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Research Paper / Araştırma Makalesi

Nickel and Copper Removal from Aqueous Media using Polyaniline/Sugar Beet Pulp (PANI/SBP) Composite

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ABSTRACT

In this study, polyaniline/sugar beet pulp (PANI/SBP) composites were synthesized, and the potential use of composites was determined for the removal of copper [Cu (II)] and nickel [Ni (II)] from wastewater. The structural and morphological properties of composites were determined by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM), respectively. The metal removal of composites from aqueous solutions was monitored by Ultraviolet Visible Absorption Spectrometer (UV-Vis). At this stage, some parameters, such as adsorbent dosage, stirring speed and contact time, the initial concentration of metal solutions and pH, were changed, and the most suitable condition was selected for metal removal. Metal removal from wastewater was determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) at optimum conditions. FTIR and SEM results supported the formation of PANI/SBP composites. Under optimum conditions, ICP-OES results for wastewater treated with PANI/SBP composite showed that this composite can be used for the removal of copper and nickel from wastewater.

Keywords: Polyaniline, Sugar beet pulp, Copper, Nickel, Adsorption

Polianilin/Şeker Pancarı Posası (PANI/SBP) Kompoziti Kullanılarak Sulu Ortamdan Nikel ve Bakırın Uzaklaştırılması

ÖZ

Bu çalışmada polianilin/şeker pancarı posası (PANI/SBP) kompozitleri sentezlenmiş ve atık sudan bakır ve nikelin uzaklaştırılmasında kompozitlerin potansiyel kullanımı araştırılmıştır. Kompozitlerin yapısal ve morfolojik özellikleri sırasıyla Fourier Dönüşümü Kızılötesi Spektroskopisi (FTIR) ve Taramalı Elektron Mikroskobu (SEM) ile incelenmiştir. Sulu çözeltilerden metal uzaklaştırma çalışmaları Ultraviyole Görünür Absorpsiyon Spektrometresi (UV-Vis) ile izlenmiştir. Bu aşamada adsorban dozajı, karıştırma hızı ve karıştırma süresi, metal çözeltilerin başlangıç konsantrasyonu ve pH gibi bazı parametreler değiştirilerek metal uzaklaştırma için optimum koşullar belirlenmiştir. Atık sudan metal uzaklaştırma çalışmaları, Endüktif Olarak Eşleştirilmiş Plazma Optik Emisyon Spektrometresi (ICP-OES) ile optimum koşullarda gerçekleştirilmiştir. FTIR ve SEM sonuçları, PANI/SBP kompozitlerinin oluşumunu desteklemektedir. Optimum koşullarda, PANI/SBP kompoziti ile muamele edilmiş atık su için elde edilen ICP-OES sonuçları, kompozitin atık sudan bakır ve nikelin uzaklaştırılmasında kullanılabileceğini göstermiştir.

Anahtar Kelimeler: Polianilin, Şeker pancarı posası, Bakır, Nikel, Adsorpsiyon

INTRODUCTION

Some cellulosic agricultural waste materials such as sugarcane bagasse, rice husk, sawdust, coconut husk, etc., have been used as cost-effective sorbents for the removal of heavy metals from industrial waste water due to their several advantages [1-4]. They have some functional groups to bind metal ions (i.e. caboxylic and hydroxy). Modification of these materials can be made easily with various chemicals and materials to increase the adsorption capacity. Sugar beet pulp (SBP) is one of these cellulosic waste materials. SBP is the remaining waste material after taking as many crystals as possible from sugar beet syrup prepared in factories under technological and economic conditions. This waste material is used substantially for animal feeding. SBP consist of functional groups associated with heavy metals binding. Especially carboxyl groups have a great biosorption and heavy metal removal potential capacity [5]. So that, the sugar beet pulp has been widely used in many studies for heavy metal removal [6-8].

Water pollution by heavy metal ions is increasingly becoming a major environmental problem because of the high toxicity of some of these elements and their tendency to accumulate through the food chain due to their high solubility in the aqueous phases, affecting all living organisms in a given ecological system. In the recent years, a great number of adsorptive materials have been used as effective materials for heavy metal removal. Among these materials there has been an increase research interest in the use of conductive polymers such as polyaniline (PANI) in the removal of heavy metals [9, 10]. The advantages of PANI are different structures, special doping mechanism and excellent environmental stability of PAn. Additionally, aniline is cheap and polyaniline can be easily prepared and coated chemically on cellulosic substrates [11-13]. These distinctive properties of PANI make it a good candidate for metal adsorption on it.

The aim of this study was to determine the potential use of PANI/SBP composite for the removal of Ni (II) and Cu (II) from aqueous solution. The adsorption process was specifically designed with respect to the effect of factors such as pH, adsorbent dosage, contact time and initial concentration on metal removal. PANI/SBP composite was characterized structurally and morphologically by FTIR and SEM analysis, respectively. In addition, PANI/SBP was used for the removal of the Ni (II) and Cu (II) from industrial wastewater.

