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Copper removal from ammoniacal spent etchant by using magnetic nanoparticles

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ABSTRACT

Using magnetic nanoparticles (MNPs) is becoming popular method to remove heavy metal ions from different waste streams because it is simple, low-cost and effective. In this study, the bare and polymer coated Magnetite Iron Oxide (Fe_3O_4) MNPs were assessed for their adsorption capability in removing cupric (Cu^{2+}) ions from ammoniacal spent etchant solution, which is originated from the production of Printed Circuit boards (PCBs). The polymers used to coat the MNP in this study were chitosan, levan and oleic acid. The batch adsorption experiments were conducted at a temperature of 20oC and the pH of the solution was between 9.0 and 9.5. Experimental results showed that adsorption was achieved within 2 hours, and the maximum amount of Cu^{2+} ions adsorbed by unit weight of MNP was observed by chitosan coated MNP with an adsorption capacity of 125 mg g^{-1}. In addition, Zeta potential measurements showed that all MNPs used in adsorption tests had negative surface charges at around pH 9.0. The more negatively surface charge MNPs the more copper ions they can adsorb. From this experiment it can be concluded that chitosan coated magnetic nanoparticle can be widely used for the removal of copper ions from water and wastewaters.

Keywords: Copper adsorption, magnetic nanoparticles, printed circuit boards, spent etchant

1. INTRODUCTION

Heavy metals released into the environment from industries like plating plants, mining, metal finishing, welding and alloy manufacturing pose a significant threat to the environment and public health [1]. Unlike some organic pollutants, heavy metals cannot be degraded into lower-toxic substances and, therefore, they can accumulate in soil and water reservoirs, leading to harmful effects on living species via the biological accumulation of food chain [2]. The metals that cause serious pollution and toxicity problems include chromium (Cr), mercury (Hg), copper (Cu), nickel (Ni), zinc (Zn) and cadmium (Cd) [3].

Copper, which is a common harmful heavy metal ion in industrial wastewaters, is one of the essential elements that are required to maintain the normal structure and function of cells. However, excessive amount of copper can cause abnormal metabolism [4]. The consumption of water that contains copper at concentrations more than the permissible level of 2

mg L^{-1} could cause stomach and intestinal distress, anaemia, liver and kidney damage [5]. In addition, if copper is ingested excessively in human diet, it may result in vomit, cramps, convulsion, and even death [6]. According to the United States Environmental Protection Agency (USEPA) and the World Health Organization (WHO), the permissible levels for copper in drinking water are 1.3 and 2 mg L^{-1}, respectively [7].

One of the industrial wastewaters that contain high amount of copper in their effluents is Spent Etchant. The spent etchant solution, which is the waste product of etching operation from printed circuit board (PCB) industries, is a high concentration hazardous waste [8]. PCBs are important components of modern electronic products, which have generated 40 billion of US dollars globally in 2009 [9]. The PCB processes result in the production of around 0.7 million m^3 of the waste yearly if keeping using the conventional way of maintaining constant etching rate, known as chemical regeneration [10]. PCBs use

around 28% of metal content, 10–20% of which is copper, 1–5% is lead and 1–3% is nickel [11].

The manufacture of PCBs involves several technical processes, and etching is one of the most important steps. According to the design of PCB, the unmasked copper is chemically dissolved into the etchant and the desired circuit pattern is produced. Numerous etching solutions have been used including ferric chloride, chromic acid, sulfuric acid, hydrogen peroxide, acidic copper chloride and ammoniacal (alkali) etchant solutions. Among these, the ammoniacal etchant solution presents advantages of fast etching, stability and high efficiency, so it is widely used in PCB process [12].

Spent ammoniacal etchant solution is a hazardous solution produced when copper is etched with ammoniacal etchant. This waste solution is alkaline solution at a pH of 8.5-9.5, having a typical copper concentration of 130-160 g L^{-1}, a chloride concentration of 175-190 g L^{-1}, ammonia concentration of 170-201 g L^{-1} and a molar ratio of ammonia to copper 4:1. Usually the solution contains also trace quantities of organic and/or inorganic chemical additives required for the etching process [13].

