Elimination of Copper and Nickel from Wastewater by Electrooxidation

Method

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Abstract: Electrooxidation method was used to remove copper and nickel from water by iron sacrificial sheets in an electrolytic cell. The effect of various voltages, electrooxidation time, and the initial pH of water has been studied on removal efficiency. The concentration of heavy metals before and after treatment was determined by an AAS instrument. The sludge obtained after treatment has been characterized using XRD, FESEM, and VSM. Our results show that the operational parameters play an important role on removal process. AAS results confirmed that the concentration of heavy metal pollutants in the water effectively decreases by increasing the applied voltage, electrochemical reaction time, or the initial pH of water. Based on these results it is possible to highly decrease the concentration of Ni or Cu from water at pH ~ 4.5 by applying ~ 28 V for 60 min. The FESEM images showed the nano-size of synthesized particles during water treatment. The element maps confirmed the presence of iron, oxygen, and heavy metal pollutants in precipitate after water treatment. The XRD patterns of powder sample obtained after removal of Ni or Cu show the reflections of Fe₃O₄ and some small peaks which are correspond to different compound of metal pollutants. VSM results showed that the sludge samples are magnetically soft and their specific magnetization depends on removal conditions. The magnetic property of the sludge samples helps to separate them easily from water using magnetic field.

Keywords: Copper; Nickel; Nano-sorbents; Electrooxidation; Wastewater treatment

1. Introduction

Water is the most essential substance for life on earth. Access to clean water is one of the most basic humanitarian goals, and it is a major global challenge for the current century [1]. With the rapid development and increased extension of factories, industries, and mining operations, heavy metals wastewaters are discharged into the surface and ground water and environment. Heavy metal ions as inorganic pollutants form a major class of environment contaminants. Most of the metal ions are known to be toxic and harmful agents to living organisms and they may cause serious health risks to the environment. Due to their high solubility in the aquatic environments, they can be easily absorbed by animals and plants and may accumulate in the human body by means of the food chain. Therefore heavy metal in wastewater has become one of the severe environmental concerns [2-8]. Due to the harmful effect of heavy metals in wastewater, it is very urgent and necessary to find an efficient, practicable, and advantageous method to treat wastewater containing toxic metal pollutants and remove their hazardous effects on human health and ecology. How to effectively and deeply remove toxic metals from wastewater is still a very important challenging task for environmental engineers and scientist [9]. In order to minimize the health risks of heavy metals pollutants from wastewaters many methods have been suggested by different research groups such as chemical precipitation, ion-exchange, membrane filtration, adsorption, electrochemical treatment [2-4,10-14].

Elimination of heavy metals from water has been traditionally carried out using chemical precipitation because of its simplicity and low cost. However, chemical precipitation is almost an ineffective technique when the concentration of metal ions in water is low. On the other hand, the chemical precipitation usually produces large amount of sludge and is not an economical method. Ion exchange is another technique which has been employed for removal of heavy metals from wastewater. A difficulty with this method is that the ion-exchange resins must be regenerated by chemical reagents and the regeneration process may cause serious secondary pollution. Also, this method is expensive and cannot be used for water treatment at large scale. Membrane filtration is an efficient method for removal of heavy metals from water, but membrane fouling and low permeate flux, process complication, and high cost are some problems which can limit the application of this technique in wastewater treatment. Adsorption has been known as an attractive, simple, and inexpensive route for removal of heavy metals from wastewater containing low concentration of pollutants. However, the adsorption efficiency highly depends on the type of adsorbents. Electrochemical technique is a process consisting electro-dissolution of a metal at the anode and production of hydrogen and hydroxide ions at the cathode. Some chemical and physical phenomena including

anodic oxidation, cathodic reduction, coagulation, electrophoretic migration, and adsorption occur in an electrochemical process. This method is known as a fast and well-controlled method that requires fewer chemicals and produces less sludge [2,6-9,15-18]. Recently many of scientists are focused on using the magnetic materials on removal of pollutants from water [19-24]. Although all above techniques can be employed for the wastewater treatment, many factors must be considered for selection of the most suitable treatment method such as removal performance, efficiency, flexibility, and safety. Also, the best removal method should be a fast, clean, inexpensive, and environmental friendly technique [2]. Electrooxidation is an efficient technique where the nanosorbents are generated in situ by electrooxidation of a sacrificial anode [25-28]. The generation of nanosorbents can be controlled by tuning the experimental parameters such as applied voltage, current, and time [17,18].