EXPERIMENTAL

Instrumentation

PANI, SBP and PANI/SBP composite were characterized by scanning electron microscope (SEM) and Fourier Transform Infrared (FTIR) spectroscopy in detail. The morphological structures of samples were determined by Philips XL 30S FEG model SEM (FEI-Phillips, Hillsboro, Oregon, USA). The structural analysis of samples was performed by Perkin-Elmer Spectrum BX model FTIR spectrometer (HP91Q) (PerkinElmer, Waltham, Massachusetts, USA). Adsorption studies were monitored by PG Instruments Limited T60UV model UV-Vis spectrometer (PG Instruments Limited, UK). Metal treatment of PANI/SBP composite was achived by Bandelin Sonorex RK 52 model ultrasonic bath (Bandelin Electronic Co., Berlin, Germany). pH measurents were performed by Hanna Instruments 2211 pH/ORP model pH meter (Hanna Instruments, Smithfield, RI, USA). The real water sample was analized by Optima 8000 model Inductive Coupled Plasma Optic Emission Spectrometer (ICP-OES) (Perkin Elmer, CT, USA) to confirm the UV-vis analysis of sample.

Reagents and Solutions

Aniline (Sigma-Aldrich, St. Louis, MO, USA) was purified by distillation at reduced pressure before it was used. Nickel(II) chloride hexahydrate ($NiCl_2.6H_2O$) (Merck, Darmstadt, Germany) and Copper(II) chloride dehydrate ($CuCl_2.2H_2O$) (Merck, Darmstadt, Germany) were used without further purification. Ammonium peroxydisulfate ($(NH_4)_2S_2O_8$), was purchased from Merck (Darmstadt, Germany). Double-distilled water was used for preparation of solutions. Methanol was purchased from Merck (Darmstadt, Germany).

Synthesis of Polyaniline

The ratio of monomer to oxidizing agent was 2. Aniline (2 mmol) was dissolved in 125 mL 1 M H_2SO_4. The solution was maintained in an inert N_2 atmosphere during 15 minutes. Polymerization was initiated by the drop wise addition of (1 mmol) ammonium peroxodisulfate ($(NH_4)_2S_2O_8$) as the oxidizing agent in 125 mL 1 M H_2SO_4 under constant stirring at 0-5°C. The reaction mixture was kept under constant stirring for 4 h. After polymerization period methanol was added to the mixture to precipitate the composite. The precipitated polymer was filtered and washed in goach crucible with distilled water prior to filtration. Finally, the composite was dried at 50°C for 24 h under vacuum environment.

Synthesis of Polyaniline/Sugar Beet Pulp Composite (PANI/SBP)

Sugar beet pulp was dried and ground until getting shape like flour (Figure 1). Then, 2.5 g ground sugar beet pulp was added into 125 mL 1 M H_2SO_4 solution containing 2 mmol aniline. After that stage, polymerization process was same with polyaniline. Synthesized composite was stored at room temperature for use in adsorption studies.

(a) (b)

Figure 1. (a) Dried and (b) ground sugar beet pulp

Batch Experiments for the Removal of Nickel and Copper from Aqueous Media

To conduct adsorption studies, Ni(II) (50 mg/L) and Cu(II) (50 mg/L) solutions were prepared in distilled water. To examine the influence of pH on the adsorption properties of PANI/SBP, 25 mL of Cu (II) and Ni (II) aqueous solutions at different pH were taken and 0.20 g PANI/SBP was added on it and mixed for 45 minutes at room temperature. Then, the mixture was filtered and heavy metal ion concentrations in the filtered solution were determined by UV-Vis technique. After determining the appropriate pH value, a calibration graph was prepared and experiments were repeated by changing contact time, stirring speed, adsorbent dosage and initial concentrations. All experiments were duplicated. The removal efficiencies of the Ni (II) and Cu(II) ions were determined using the following expression (1):

$$\text{Removal efficiency} = [(C_0-C_e) / C_0] \times 100 \quad (1)$$

where C_0 (mg/L) and C_e (mg/L) are the initial and final concentrations (at any time) of Ni(II) and Cu(II) ions before and after adsorption, respectively. The pH of the metal solutions was adjusted using saturated HCl or NaOH solutions. The working ranges for optimized parameters were shown at Table 1.

Table 1. Working ranges for studied parameters

Parameters	Ni(II)	Cu(II)
pH	6-8	4-7.5
Adsorbent dosage (g)	0.03-0.10	0.05-0.20
Contact time (min)	30-60	15-60
Mixing speed (rpm)	200-400	200-400
Initial concentration (mg/L)	25-75	25-75

Ni (II) and Cu(II) Removal from Wastewater

The adsorption capacity of PANI/SBP composite was tested at optimum conditions for real wastewater and the results monitored with the ICP-OES instrument. The Ni(II) and Cu(II) contaminated wastewater was received from the Organized Industrial Region, Burdur, Turkey. Experiments were performed to purify 25 mL wastewater by applying the optimum conditions.

