Cumhuriyet Science Journal
CSJ

e-ISSN: 2587-246X
ISSN: 2587-2680

Cumhuriyet Sci. J., Vol.40-2(2019) 406-413

Humic Acid/Quercetin Coated Magnetic Fe_3O_4 Nanoparticles For Adsorptive Removal of Cu^{2+} and Ni^{2+}

Fatoş Ayça ÖZDEMİR OLGUN [1,*], ***Birsen DEMİRATA ÖZTÜRK*** [1]

[1] *Istanbul Technical University, Department of Chemistry, Istanbul TURKEY*

Received: 03.01.2018; Accepted: 04.10.2019 *http://dx.doi.org/10.17776/csj.374057*

Abstract. Removal of metals and heavy metals from industrial wastewaters is a serious concern for water systems. In this study, environmentally friendly natural polymer coated, cost-effective, easy to operate HA/QR magnetic nanoparticles were suggested to overcome this problem, for the first time in literature. Fe_3O_4 magnetic nanoparticles were synthesized with co-precipitation technique and a core-shell structure was obtained with humic acid sodium salt (HA) solution. At the second step of the procedure, synthesized magnetic nanoparticles were coated with quercetin solution. Scanning electron microscopy (SEM), X-Ray diffraction (XRD) and particle size analyses were performed to enlighten and characterize the structure. The newly synthesized nanoparticles were used for the batch-wise adsorption of copper and nickel metals, successfully. Maximum adsorption capacities were calculated as 14.61 mg/g for copper and 28.30 mg/g using 0.03 g adsorbents, at pH=7. Adsorption isotherms were evaluated and it was concluded that adsorption equilibrium fitted to both Langmuir and Freundlich isotherm models, better correlated with Langmuir isotherm model.

Keywords: Humic acid, Fe_3O_4 magnetic nanoparticles, metal removal, adsorption isotherm.

Hümik Asit/Kuversetin Kaplı Fe_3O_4 Manyetik Nanoparçacıklar ile Cu^{2+} ve Ni^{2+} Metallerinin Adsorpsiyon Yöntemiyle Giderimi

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Özet. Endüstriyel atıksulardan metal ya da ağır metal giderilmesi su sistemleri için ciddi sorunlar oluşturabilmektedir. Bu çalışmada, bu sorunları tamamen gidermek ya da en aza indirmek için bir çözüm yolu önerildi. Çalışma kapsamında, literatürde ilk kez, doğal polimer olan hümik asit sodyum tuzu ile kaplı olduğu için çevre dostu olan, ekonomik ve manyetik özelliğinden dolayı kullanım kolaylığı sağlayan HA/QR manyetik nanoparçacıklar sentezlendi. Sentez prosedürünün birinci adımında birlikte çöktürme tekniğiyle Fe_3O_4 manyetik nanoparçacıklar sentezlendi ve çekirdek-kabuk (core-shell) modeline uygun olarak hümik asit çözeltisi ile muamale edilerek kaplandı. İkinci adımda ise, sentezlenen partiküller kuersetin çözeltisi ile kaplandı. Oluşan nano yapının aydınlatılması için SEM (Taramalı Elektron Mikroskopisi), X ışını kırınımı (XRD) ve parçacık boyut analizi teknikleri kullanıldı. Yeni sentezlenen parçacıklar Cu^{2+} ve Ni^{2+} metallerinin giderimi için adsorban olarak başarıyla kullanıldı. pH=7 değerinde 0.03 g adsorban kullanılarak hesaplanan adsorpsiyon kapasiteleri Cu^{2+} için 14.61 mg/g; Ni^{2+} için 28.30 mg/g olarak hesaplandı. Adsorpsiyon izotermleri değerlendirildiğinde, elde edilen adsorpsiyon izoterm eğrisinin hem Langmuir hem Freundlich modeline uyum sağladığı gözlemlendi.

Anahtar Kelimeler: Hümik asit, Fe3O4 manyetik nanoparçacıklar, metal giderimi, adsorpsiyon izotermi.