In this study we attempt to remove both copper and nickel ions from water in an electrolytic bath by electrooxidation. Here, the polluted water acts as the electrolyte and the electrodes are two iron sheets. By applying an appropriate potential difference between two iron plates in polluted water, the magnetic nano-sorbents with large surface area are generated in situ by electrolytic oxidation of iron anode and reduction of water at the surface of cathode. During electrooxidation of iron, charged ionic species are removed from wastewater by allowing ions to react with oppositely charged ions, or with nano-sorbents generated in the electrolytic bath. We are interested to study the influence of operational parameters such as applied voltage, removal time, and pH of water on removal efficiency of nickel and copper from water.

2. Experimental

2.1. Materials and Methods

Synthetic copper and nickel wastewater was prepared by dissolving a specific mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Merck Co.) into a known volume of deionized (DI) water, respectively. Two $1 \times 2 \text{ cm}^2$ and $2 \times 3 \text{ cm}^2$ iron sheets (purity >99%) were used as sacrificial anode and cathode, respectively. In order to remove the impurities from the surface of electrodes, they were first polished mechanically with fine grain emery paper and then ultrasonically cleaned with ethanol. The cleaned electrodes were placed in an electrolytic cell containing 200 mL of water sample polluted with copper or nickel and the reaction was conducted potentiostatically. In order to study the effect of applied voltage on removal efficiency of nickel and copper two series of samples were prepared by applying different voltages ranging from 5 V to 30 V. To understand the influence of removal time on elimination of copper and nickel from water the reaction time changes from 20 to 100 min. Also, some more samples have been

synthesized at different pH of water and characterized to obtain more information about the best experimental condition for removal of these metal ions from water. To understand the effect of nickel and copper salt on the properties of precipitate obtained after water treatment, one reference (ref.) sample was prepared with no heavy metal pollutants in the water. As the reaction takes place, water is reduced to hydrogen and hydroxyl anions at the cathode, while iron metal is oxidized to iron ions at the anode. In the solution, the ion species react to form an orange-brown iron hydroxide precipitate which then can be dehydrates to produce the iron oxide. The experimental conditions affect the final composition of the precipice formed. The prepared precipitate was separated from water and left to dry.

2.2. Analytical procedure and Sludge characterization techniques

The concentration of copper and nickel in water before and after treatment was analyzed using a ContraAA 700 Atomic Absorption Spectrophotometer (AAS). The structure of the produced sludge after removal process analyzed by a PW1840 X-ray diffractometer (XRD), using CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$). Magnetic measurements were conducted using a vibrating-sample magnetometer (VSM) made by an Iranian company (Meghnatis Daghigh Kashan Co.). The nanostructure of the precipitate obtained after water treatment has been studied using a MIRA3 FESEM.

3. Results and discussion

The applied voltage is an important parameter in all electrochemical systems. In this study the effect of different voltages, ranging from 5 V to 30 V, has been studied on removal of copper and nickel from laboratory water sample (pH $\sim$ 4.5) for half an hour. Figure 1 presents the concentration of copper and nickel as a function of voltage where C_0 and C are the concentration of pollutants in water before and after treatment, respectively. The mass of precipitate obtained after removal of copper and nickel versus voltage are shown in Figure 2. Obviously, one can see that there is the same trend for concentration of pollutants and the mass of precipitate versus voltage. It is known that during the oxidation of the iron electrode, two processes take place, charge transfer and iron ions diffusion into the electrolytic solution. At higher voltage the oxide layer and whole deposit from the surface of the anode and the residue on the surface of the cathode are being removed, allowing a better charge transfer between the electrodes. Increasing the voltage leads to cleaning and degassing of the electrode surface, decreasing the thickness of diffusion layer, and improving the reaction and the hydrolysis rates, so that overall mass transport is enhanced.