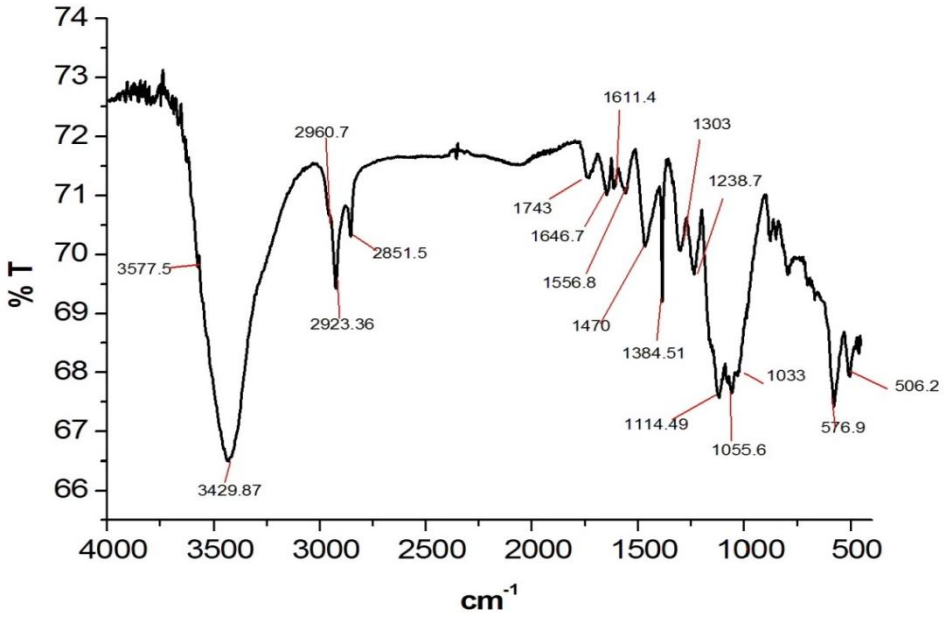
RESULTS and DISCUSSION

Characterization

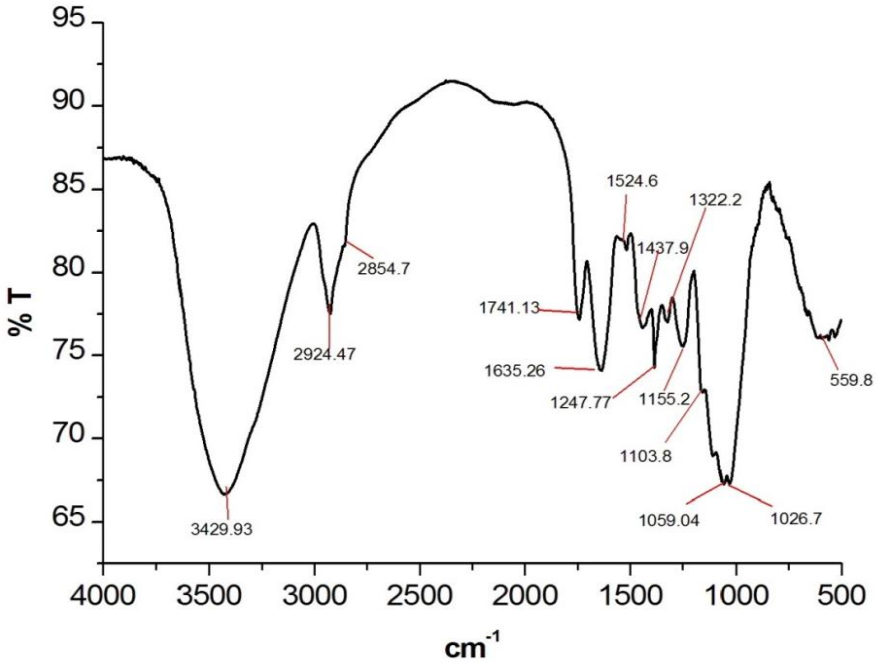
FTIR Results

Structural characterizations of PANI and PANI/SBP composites were obtained by FTIR analysis (Figure 2a-c). FTIR spectra show that both quinoidal and benzoid stretching clearly exist which indicating the polymer is in the form of emeraldine base (EB) [14]. Base form of PANI has five important regions in FTIR; the first region is attributed to N-H stretch in benzenoid-N-H-benzenoid units (B-NH-B) in the range of 3500-3100 cm^{-1}. The main absorbance peaks are located at 3429 cm^{-1} and 3430 cm^{-1} in this range for PANI and PANI/SBP, respectively. The second region is in the range of 3100-2800 cm^{-1} which shows the C-H stretch. The absorbance of PANI is even weaker in this region (Figure 2b). The third region is from 1600 to 1450 cm^{-1}; aromatic ring stretch, N-H deformation and C=N stretch are vibrations that give absorption in this region. The bands at 1556 cm^{-1} and 1632 cm^{-1} which are seen in PANI/SBP composite spectrum are belong to benzenoid ring stretch and quinoid ring stretch (Figure 2c). The fourth region is belonges to C-N stretch (from 1400 to 1240 cm^{-1}) for aromatic amines. Self-conducting PANI shows three characterisic peaks in this region which are at 1303 cm^{-1}, 1384 and 1238 cm^{-1}. These bands are seen in the PANI/SBP composite at 1309, 1384 and 1238 cm^{-1}, respectively. The last region is from 1200 to 500 cm^{-1}, that is the C-H in-plane and out-of-plane