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[*] Corresponding author. *Email address: ozdemirfa@itu.edu.tr*

1. INTRODUCTION

As industry develops, waste products become a concerning issue. Heavy metals found in discharged sewage show toxic impacts with their resistance against biodegradation and ability of accumulation. Livers, nervous system, female and male reproductive system, connective tissues such as hair, skin and nails are the first places affected by metal accumulation [1]. Heavy metals such as nickel and copper are used in many production plants and often met in their aqueous effluents [2]. The ability of metal ions to accumulate in plant, fish and mammals tissues poses a serious threat to human health through bioaccumulation in the food chain [3,4]. Several methods for heavy metal removal are found in literature such as; ultrafiltration, ion exchange chromatography, precipitation [5-7], reverse osmosis [8], nanofiltration [9]. Among these methods, adsorption process is commonly used with its flexible operation and high-quality effluent production [10]. In recent years, advances in nanoscale sciences, offer more effective adsorbents with many specific physiochemical properties. Nanosized ferric oxides are preferable for adsorption process with their low-cost, eco-friendly and easy-to-operate magnetic properties [11]. Moreover surface modified Fe_3O_4 nanoparticles are more efficient as their surface functionality improved. Humic acid, which is the end product of microbiological decomposition of plants and animals, is a good candidate for a surface coating material to provide a long-time stability. Quercetin, a naturally derived polyhydroxy (3, 3', 4', 5,7-OH) compound that can form complexes with metal cations, also prevents oxidation and growth of bacteria in water.

In this study Fe_3O_4 magnetic nanoparticles were synthesized and coated with humic acid sodium salt and quercetin, respectively. HA/QR magnetic nanoparticles were installed in copper and nickel adsorption process in batch-wise. Essential adsorption parameters as pH, adsorbent dose and incubation time [12] were investigated for the optimization. Adsorption equilibrium data were studied for a better understanding of adsorption process.

2. MATERIALS AND METHOD

All the reagents used in the experiments were of analytical grade. Iron (III) chloride hexahydrate (98%, Merck), ammonium iron (II) sulfate hexahydrate, humic acid sodium salt (Sigma Aldrich), quercetin (Sigma Aldrich), hydrochloric acid (Merck), ammonia solution (25%, Merck), NaOH (Merck), standard solutions of Cu^{2+} and Ni^{2+} for atomic absorption spectrometry were used during experiments. Ultrapure water was used when required, at each step of procedure.

Gec Avery analytical balance was used to weigh the chemicals at solid phase. Magnetic stirrer (VWR) and ultrasonic bath (Bandelin Sonorex) were used at solution preparation step. MSE Mistral 2000 centrifuge was used at synthesis of nanoparticles. The batch adsorption experiments were performed with the aid of shaker (Edmund Bühler 7400 Tubingen). For pH measurements Knick pH-meter was used. JOEL JSM-7600F Scanning Electron Microscope and FEI Quanta 250 FEG was used for the SEM analysis. Ultrapure water used during all experiments were obtained by Millipore Direct Q-UV 3. Varian 280-FS atomic absorption spectrometer was used for the determination of metals. Air/ acetylene gas mixture was used for atomization step. Hollow cathode lamps peculiar to each metal were installed during analyses. The absorbance measurements were performed at 324.8nm for Cu and 232.0 nm for Ni^{2+}.

2.1. Preparation of Solutions

1000 mgL^{-1} humic acid sodium salt solution was prepared by dissolving 0.25 g humic acid sodium salt in 0.25 L ultrapure water. 1×10^{-2} M quercetin solution in ethyl alcohol medium and 1% (w/v) SDS solution were prepared to use at nanoparticle synthesis step. Standard solutions of Cu^{2+} and Ni^{2+} were prepared by dilution of 1000 mgL^{-1} stock solutions to be in the required concentration level.

2.2. Synthesis of Nanoparticles

15.25 g $FeCl_3.6H_2O$ and 10.50 g $NH_4FeSO_4.6H_2O$ were weighed and mixed and dissolved in 250.0 mL of ultrapure water. 5.0 mL of 25% ammonia solution was added to 50.0 mL portion of the mixture mentioned above. After the addition 25% ammonia solution, precipitation occurred. In order to modify and improve the surface properties of nanoparticles, 25.0 mL of humic acid sodium salt solution and 25.0 mL 1× 10^{-2} M quercetin solutions were added, respectively. The synthesis procedure occurred at 90 ^{0}C for 1h. After humic acid quercetin magnetic nanoparticles were obtained, the particles were washed twice with ultrapure water to remove the excess impurities. Finally, synthesized nanoparticles were filtered and allowed to dry at 50^{0}C for 12 h in drying oven. Dried particles were pestled in mortar to powder form.