The presence of ammonia and other heavy metals in the solution make it hazardous and cause health and environmental problems. The most difficult problem of the solution is caused by due to the complex formed between copper and ammonia. Tetraamminecopper (II) ion [$Cu(NH_3)_4^{2+}$] is the major complex specie formed in spent ammoniacal etchant. The complex is very difficult to break and prevents the precipitation of metal [14]. If this waste solution is discharged in to the environment without treating, it can cause a complicated environmental and health problems. Thus, the rapid and effective removal of Cu^{2+} from wastewater is among the most important issues in wastewater treatments.

Nowadays, adsorption of Cu^{2+} ions on magnetic nanoparticles is becoming popular to remove copper from different waste streams because it is simple, low-cost and effective. Therefore, the aim of this study is to assess bare and polymer coated Fe_3O_4 MNP for their adsorption efficiencies of Cu^{2+} ions from ammoniacal spent etchant wastewater. The polymers used to coat the MNP in this study were chitosan, levan and oleic acid. In this work, the synthetic ammoniacal spent etchant (copper stock solution), MNP and levan were produced in Marmara University Environmental, Metallurgical and Materials, and Bioengineering departments respectively.

2. MATERIALS AND METHODS

In this work, hydrated copper chloride ($CuCl_2.2H_2O$) and ammonia (NH_3) were used for the synthesis of copper stock solution to simulate the waste effluent generated from the etching stage of PCB. Whereas, Iron (II) chloride (0.5 Molar), iron (III) chloride (0.5M), ammonium hydroxide (NH_4OH) (4M) and ethanol were used for the preparation of MNP. Levan polymer was produced from *Halomonas smyrnensis* AAD6^T, which is a Gram-negative, aerobic,

exopolysaccharide-producing, and moderately halophilic bacterium.

The detailed description for the synthesis of copper stock solution was as follows: 16.1142 grams of $CuCl_2.2H_2O$ and 28.2 mL of NH_3 (25%) solutions were mixed in 2L of ultra pure water. The mixture was stirred by magnetic stirrer for 20-30 minutes at room temperature. Finally the mixture turned to blue color, which is the true color of spent ammoniacal etchant.

The synthesis of Fe_3O_4 MNP was clearly described in the following procedures: 20.3 g of 0.5 M ferric chloride ($FeCl_3$) and 9.94 g of 0.5 M ferrous chloride ($FeCl_2$) were added in to two different beakers containing 150 and 100 mL of distilled water respectively and stirred with magnetic stirrer at 250 revolutions per minute (rpm) for 5 minutes. Then, the two solutions were combined in another beaker and stirred again at 550 rpm for 5 minutes. After that 100 mL of 4 M NH_4OH was added until the pH was 9. Then the mixture was mixed with mechanical stirrer for 30 minutes. The solution was heated for 20 minutes till 70 ^{o}C and then cooled to room temperature. After cooling, the MNP was separated by using magnetic separation. The separated MNP was washed by distilled water and ethanol to remove all other contaminants. Finally the MNP was dried in furnace for 24 hours at 100 ^{o}C. Similar procedures were followed to prepare levan, oleic acid and chitosan coated MNPs in such away that the coating organic compounds were added and stirred at 550 rpm for 5 minutes before adding NH_4OH [15]. The structures of magnetite iron oxide, levan, chitosan and oleic acid are shown in Fig 1.
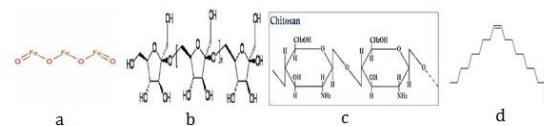
Fig 1. Structures of Fe_3O_4 (a), levan (b), chitosan (c) oleic acid (d)