bending vibrations in aromatic rings. For intrinsic conducting PANI, the main absorbance bands are located at 1150 and 800 cm^{-1} and some other bands can also be seen [15, 16]. The band at 1114 cm^{-1} for PANI is described as the 'electronic-like band' by the MacDiarmid group and is considered as a measure of the degree of delocalization of electrons on the PANI [17]. It can be evaluated as the characteristic band of PANI conductivity [18]. This band is around 1155 cm^{-1} in composite. The bands at about 800 cm^{-1} and 500 cm^{-1} are due to the C-H out-of-plane bending and the aromatic ring deformation, respectively. The band at 1741 cm^{-1} in the spectrum of SBP was attributed to ester groups of hemicelluloses and the ester linkage of carboxylic groups in lignin [19]. The band referred to benzenoid ring stretch and quinoid ring stretch at 1646 cm^{-1} for PANI shifted to 1632 cm^{-1} for PANI/SBP composite. Similarly, the band at 1055 cm^{-1} that belongs to C-H in-plane and out-of-plane bending vibrations in aromatic ring for PANI shifted to 1051 cm^{-1} for composite. As a result, it is supported by FTIR results that PANI forms PANI/SBP composites by being properly coated on sugar beet pulp by a chemical polymerization method.



(a)



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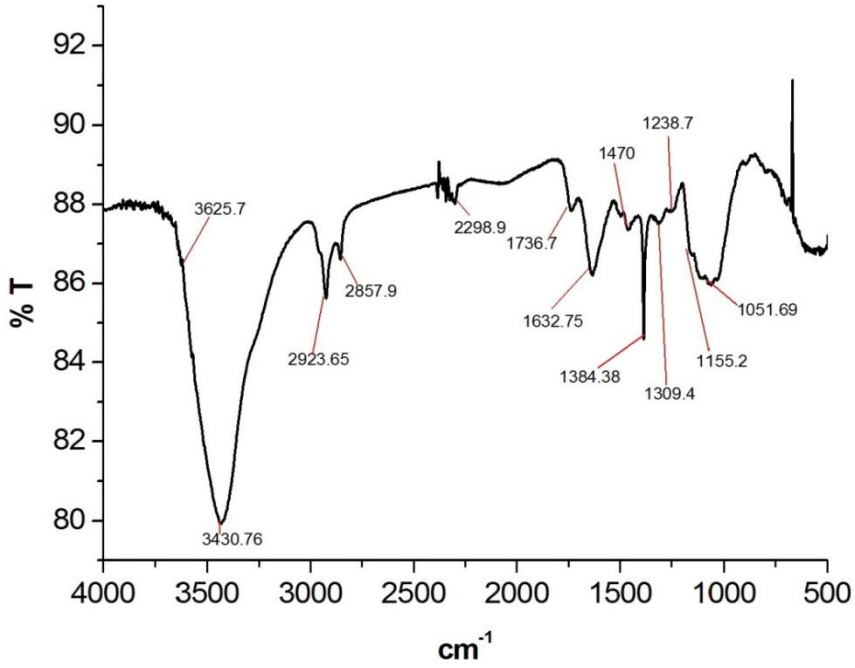

(c)

Figure 2. FTIR spectra of (a) Polyaniline (PANI), (b) Sugar beet pulp (SBP) and (c) PANI/SBP

SEM Results

SEM micrographs of PANI, SBP and PANI/SBP are shown in Figure 3(a-e). The SEM image of the PANI is shown in Figure 3(a), indicating that the material is made of capsule, granular and porous surface particles [20]. The micrograph of sugar beet pulp exhibits a homogeneous sponge-like native structure results from the destructuring undergone by the beet during the industrial sugar extraction process. The typical rectilinear cellulose fibrous structure was not observed (Figure 3b) [21]. When the surface morphology of PANI/SBP was examined, it can be seen that the PANI particles were homogeneously distributed in SBP morphology (Figure 3c). This structure supported the formation of composite. Besides, surface topography of PANI/SBP, before and after treated with metals was observed that the morphology was affected. After treating with Ni (II), minor changes in morphology were observed (Figure 3d). However, marked differences were observed between PANI/SBP and Cu(II) treated PANI/SBP (Figure 3e) such as a very rigid and solid surface structure.