2.3. Characterization of Synthesized Nano particles

As the HA/QR magnetic nanoparticles were synthesized for the first time in the literature, the structure should be understood. For this reason, SEM, XRD and particle size analyses were performed.

Qualitative analyses of synthesized nanoparticles were performed by X-ray diffractometer. The analyte was stabilized between the positions of 0^{0}C-90^{0}C 2θ angles. By using the software of the instrument the collected data was transferred to graphic art for a better understanding.

Particle sizes of nanoparticles were measured by size analyzer. Synthesized nanoparticles were added to the reservoir of the instrument after ultrapure water. At pre-analysis step the particles were exposed to ultrasonic waves for 5 minutes allowing the particles dispersed in water. The results were achieved by taking the refractive index values of water and analyte into consideration. The reservoir was discharged and washed regularly after each measurement.

2.4. Adsorption Studies

Batch adsorption method was used to investigate the adsorption characteristics of the synthesized HA/QR magnetic nanoparticles. Batch-wise experiments were performed in glass flasks with a reaction volume of 50.0 mL at room temperature (25.0±0.1 ^{0}C). Metal solutions with desired concentration values were shaken with synthesized QR/HA magnetic nanoparticles. The particles were easily collected from the slurry with a regular magnet, leaving a clear effluent behind. Prior to the adsorption isotherm studies, adsorption parameters such as; pH, contact time and amount of adsorbent were optimized. For pH optimization, 2 mgL^{-1} Cu^{2+} and 3 mgL^{-1} Ni^{2+} solutions were prepared by adequate dilutions of their stock solutions. The pH values of the prepared solutions were adjusted with 0.1 M NaOH and 0.1 M HCl solutions. 0.01g of HA/QR magnetic nanoparticles were let to contact with freshly prepared solutions at varying pH values for 10 min at 400 rpm. The effect of contact time was investigated by allowing to contact 0.1 g of HA/QR magnetic nanoparticles with 2 mgL^{-1} Cu^{2+} and 3 mgL^{-1} Ni^{2+} solutions at pH=7, for increasing periods of time. Finally, the amount of HA/QR magnetic nanoparticles to be used in adsorption experiments were optimized at pH=7, using 2 mgL^{-1} Cu^{2+} and 3 mgL^{-1} Ni^{2+} solutions. After these optimizations, the adjusted adsorption parameters were employed in subsequent experiments.

The concentration of the residual metal in solution was determined by fast-sequential flame atomic absorption spectrometer. Solutions not to contain metal were used as blank. The difference between the initial and final concentration values was calculated in order to obtain adsorbed metal concentration and adsorbent capacity.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of HA/QR magnetic nanoparticles

The scanning electron microscopy (SEM) images of the synthesized nanoparticles was displayed in Figure 1. Lighter and brighter shades of the image belong to the coated nanoparticles. The particles exhibit a uniform size of approximately 40 nm.

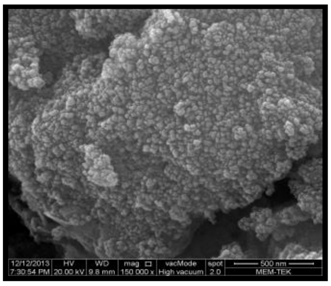

Figure 1. SEM micrograph of HA/QR magnetic nanoparticles.

The crystal structures of the samples were analyzed using X-ray diffraction method. The samples were analyzed between 0^0C- 90^0C at diffraction angle of 2θ. In Figure 2, the first image belongs to the core-shell magnetic nanoparticle before coating and the second image belongs to the magnetite coated with QR and HA solutions. As we compare the scan images, it can be concluded that five peaks existing in both of the images are the characteristics of the magnetic nanoparticle. The sharpest peak of number 2 only existing in the first scan image is thought to be as a result of coating procedure.

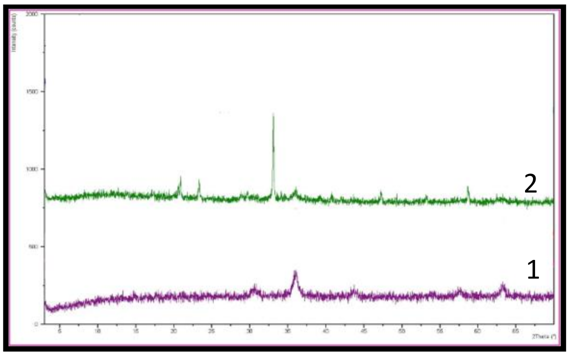

Figure 2. XRD patterns of 1)Magnetic nanoparticle 2) HA/QR coated magnetic nanoparticle.