There are more effects of voltage upon an electrochemical cell, such as general improvement of hydrodynamics and movement of species which alter the kinetic, current, and reaction mechanism. It is known that increasing the voltage significantly speeds up the reaction rate [29-31]. Therefore, more precipitate will be produced to capture more pollutants from water. Our results show that the removal efficiency of Cu and Ni increases by increasing the applied voltage. Therefore a voltage of ~ 28 V was chosen as the optimum voltage for the subsequent experiments.

In order to study the effect of electrooxidation time on removal of pollutants from water (pH ~ 4.5), some experiments were carried out by applying ~ 28 V at different times. Figures 3 and 4 show the ratio of C/C_0 and the mass of precipitate after elimination of copper and nickel versus time. Based on these data we found that the electrooxidation at longer time produces more precipitate which can capture more pollutants from water. The only exception is the water sample treated after 90 min where the slightly increase in the concentration of copper and nickel in the water could be due to desorption of pollutants from the surface of precipitate after 90 min of absorption. Our results suggest that it is possible to remove 100% of Ni from water at pH ~ 4.5 using electrooxidation of iron under ~ 28 V for 1 hour.

The initial pH has a considerable influence on the performance of an electrochemical process [7]. The effect of the initial pH of wastewater on Cu and Ni removal was explored in the range of pH 1 – 5 under a voltage of ~ 28 V for an hour. At pH higher than 5, some precipitates formed in the water immediately after increasing a few drops of NaOH or NH_4OH solution. Therefore, the effect of different pH ranging from 1 – 5 on removal of pollutants by electrooxidation has been studied. Our results show that in the case of Cu, by decreasing the pH from ~ 1.1 to ~ 2.2 the ratio of C/C_0 slightly increases from about 0.22 to 0.24 and then again decreases to 0.22 at pH ~ 4.5. While for those water samples polluted with Ni at pH from ~ 1.3 to ~ 4.5 the value of C/C_0 ranges from about 0.14 to 0.

In order to obtain more information about the precipitate produced after water treatment, some of sludge samples have been characterized using FESEM, XRD, and VSM. An energy-dispersive x-ray (EDX) detector is used to separate the characteristic x-rays of different elements into an energy spectrum, and EDX system software is used to analyze the energy spectrum in order to determine different elements in the sample. In this study EDX were used to find the chemical composition of materials down to a spot size of a few microns, and to create element composition maps over a much broader raster area. The element maps are the images showing the spatial distribution of elements in the sample. The maps of different elements over the same area can help to determine what phases are present.

Figure 5 and 6 shows typical FESEM images and the element maps of different precipitate samples obtained after removal of Ni and Cu, respectively. These images clearly confirm the nano-size structures of particles formed during the water treatment by electrooxidation of iron. The element maps show that the precipitate prepared after electrooxidation of iron composed of iron, oxygen, and heavy metal pollutants either nickel or copper. It is known that nanoparticles are interesting materials and possess novel and significantly changed physical and chemical properties. Nanoparticles present high absorption, interaction, and reaction capabilities. As particles get smaller, their surface area to volume ratio gets larger. The smaller particles with more surface area react much faster, because more surface area provides more reaction sites for the same volume, leading to more chemical reactivity. In fact, the quantum size effects and the higher surface area to volume ratio of nanomaterials enhances the reactivity with environmental contaminants and provides a tremendous driving force for absorption of pollutants from water [3,32].