Adsorption Studies

Effect of pH

The pH of the working solution is one of the most important parameters in the metal adsorption processes. Aqueous solution pH affect the chemical speciation of the metal ions and the surface charge characteristics of functional groups onto the adsorbent surface [22, 23]. The effect of pH on the adsoption of metal ions was studied and indicated in Figure 4a, b. The experiments were performed with different solution pH values ranged between 6-8 and 4-7.5 for Ni(II) and Cu(II), respectively.

It was observed that an increase in pH supports the removal of nickel metal until pH 7.5, and adsorption decreases above pH 7.5. Optimum pH value was determined as 7.5 for Ni(II). This optimum pH value is in harmony with the literature [24]. It was that pH increase negatively affects the removal of copper metal from aqueous solutions, and the highest removal is at pH 4. In the adsorption experiment, when the pH value was greater than 7, there was a significant decrease in the adsorption percentage. The reason for this is that if the pH value is greater than 7, the OH- ion dominates and creates competition for OH- and Cu (II) ions between the adsorbent surface and the solution. As a result, the adsorption of Cu (II) ions on the surface decreases. This result is in good agreement with some previous studies [25]. It is seen that the adsorption of Cu (II) ions at pH 4 is 55.01% and at pH 5 it is 52.45%. Since there is not much difference between the adsorption values of pH 4 and pH 5, the optimum pH was determined as 5.

Effect of PANI/SBP Dosage

Adsorbent dosage is one of the most important variables, which specifies the capacity of an adsorbent for metal solutions at optimum condition. After determining the optimum pH values, the effect of adsorbent dosage on the removal of metal ions was investigated (Figure 5). The effect of different adsorbent dosages on the removal of Ni (II) and Cu (II) from copper and nickel solutions at the initial concentration were investigated. Maximum adsorption values were determined by using different adsorbent dosages at optimum pH. Adsorbent dosage was tested in the range

of 0.05-0.2g in removing copper ions [25]. The optimum adsorbent dosage was determined as 0.15g. Adsorbent dosage was in the range of 0.03-0.1g for the removal of nickel ions [24]. Since 94.88% of nickel ions are removed at 0.05g, the optimum adsorbent dosage was determined as 0.05g. The removal of Ni (II) ions decreases after 0.05 g PANI/SBP. This may be due to the fact that the adsorption capacity is not fully utilized at higher adsorbent dosages in comparison to lower adsorbent dosages. These results may be due to the overlapping of the adsorption sites as a result of overcrowding of adsorbent particles [26].

