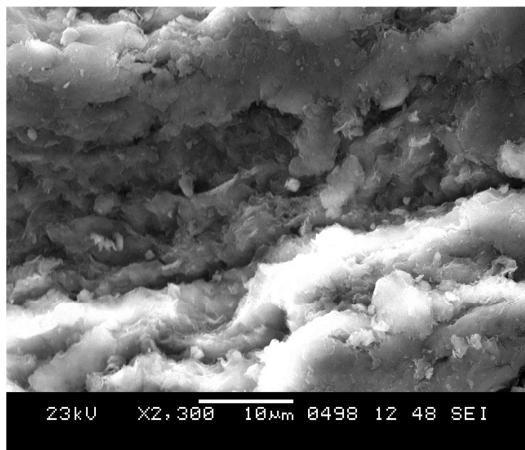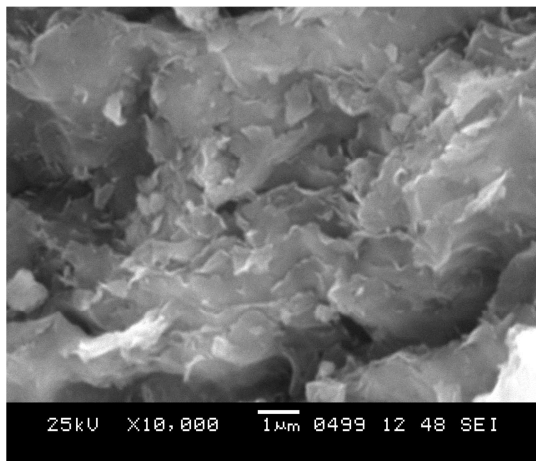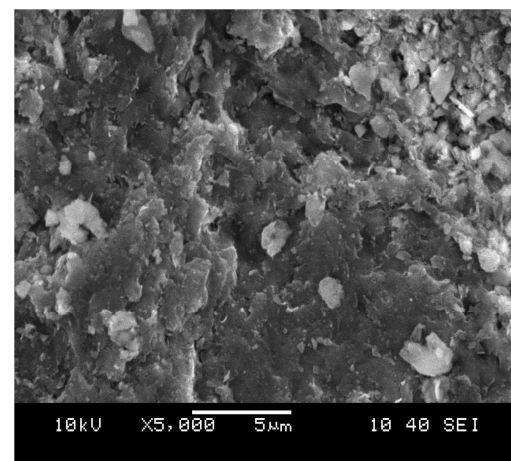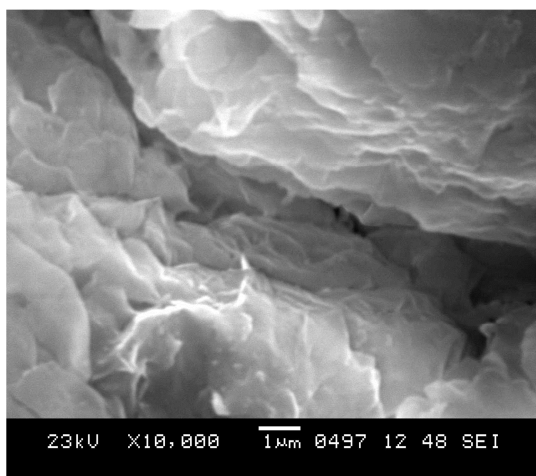
Pristine clay
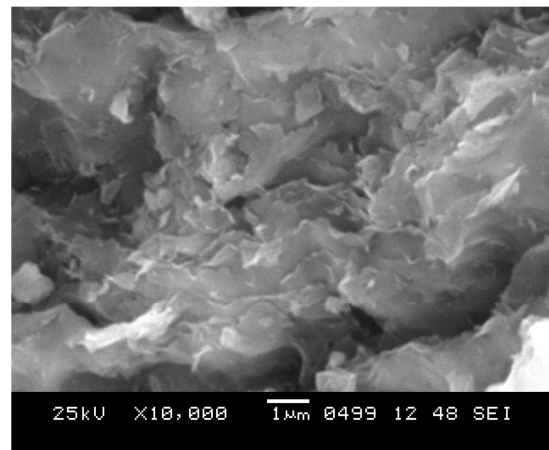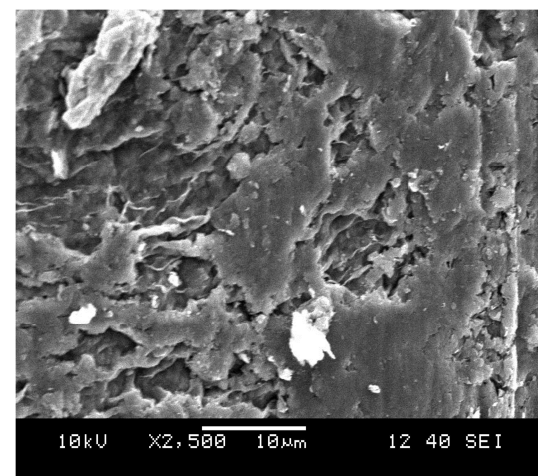