The crystal structure of the sludge samples was studied using a PW1840 XRD. Figure 7 shows XRD patterns of the reference sample prepared without any heavy metal pollutant in the water and different typical sludge samples obtained after removal of nickel and copper at pH ~ 4.5 under ~ 28 V for 60 min and 90 min. All indexed peak in the XRD pattern of the reference sample show that the particles have an inverse cubic spinel structure, with the space group $Fd\bar{3}m$. Based on XRD patterns the structure of produced precipitates after removal of heavy metal ions is different. The presence of secondary phases in the XRD pattern of the sludge samples obtained after removal of Ni and Cu was detected. These small peaks which marked with asterisks in Figure 7 show the formation of different compound of nickel and copper in the water. The x-ray diffractogram of powder sample prepared after 60 min and 90 min removal of Ni show the reflections of Fe_3O_4 and some small peaks which are correspond to nickel oxide or sulfate. The peaks observed in the XRD pattern of these two sample indexed with (110) and (002) correspond to crystal structure of Ni_2O_3 (reference code: JCPDS 00-014-0481) and orthorhombic crystal structure of nickel sulfate (reference code: JCPDS 1-076-0220). Also, compared with JCPDS card no. 1-085-1977, the XRD pattern of the sample made after 60 min of Ni removal the peak (003), comes from the presence of NiO_2 structure in the precipitate sample. The peaks observed in the XRD patterns of the precipitates made during removal of Cu are mainly correspond to the Fe_3O_4 structure. From XRD pattern of the samples after 60 min water treatment two peaks (112) and (012) arise from Cu_8O_7 and $Cu_{64}O$ in agreement with reference code: JCPDS 0-003-0879 and JCPDS 01-077-1898.

Magnetism is a physical property that independently helps in water purification by influencing the physical properties of contaminants in water. Adsorption procedure combined with magnetic separation can be used as a promising technique in wastewater treatment and environmental cleanup [3]. The magnetic properties of nanoparticles have been characterized using a VSM. Figure 8 presents the magnetization curve of the reference sample and different sludge samples obtained after removal of nickel and copper at pH ~ 4.5 under ~ 28 V for 60 min and 90 min. One can see that all of these samples are magnetically soft with only a little hysteresis, but the specific magnetization highly dependent on experimental conditions. The magnetization of the reference sample with Fe₃O₄ crystal structure ~ 55 emu g⁻¹ is higher than those samples containing nickel or copper compound as secondary phases. Figure 8 clearly show that the specific magnetization of the sludge samples containing a mixture of heavy metal pollutants and iron oxide are lower. The magnetic property of the precipitate after water treatment gives us the ability to separate the sludge from water by magnetic separation.

4. Conclusions

In this study the removal of nickel and copper from water sample has been studied using electrooxidation method. The effect of different experimental conditions such as applied voltage, removal time, and the pH of water on removal efficiency has been investigated. AAS results showed that it is possible to highly decrease the concentration of Ni or Cu from water at pH ~ 4.5 by applying ~ 28 V for 60 min. The sludge samples have been characterized using FESEM, XRD, and VSM. XRD results show that the structure of precipitate synthesized during removal of Ni and Cu could be a mixture of different compounds containing iron, Ni, or Cu. The FESEM images showed the nanostructures of particles and the element maps confirmed the prepared precipitates is composed of iron, oxygen, and heavy metal pollutants. VSM results show that the specific magnetization of the sludge containing metal pollutants and iron oxide are lower than the reference Fe₃O₄ sample which is ~ 55 emu g⁻¹. The magnetization of precipitates helps to collect and separate them from water medium by magnetic separation after water treatment.

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Figure captions

Figure 1: The concentration of copper and nickel as a function of applied voltage.

Figure 2: The mass of precipitate obtained after removal of copper and nickel versus voltage.

Figure 3: The ratio of C/C_0 after elimination of copper and nickel versus time.

Figure 4: The mass of precipitate after elimination of copper and nickel versus time.

Figure 5: Typical FESEM images and the element maps of different precipitates obtained after removal of Ni.

Figure 6: Typical FESEM images and the element maps of different precipitates prepared after removal of Cu.

Figure 7: XRD patterns of the reference sample and typical sludge samples synthesized after removal of nickel and copper.

Figure 8: The magnetization curve of the reference sample and sludge samples obtained after elimination of nickel and copper.

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Figure 1.

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Figure 8.

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