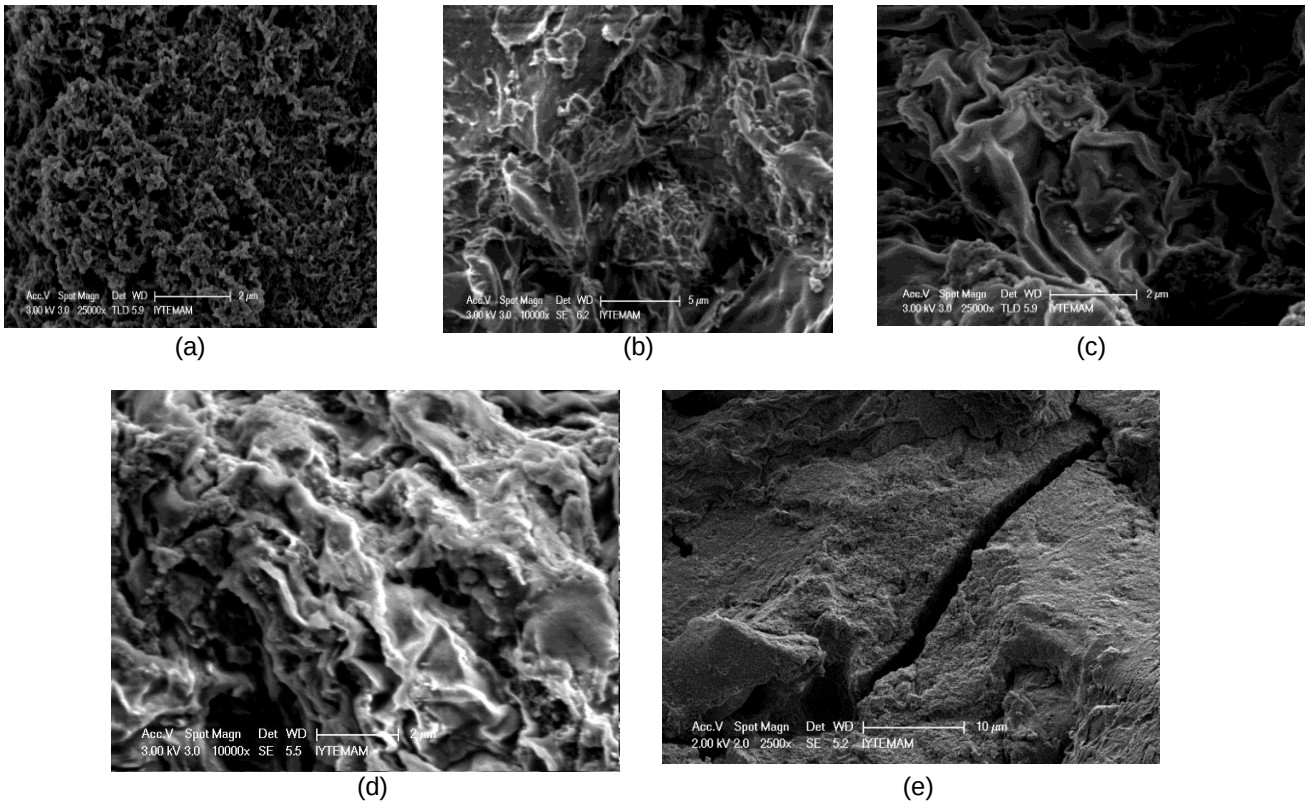

Figure 3. SEM images of (a) PANI, (b) SBP, (c) SBP/PANI, (d) SBP/PANI treated with Ni(II) and (e) SBP/PANI treated with Cu(II)

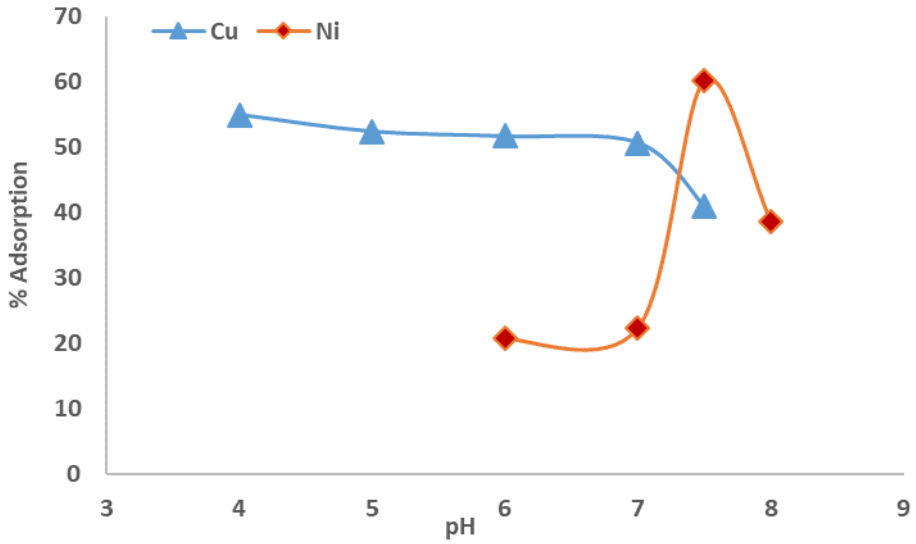

Figure 4. Effect of pH on the removal of Ni(II) and Cu(II) ions

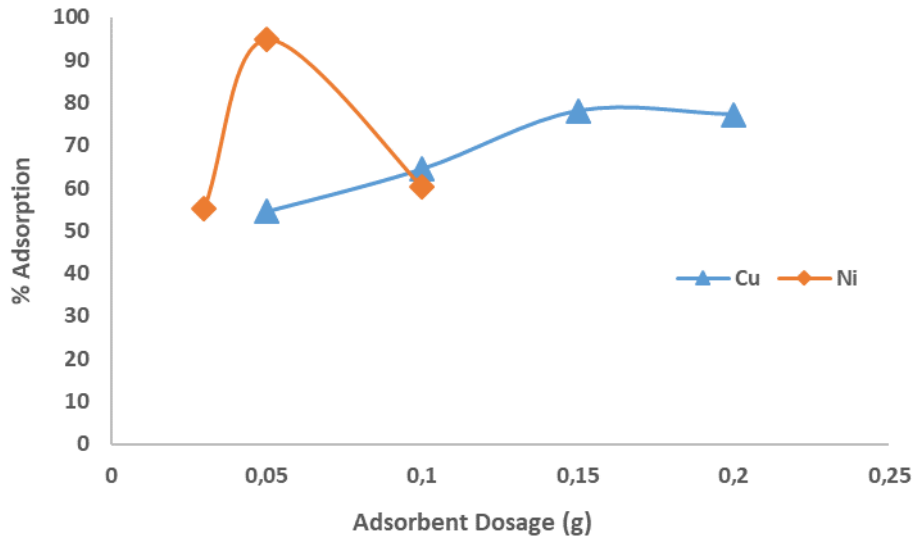

Figure 5. Effect of polyaniline/sugar beet pulp (PANI/SBP) dosage on the removal of Ni (II) and Cu (II)

Effect of Stirring Speed

The effect of mixing speed on adsorption was investigated by keeping the optimum pH and optimum adsorbent dosages constant for nickel and copper solutions. Optimization was completed by changing the mixing speeds in the range of 200-400 rpm (Figure 6). Adsorption values increased at 300 rpm according to 200 rpm for metal ions. The adsorption reduction that occurs at higher mixing speed than 300 rpm may be due to excessive agitation of the ions in the mixed solution. Higher stirring speed may reduce the adsorption by increasing the repulsion forces on the adsorption surface. The attraction between PANI/SBP and metal ions may be reduced by these forces [27]. Thus, the optimum stirring speed for the removal of both metal ions was determined as 300 rpm.