Pristine clay

Figure 7**.** SEM image of pristine clay

Pristine clay

Organoclay (25%CEC)

Organoclay (100% CEC)

Clay+CPC(50%)

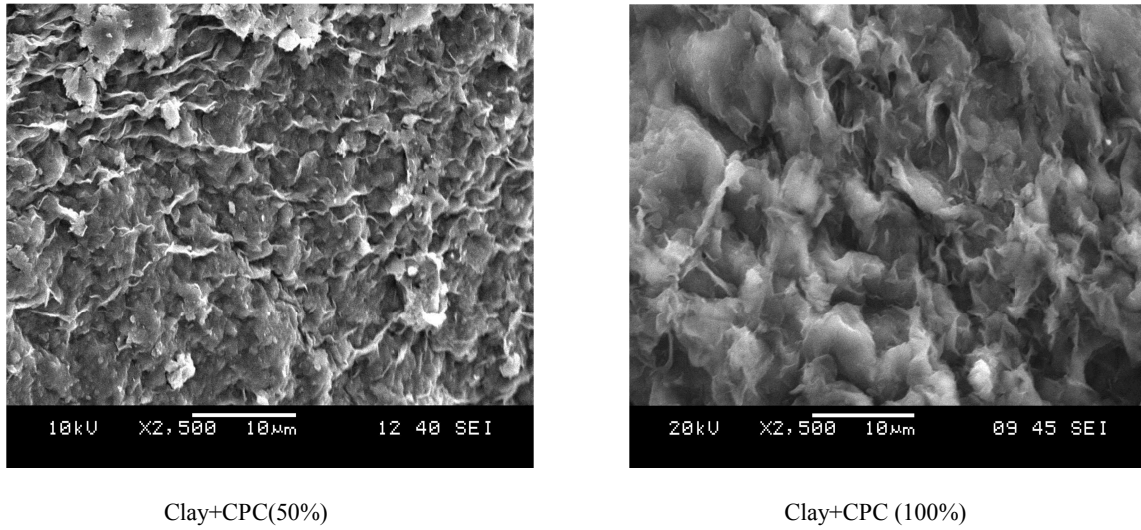Clay+CPC(50%)   Clay+CPC (100%)