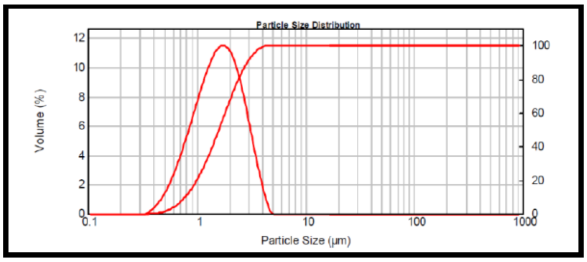

Figure 3. Particle size distribution of HA/QR magnetic nanoparticles measured by particle size analyzer.

Particle size analyzer was used to measure the particle size distribution and surface area of the synthesized HA/QR magnetic nanoparticles. Figure 3 shows the distribution of the synthesized nanoparticles after ultrasonicated in water for complete dispersion.

Using Figure 3, the average particle diameter was measured at 1.59 µm with a surface area of 4.42 m^2/g. The values measured by particle size analyzer are higher than those measured by SEM, as the attractive forces between dry particles are so great. This can be explained by the dispersion of HA/QR magnetic nanoparticles in water and subsequent sonication. Besides, the average particle diameter and surface area of uncoated magnetic nanoparticles were also measured. As the results were compared, the average particle diameter decreased after coating (17.53 µm for uncoated; 1.59 µm for HA/QR coated) when the surface area increased (0.97 m^2/g for uncoated; 4.42 µm for coated).

3.2. Adsorption of Cu^{2+} and Ni^{2+} with HA/QR Magnetic Nanoparticles

3.2.1. Optimization of Adsorption Parameters

In order to explain the adsorption characteristics of the synthesized nanoparticles, some basic parameters such as pH, contact time should be examined. One parameter at a time procedure was employed during optimization experiments.

For the optimization of pH value, 2 mgL^{-1} Cu^{2+} and 3 mgL^{-1} Ni^{2+} solutions were prepared. 0.01g of synthesized nanoparticles were shaken with freshly prepared solutions at varying pH values for 10 min at 400rpm. Removal percentages were calculated using the equation given below.

$$\%Removal= [(c_i-c_f)/ c_i] \times 100 \qquad (1)$$

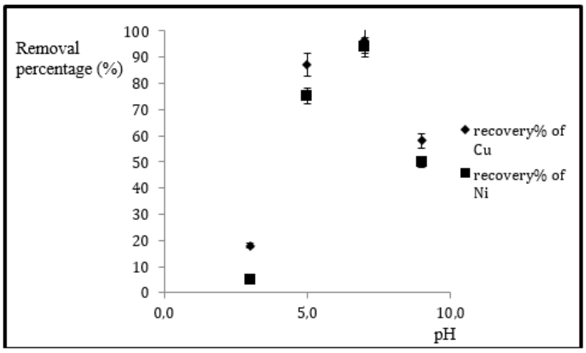

Figure 4. Effect of pH on Cu^{2+} and Ni^{2+} adsorption by HA/QR magnetic nanoparticles.

As it is seen from the graph above, maximum removal percentage of both metal is at pH=7. The most effective amount of adsorbent to be used in further adsorption experiments must be decided. For this purpose, 0.01g ; 0.02g, 0.03g and 0.04g of adsorbent were weighed. 2 $mgL^{-1}Cu^{2+}$ and 4 $mgL^{-1}Ni^{2+}$ solutions were prepared by accurate dilution of stock solutions. The particles were allowed to contact with the metal solutions for 10 min with a rotation rate of 400 rpm. in batch system. It is obviously seen from Figure 5 that, the maximum metal removal was obtained with 0.03 mg of nanoparticle. Afterward, the more particles used in batch system do not make a remarkable change in removal percentage.