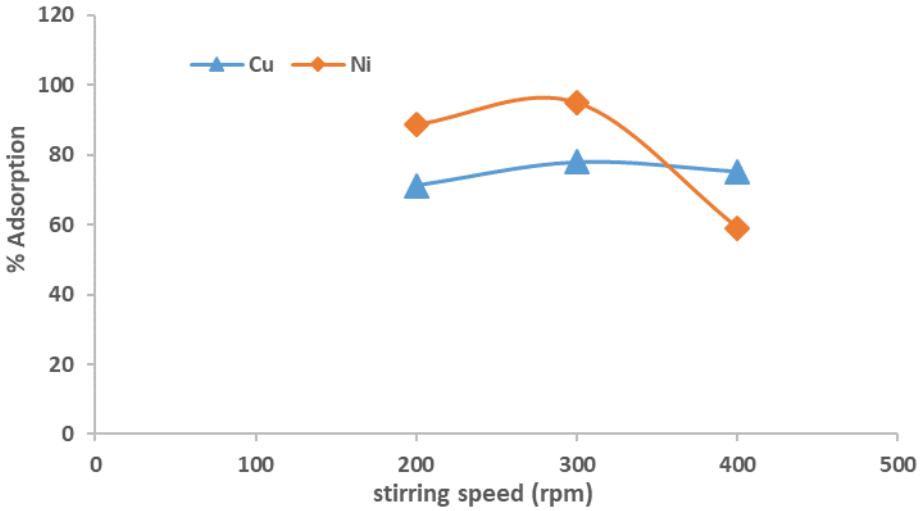

Figure 6. Effect of stirring speed on the removal of Ni (II) and Cu(II)

Effect of Contact Time

In order to investigate the effect of mixing time on the removal of metal ions, the effect of different mixing times on adsorption at initial concentrations, optimum pH, adsorbent dosage and mixing speed was investigated. Figure 7 indicates the effect of the contact time on the removal efficiency of Ni(II) and Cu(II). The mixing time was changed in the range of 15-60 minutes to remove copper ions. While there was an increase in metal removal up to 30 minutes, a decrease was observed over 30 minutes and the optimum time was determined as 30 minutes. It worked well within 30-60 minutes for the removal of nickel ions. It was observed that metal removal decreased between 30 and 45 minutes, and metal removal increased between 45 and 60 minutes. Since 94.88% metal was removed in 60 minutes, there was no need to increase time further and the optimum time was determined as 60 minutes.

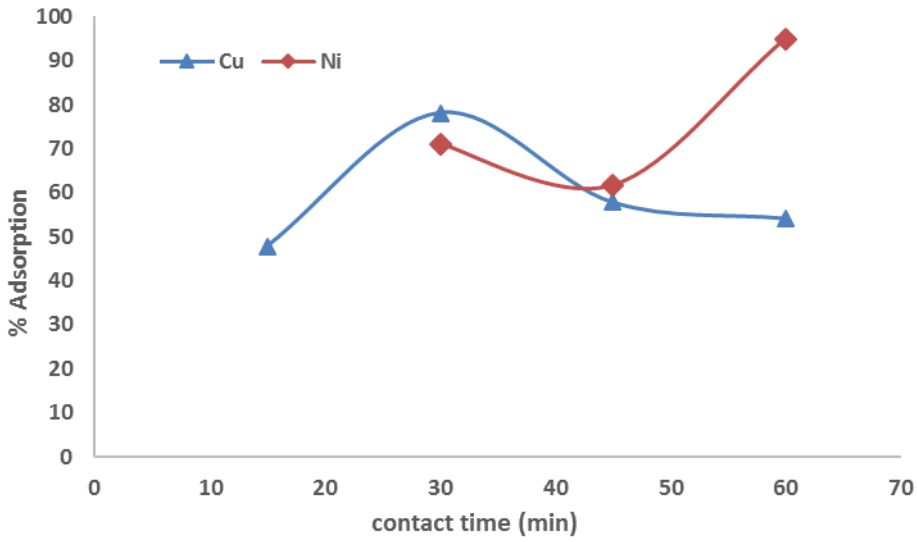

Figure 7. Effect of contact time on the removal of Ni (II) and Cu (II)

Effect of Initial Concentration

Figure 8 shows that the metal ion adsorptivity depended on the initial Ni (II) and Cu (II) ions concentrations. The initial metal ion concentration appears to be an important factor driving ionic mass transfer between the aqueous phase and the adsorbent [28]. After determining the optimum pH, adsorbent dosage, mixing speed and contact time, the effect of initial concentration on the removal of metal ions was examined. Metal removal studies were carried out by changing the solution concentrations 25 to 75 mg/L. The optimum initial concentration was determined as 50 mg/L for both metals.