Figure 8. Comparison of surface morphologies

Organoclay+39 ppm bakır | Organoclay+79 ppm bakır

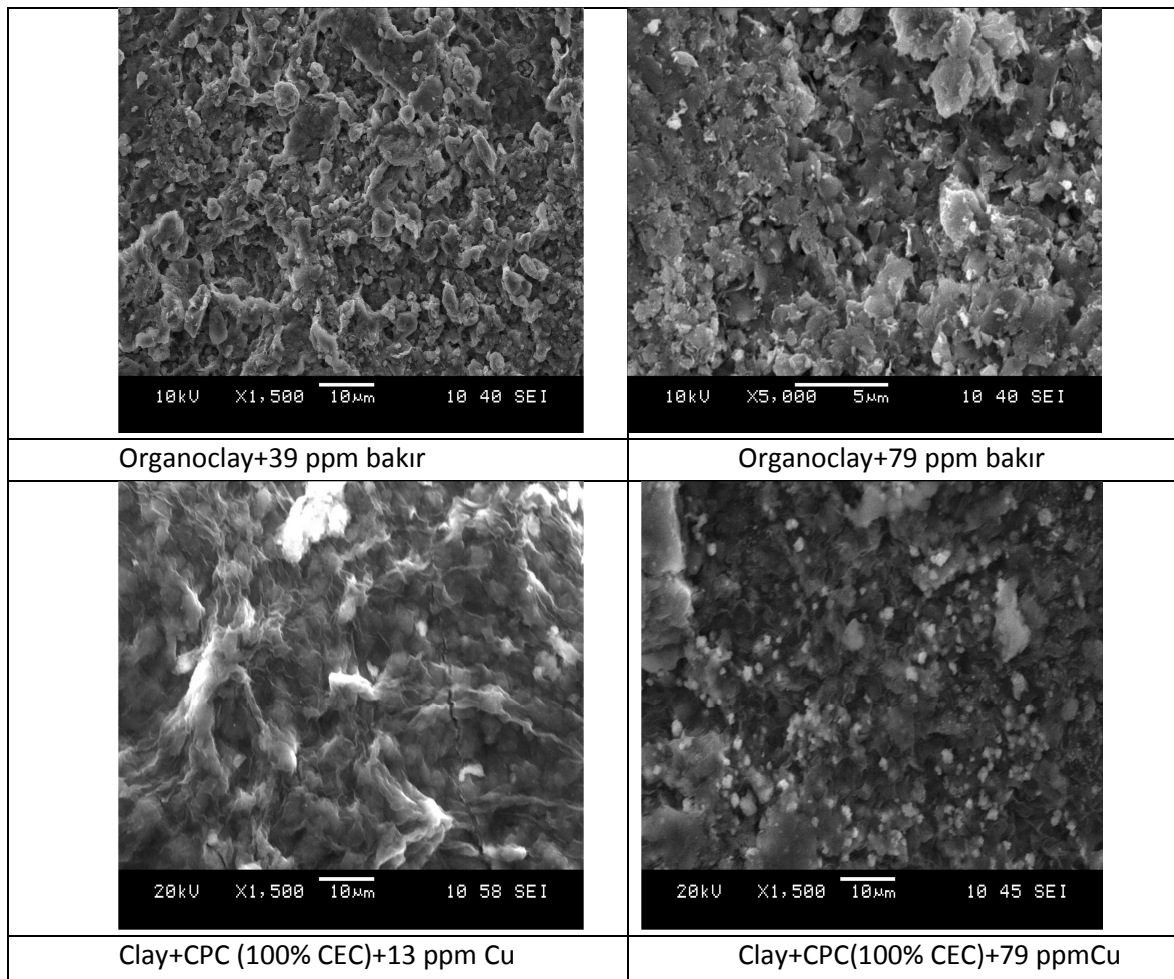Clay+CPC (100% CEC)+13 ppm Cu | Clay+CPC(100% CEC)+79 ppmCu

Figure 9. Effect of Cu^{2+} on surface morphology

During the adsorption –flocculation experiments, Cl^- anions will exist in the medium as a result of the dissociation of cetylpridium and they probably will cause the precipitation of copper as $CuCl_2$ on the surface. Moreover, the existence of $CuCl_2$ on the surface is distinguished in Figure 9 even for a small amount of copper. In the case of organoclays no further change depending on adsorption of copper is observed on the surface. Under these circumstances, the adsorption and also precipitation are effective mechanisms in the removal of copper during the adsorption-flocculation process.

3.3.   Adsorption-Flocculation Studies

Pseudo second order kinetic model given below was applied to the data obtained from kinetic experiments.

The parameters and correlation coefficients are given in Table 3.

$$\frac{dQ_t}{dt} = k_2\left(Q_e - Q_t\right)^2 \qquad (2)$$

and the integrated form of the equation for $Q_t=0$ at $t=0$ and $Q_t=Q_t$ at $t=t$

$$\frac{t}{Q_t} = \frac{1}{k_2Q_e^2} + \frac{1}{Q_e}t \qquad (3)$$

here $k_2Q_e^2$ is the initial adsorption rate and k_2 adsorption rate constant.

Table 3. Kinetic model parameters of Cu^{2+} and cetylprydinium cations

Adsorbate	k_2 (g/mg h)	a_e (mg/g)	$k_2a_e^2.10^{-4}$ (mg/g h)	R^2
CPC	0.22	238	1.25	0.99
Cu^{2+}	0.21	26.3	0.015	0.99

$k_2a_e^2$: Initial adsorption rate k_2 : Adsorption rate constant

A close examination of the Table reveals that CPC has a considerable higher initial adsorption rate than Cu^{2+} whereas the adsorption rate constants of both cations are nearly same. Under these circumstances, the amount of CPC on the surface will probably higher at very beginning of the adsorption but the competition between Cu^{2+} and CP cations is almost negligible.