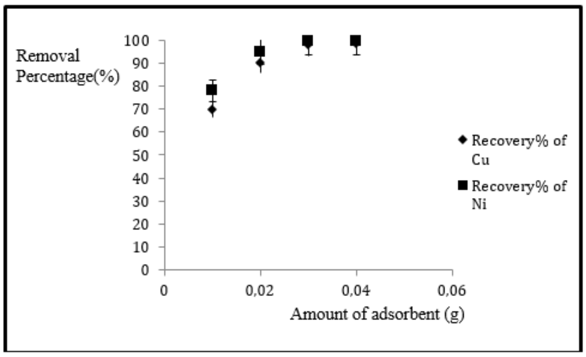

Figure 5. Effect of amount of HA/QR magnetite on Cu^{2+} and Ni^{2+} adsorption by HA/QR magnetite nanoparticles.

Using the adsorption parameters optimized in previous experiments (0.03 g of magnetite; pH=7), removal percentages of metals were calculated at increasing periods of time. For 30 min of contact time, it was observed that removal percentage reaches its maximum (99.5% for Ni; 98.0% for Cu^{2+}) and stays stable as time passes.

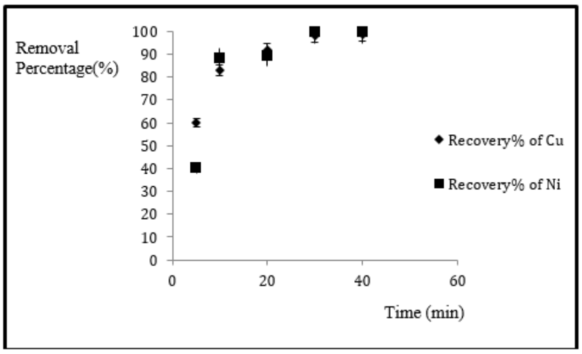

Figure 6. Effect of batch-wise contact time on Cu^{2+} and Ni^{2+} adsorption by HA/QR magnetite nanoparticle adsorption.

3.2.2. Adsorption Isotherms

Adsorption equilibrium must be well investigated and analyzed in order to have an opinion about the design of adsorption process. In this study Langmuir and Freundlich isotherm models were used to define the adsorption of metal ions by synthesized magnetite nanoparticles. For a more realistic approach to adsorption phenomena as a function of concentration, the concentration range was selected in geometric order (between 0.01-0.08 mgL^{-1}). Langmuir isotherm that represents the simplest theoretical model for monolayer adsorption is in the following form;

$$1/q_e = 1/Q_{max} + 1/\ Q_{max}\ K_L \quad (2)$$

where; $q_e = [(c_i - c_f)/V]\ /m \quad (3)$

In the equation given above; Q_{max} (Maximum adsorption capacity of the adsorbent) and K_L (Equilibrium constant represented in Gibbs free energy change of adsorption) represent the Langmuir adsorption parameters. The concentration terms c_i and c_f represent the initial and equilibrium concentrations of metals in solution, V represents the volume of solution and m stands for the amount of magnetite used during batch experiments.

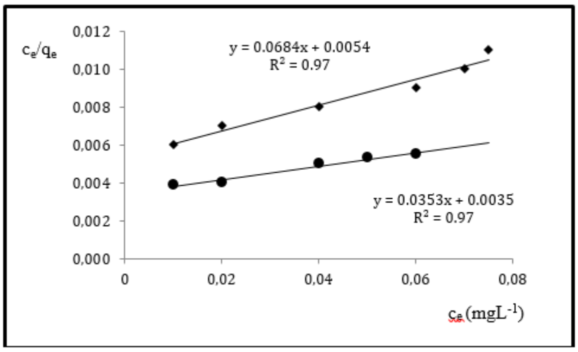

Figure 7. Linearized Langmuir isotherm graphs of Cu^{2+} and Ni^{2+} adsorption by HA/QR magnetite nanoparticles.

The Freundlich isotherm equation is as follows;

$$q_e = K_f \times C_e^{1/n} \quad (4)$$

may be linearized with a similar algorithm;

$$\ln q_e = K_f + 1/n \ C_e \quad (5)$$

Freundlich equation represents a line with a slope of 1/n and an intercept of K_f corresponding to the adsorption capacity and intensity, respectively[13].