2.1. Batch Adsorption Experiment

Batch adsorption experiments were carried out at 20 ^{o}C in aqueous solutions containing copper (II) ions. For this purpose, 50mL of stock solutions were added in to flasks containing 0.1, 0.2, 0.3, and 0.4 grams of MNPs. Blank samples were also prepared without the addition of MNP. All flasks were sonicated in ultrasound bath for 15 minutes. Batch adsorption experiments were conducted by using IKA KS 4000ic control shaker for two hours at 200 rpm and 20 ^{o}C. The initial and final pH was measured after sonication and shaking respectively and found to be between 9.0-9.5. After equilibrium was reached, the MNPs were separated from the solutions by magnetic separation technique and the supernatant was collected and filtered with syringes. 2% nitric acid was added to the supernatant to remove any black precipitation. 100 µL of supernatant was taken and diluted to 500 for the determination of the remaining copper ion concentration in the solution that was measured by Atomic Absorption Spectrometer (AAS). The amount

of copper ions adsorbed by unit weight of MNP was calculated by using equation 1.

$$q_{(t)} = \frac{(C_0 - C_t)}{m} \times V \tag{1}$$

where $q_{(t)}$ (mg g^{-1}) is the amount of copper ions adsorbed by unit weight of MNP; C_o and C_t (mg L^{-1}) are the initial and final Cu^{2+} ion concentrations respectively; V is the solution volume (L), and m (g) is weight of MNP.

3. RESULTS AND DISCUSSION

3.1. Adsorption Studies Results

Batch adsorption studies were conducted according to the procedures described above. The MNPs used in the adsorption studies were uncoated iron oxide, iron oxide coated with levan, oleic acid and chitosan. According to equation 1, the copper ions adsorbed by unit weight of the above mentioned MNPs were 69 mg g^{-1}, 46 mg g^{-1}, 66 mg g^{-1} and 125 mg g^{-1} respectively. The adsorbed copper ions (q_e, mg g^{-1}) versus equilibrium copper ion concentration in solution (C_e, mg L^{-1}) is given in Fig 2.
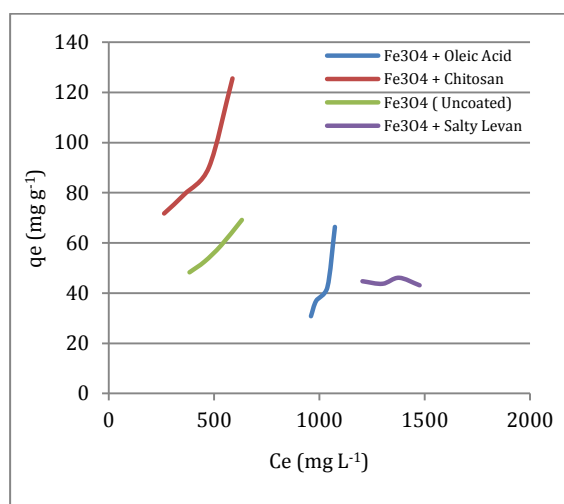

Fig 2. C_e vs q_e graph

From Fig 2, it was observed that the adsorption capacity increases with decreasing the mass of MNPs except for the MNP coated with levan which had almost constant adsorption value for all MNP masses. This indicates that levan coated MNP showed Langmuir adsorption that reached to maximum adsorption (q_{max}) which is a parameter in Langmuir adsorption isotherm. However, the MNP coated with oleic acid showed less adsorption behavior than even the uncoated MNP. The maximum amount of copper ions adsorbed by unit weight of MNP was observed by chitosan coated MNP with an adsorption capacity of 125 mg g^{-1}. This is due to the fact that the strong attraction between the negatively charged amine groups found on the surface of chitosan and the positively charged copper ions in the aqueous enable more copper ions be adsorbed on the surface of chitosan [16]. The values of the adsorption capacities found in this work is higher than many reported

results also using amino-functionalized MNPs (~27 mg g^{-1} [17]), (~30 mg g^{-1} [18]) and (~46 mg g^{-1} [19]). However, high adsorption capacity of copper (maximum 625 mg g^{-1}) was also reported using glycine-functionalized maghemite (γ-Fe$_2$O$_3$) MNP [20].