The existence of CPC in the adsorption medium has two controversial effects; in one hand it will cause an increase in the amount of clay removed, on the other hand a decrease in the active sites as a result of adsorption simultaneously on the interlayer surface. Therefore, the amount of CPC should be determined by

considering the removal of clay particles and also the coverage of active sites that cause a relative decrease in the adsorption of Cu^{2+}. Under these circumstances, the adsorption-flocculation experiments were carried out by using CPC in amounts equal to 25, 50 and 100% of CEC of the clay mineral. As shown in Figure 10, the adsorbed amounts decreases with increasing amount of CPC in the adsorption medium. Besides, the adsorption isotherms have different features. When the amount of CPC is equal to 25 and/or 50% of CEC, adsorbed amounts of Cu^{2+} increase sharply at low equilibrium concentrations and it reaches an equilibrium value. Whereas; a gradual and continuous increase is observed when the amount is increased to 100 % of CEC.
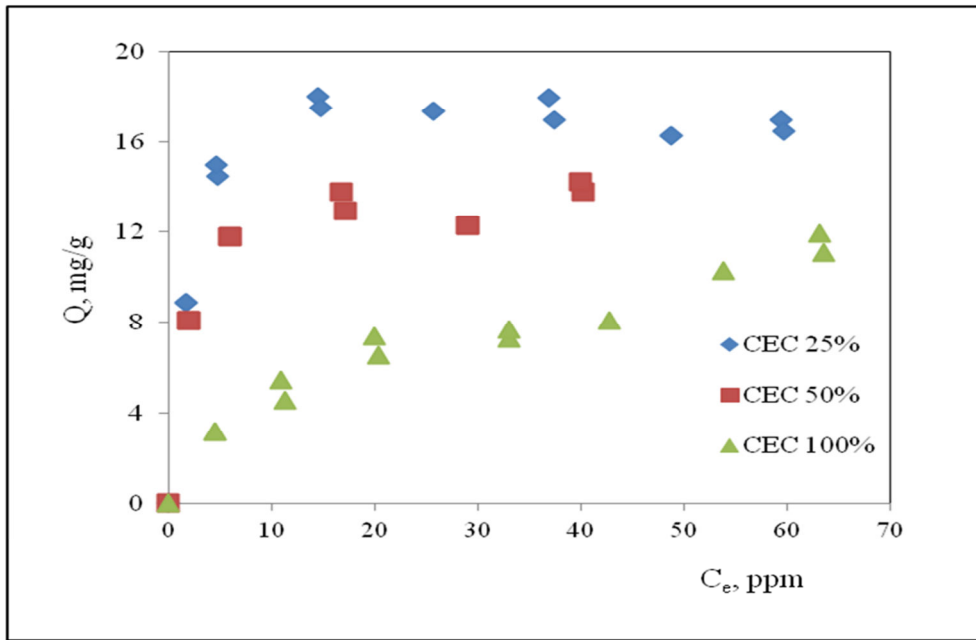
Figure 10. Change in adsorbed amounts with the amount of CPC added to adsorption-flocculation medium
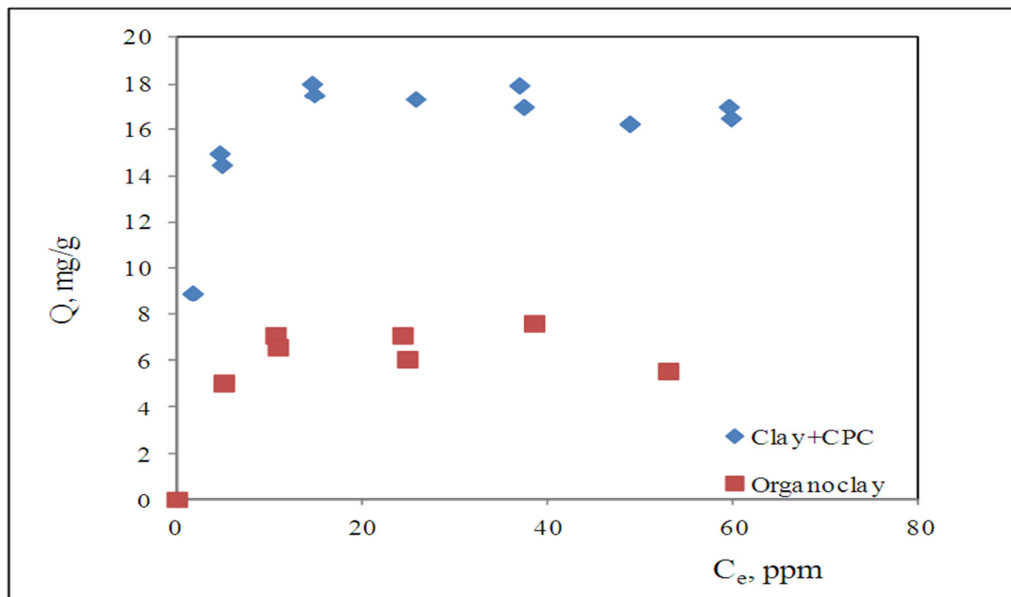