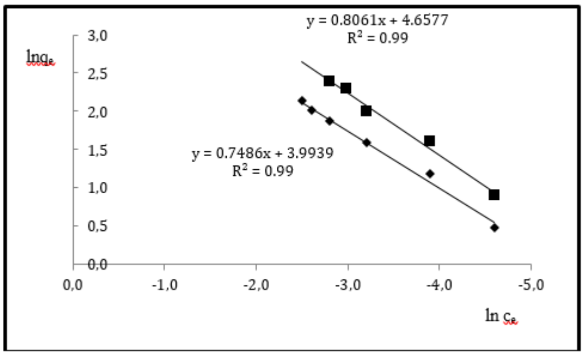

Figure 8. Linearized Freundlich isotherm graphs of Cu^{2+} and Ni^{2+} adsorption by HA/QR magnetic nanoparticles.

Freundlich equilibrium constants were determined from the graph drawn ln q_e versus ln c_e . In linearized Freundlich equation, n indicates the degree of nonlinearity[14]. When n is smaller than 1, adsorption process is assumed to be chemical phenomena; n value between 1 and 10 (which was calculated as 1.33 for Cu^{2+} and 1.24 for Ni^{2+}) adsorption is physical and good when considered [14-16].

Taking the advantage of the linearized isotherms shown in Figure 7 and Figure 8, Langmuir and Freundlich isotherm equations for batch adsorption of Cu^{2+} and Ni^{2+} metals were obtained and summarized in Table 1.

Table 1. Parameters of Linearized Langmuir and Freundlich Isotherm.

	Parameters obtained by Langmuir Isotherm				Parameters obtained by Freundlich Isotherm			
Metal Adsorbed	Langmuir Isotherm Equation	Slope $^{-1}$ of Linearized Langmuir Isotherm	K_L	R^2	Freundlich Isotherm Equation	Slope $^{-1}$ of Linearized Freundlich Isotherm	K_f	R^2
Cu^{2+}	$Q_e = 6.84\times10^{-2}$ (1+ 0.079) c_e	Q_{max}=14.61 mg/g adsorbent	12.67 L/mg	0.97	$Q_e = 3.99c_e^{0.75}$	n= 1.33 mg/g adsorbent	3.99 L/mg	0.99
Ni^{2+}	$Q_e = 3.53\times10^{-2}$ (1+ 10.09) c_e	Q_{max}=28.30 mg/g adsorbent	10.08 L/mg	0.97	$Q_e = 4.65c_e^{0.81}$	n=1.24 mg/g adsorbent	4.66 L/mg	0.98

When Table 1 is inspected carefully, one can see that the adsorption models of Cu^{2+} and Ni^{2+} metals by HA/QR magnetic nanoparticles are well fitted to both isotherm models (when the regression coefficients were taken into consideration). However, the overall data are slightly better fitted to Langmuir isotherm for both metals.

4. CONCLUSION

In this study, HA/QR magnetite nanoparticles were synthesized for the adsorption of metals from aqueous systems, as the first time in literature. Fe_3O_4 magnetic nanoparticles are rather preferred for their easy to operate properties at batch-wise adsorption process. The particles were coated with humic acid, for longtime usage. Considering economical issues in large-scaled installation of newly synthesized nano-composite materials, long-term usage is another issue to be evaluated. In previous studies found in literature, the nanoparticles were coated with many different polymers to be more stable[17-18]. However, humic acid, which is a natural, biodegradable and environmentally friendly polymer was installed for the first time within this assay. At the second step of coating, quercetin was chosen as the hydroxyls on the molecule may enhance the adsorption capability of HA/magnetite nanoparticles. And more than it was presumed, the particle size analyses showed an obvious decrease from 17.53 µm to 1.59 µm at diameters. The synthesized particles were measured to have a diameter of 40 nm. and used in adsorption experiments. Batch-wise adsorption process was easily operated with HA/QR magnetite nanoparticles taking the advantage of their magnetic behaviors. The adsorption isotherm of Cu^{2+} and Ni^{2+} -as model metals- fitted both to Langmuir and Freundlich isotherm models. The optimal removal of metals occurred contacting metal solutions with only 0.03 g adsorbent at pH=7, for 30 min. There are many studies found in literature introducing new composite materials for the adsorption of metals [19- 21] This study shows superiority to others, obtaining high removal percentages (99.5% for Ni; 98.0% for Cu^{2+}) at neutral pH values by installing a biodegradable and eco-friendly material as adsorbent.

ACKNOWLEDGMENTS

Thanks to Erciyes University Scientific Research Project (BAP) Department who supported this work under the project number FBD-10-3313.

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