3.2. Zeta Potential

Zeta potential is the electrostatic potential at the shear surface. It is usually related to the stability of a colloidal suspension. A colloidal suspension is stable if the particles remain in suspension and do not coagulate. The colloidal stability depends on the relative magnitude of the forces of attraction and the forces of repulsion [21]. Zeta potentials were performed using titration method to check the binding of polymers onto Fe$_3$O$_4$. For this purpose, 0.03 g MNPs were dispersed in 600 mL deionized water and titrated to pH 2-10 using 0.1 M HCl or NaOH solution. The pH versus Zeta potential for the MNPs is shown in Fig 3.

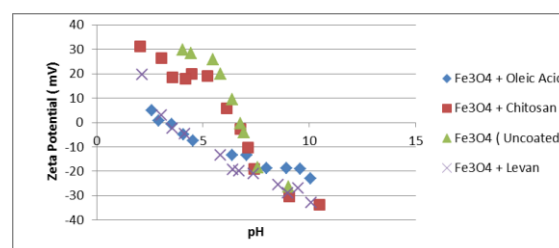**Fig 3.** *pH* versus *zeta potential*

From the results of Fig 3, it is observed that zeta potential of the magnetic nanoparticles decreases as pH increases because of the release of H$^+$ ions [22]. As a result, higher pH values can be preferred for adsorption of Cu^{2+} ions on the surface of the MNPs. The results also showed that all MNPs used in adsorption tests had negative surface charges at around pH 9.5, ranging between -20 mV (for oleic acid coated MNP) to -32 mV (for levan coated MNP). Higher pH makes the biomass surface more negative. The more negative the surface charge of the sorbent, the faster the removal rate of Cu(II) in the aqueous phase, since the binding of cationic Cu(II) ions species with the negatively charged groups is enhanced [23].

The effect of pH on metal adsorption is also explained in relation with the pH of point of zero charge (pH$_{pzc}$) that is obtained from zeta potential analysis. pH$_{pzc}$ represents the pH values where the net surface charge is zero. It is stated at pH higher than pH$_{pzc}$, the MNP surface is negative and metal adsorption is expected. But, when the pH is lower than pH$_{pzc}$, metal adsorption is reduced because the MNP surface is positive [24]. Based on the zeta potential results of Fig 3, the pH$_{pzc}$ of the uncoated Fe$_3$O$_4$ MNP was found to be around 6.6, which was consistence with the values reported in literature. After coated with the polymers, the pH$_{pzc}$ had been shifted to 6.4, 3.6 and 2.9 for the chitosan, levan and oleic acid coated MNPs respectively, showing that the coating of the polymers onto uncoated Fe$_3$O$_4$ MNP was successful. Moreover, magnetic nanoparticles modified with these polymers produce acidic surface since pH$_{pzc}$ is lower than that of

uncoated MNPs and this surface acidity is due to the introduction of several functional groups [25].

4. CONCLUSION

This study clearly reveals the potential of using bare and different polymer coated Fe_3O_4 MNPs as an excellent adsorbent for the removal of Cu (II) from aqueous solutions. The adsorption capacities of Fe_3O_4 nanoparticles were enhanced upon the surface modification polymers. The adsorption results showed that the highest copper ions adsorption was observed by the chitosan coated MNP, which was 125mg g^{-1}. This is due to the electrostatic attraction and complexation of copper ions with amine groups on the surfaces of the chitosan molecules. Moreover, zeta potential results showed zeta potential of the MNPs decrease with increasing pH and higher pH values is preferred for adsorption of copper ions on the surface of MNPs. In general the results obtained in this study were comparable with the literature values. Therefore, it is concluded that chitosan coated Fe_3O_4 MNP can be widely used in the removal of copper and other heavy metals from water and wastewaters.

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