Figure 11. Comparison of adsorbed amounts by organoclay through adsorption and pristine clay through the adsorption - flocculation

The removal of Cu^{2+} cations by leaving into contact the Cu^{2+} solutions with organoclay in the same time interval as in the case of adsorption- flocculation experiments were compared with the amounts removed at the end of the adsorption- flocculation experiments conducted using pristine clay are compared in Figure 11. Although the same amount of CPC used in both cases, adsorption –flocculation method seems more efficient in the removal of copper. This behavior is attributed to less surface coverage resulting from the leveling off CP

cations in the adsorption medium due to their consumption for the flocculation of clay particles.

4. CONCLUSIONS

The removal of Cu^{2+} cations through the adsorption-flocculation process was studied. It is concluded that the proposed method is available for the removal of Cu^{2+} cations and also loaded adsorbent simultaneously. In

this respect, the method proposed is convenient for the use in the waste water collection pools.

Acknowledgment

REFERENCES

[1] Malakul, P., Srinivasan, K.R., Wang, H.Y., Metal Adsorption and Desorption Characteristics of Surfactant-Modified Clay Complexes, Industrial Engineering Chemistry Reseach, 37, 4296-4301, 1998.

[2] Atia, A.A., Adsorption of Chromate and Molybdate by Cetylpyridinium Bentonite, Applied Clay Science, 41, 73-84, 2008.

[3] Lin, S-H., Juang, R-S., Heavy Metal Removal from Water by Sorption Using Surfactant Modified Montmorillonite, J. of Hazardous Materials, B92, 315-326, 2002.

[4] Eren, E., Removal of Copper Ions by Modified Ünye Clay, Turkey, J. of Hazardous Materials, 159, 235-244, 2008.

[5] Özdemir, G., Yapar, S., Adsorption and Desorption Behavior of Copper Ions on Na-montmorillonite: Effect of Rhamnolipids and pH, J. of Hazardous Materials, 166, 1307-1313, 2009.

[6] Shen, Y-H., Removal of Phenol from Water by Adsorption Flocculation using Organobentonite, J. of Hazardous Materials, 36, 1107-1114, 2002.

[7] Yapar, S., Physicochemical Study of Microwave-synthesized Organoclays, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 345, 75-81, 2009.

[8] Lagaly, G., Weiss, A., Kolloid-Zeitschrift & Zeitschrift für Polymere 243, 48– 55, 1970.

[9] Praus P., Turicová, M., Študentová, S., Ritz, M., Study of Ceyltrimethyl Ammonium and Cetylprydinium Adsorption on Montmorillonite, Journal of Colloid and Interface Science, 304, 29-36, 2006.

[10] Vazquez, A., Lopez, M., Kortaberria, G., Martin, L., Mondragon, I., Modification of Montmorillonite with Cationic Surfactants, Thermal and Chemical Analysis, Including CEC Determination, Applied Clay Science 41, 24-36, 2008.

[11] Abou-El-Sherbini, K., Hassanien, M.M., Study of Organically Modified Montmorillonite Clay for the Removal of Copper (II), J. of Hazardous Materials, 184, 654-661, 2010.

[12] Zhu, J., He, H., Zhu, L., wen, X., Deng, F., Characterization of Organic Phases in the Interlayer of Montmorillonite using FTIR and 13C NMR, J. of Colloid and Interface Science, 286, 239-244, 2005.

[13] Kloprogge, J.J., Mahmutagic, E., Frost, R.L., Mid-infrared and Infrared Emission Spectroscopy of Cu-exchanged Montmorillonite, Journal of Colloid and Interface Science, 296, 640-646, 2006.

[14] Madejová, J., Arvaiová, B., Komadel, P., FTIR Spectroscopic Characterization of Thermally Treated Cu^{2+}, Cd^{2+} and $Li+$ Montmorillonites, Spectrochimica Acta Part A, 55, 2467-2476, 1999.