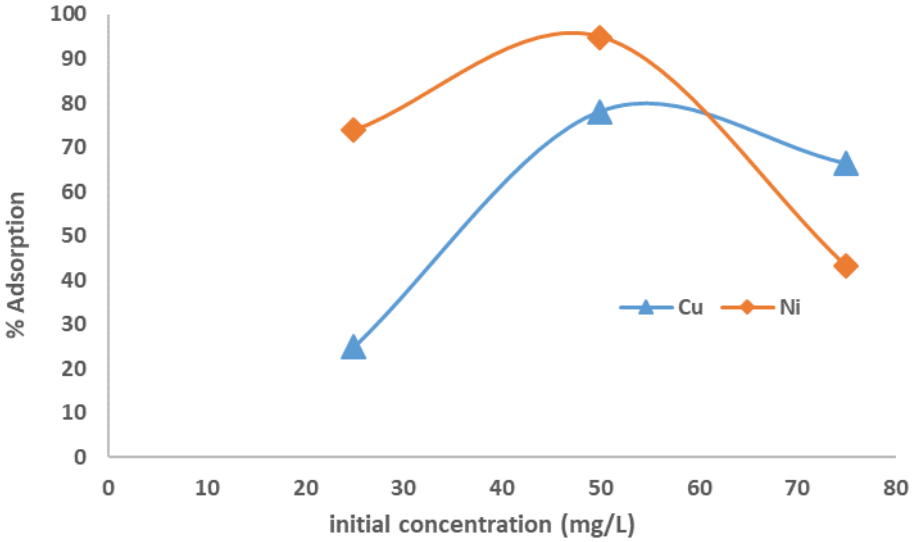

Figure 8. Effect of initial concentration on the removal of Ni (II) and Cu (II)

Waste Water Studies

The adsoption performance of PANI/SBP was tested for the industrial wastewater sample supplied from organized industrial region in our city (Burdur, Turkey), contaminated by metal cations from industrial activities using ICP-OES. The real water samples were only filtered through a filter paper prior to analysis. Experiments were performed to treat 25 mL wastewater by applying the optimum conditions given in Table 3.

In addition, metal adsorption percentages were compared by treating the real water sample with both SBP and PANI/SBP under optimum conditions, and it was determined that the composite retained Ni (II) and Cu (II) metal ions better. SBP adsorbed 75% and 65% of Ni (II) and Cu (II), respectively, while the composite adsorbed 95% and 78%. Table 4 shows the ICP-OES parameters for Ni (II) and Cu (II) standart solutions calculated from the calibration curves of metal ions and maximum adsorption values of metals (%Ads) with PANI/SBP in wastewater.

Table 3. The optimum conditions to remove Ni(II) and Cu(II) from aqueous solutions and the maximum adsorption percent of adsorbents

Parameters	Ni(II)	Cu(II)
pH	7.5	5.0
Dosage (g/50 mL)	0.05	0.15
Stirring speed (rpm)	300	300
Contact time (min)	60	30
Initial concentration (mg/L)	50	50

Table 4. ICP-OES parameters of Ni (II) and Cu (II) standart solutions

Element	Dalga Boyu (nm)	LOD (µg/L)	R^2	Max adsorption (Ads%) with PANI/SBP
Ni(II)	231.604	5.0	0.999	45
Cu(II)	327.393	2.5	0.999	72

According to the ICP-OES results, Ni(II) and Cu(II) removal from wastewater in terms of percent removal were calculated almost 45% and 72%, respectively. The removal percent of Ni(II) was lower than Cu(II) using PANI/SBP composite. It was suggested that PANI/SBP composite had a higher selectivity of Cu(II) ions than that of Ni(II) ions [29, 30]. As a result, PANI/SBP is an efficient and cost-effective adsorbent for the removal of Ni (II) and Cu(II) from industrial wastewaters.

CONCLUSION

PANI/SBP composite was synthesized successfully in aqueous media by the chemical polymerization and the adsorption ability of produced adsorbent was studied in the aqueous media for the Ni(II) and Cu (II) ions. The composite formation was investigated with FTIR and SEM techniques. FTIR results supported that PANI formed PANI/SBP composites by coating sugar beet pulp properly. SEM images supported that the granular and porous PANI was coated on sugar beet pulp, whose micrograms were crystalline, and a composite with a new morphology was formed. After the optimization of some important parameters (pH, adsorbent dosage, contact time, mixing speed, initial concentration of metal solutions), removal efficiencies were found to be 95% and 78% for Ni (II) and Cu (II), respectively. In conclusion, the effectiveness of PANI/SBP composite was good for the removal of Ni (II) and Cu (II) from wastewater.

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