Journal of Materials and Environmental Sciences
ISSN : 2028-2508

JMES, 2017 Volume 8, Issue 6, Page 2140-2146

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Pretreatment of paper recycling plant wastewater by electrocoagulation using aluminum and iron electrodes

Mohammad Ali Zazouli[1] , Malihe Ahmadi[*1], Jamshid Yazdani Charati[2]

1. *Department of Environmental Health Engineering, Faculty of Health, Health Sciences Research Center, Mazandaran University of Medical Sciences, Sari, Iran*
2. *Department of Biostatics, Health Sciences Research Center, Faculty of Health, Mazandaran University of Medical Sciences, Sari, Iran*

Received 23 Jun 2016,
Revised 07 Aug 2016,
Accepted 24 Aug 2016

Keywords
- ✓ pulp and paper industry,
- ✓ wastewater treatment,
- ✓ electrocoagulation,
- ✓ industrial wastewater

maliheahmadiii@yahoo.com
(M. Ahmadi);
Phone: +981513543085

Abstract

The aim of this work was to treat wastewater from industrial pulp and paper recycling using electrocoagulation. Aluminum (Al) and Iron (Fe) electrodes were used as the electrochemical cell set up. Factors of initial pH and initial voltage were tested during the process and optimized. Tests were done on different initial pH values of 5, 7 and 9 and initial voltage levels of 20, 40 and 60 mv. All samples were analyzed according to standard methods. Result showed that initial pH 7 and initial voltage 60 mv had better removal efficiency for COD and color removal. In these conditions, COD and color removal efficiency with the Fe electrode were 92% and 100%, respectively. Al electrodes had lower efficacy for COD and color removal than the Fe electrode.

1. Introduction

The pulp and paper industry is one of the biggest users of fresh water with large amounts of wastewater discharge per ton of product (100 – 250 m^3 per ton product). This type of wastewater often contains a high level of COD, BOD, lignin, wood debris and other contaminants. However, wastewater composition varies according to the type of raw material and amount of water used in the pulping process [1-4].

Wastewater from the pulp and paper industry needs to be treated in order to prevent it having a harmful effect on the environment and contaminating limited clean water resources. Water consumption and environmental pollution can be reduced using advanced wastewater treatment technologies so that wastewater can be reused. Current physiochemical wastewater treatment needs more chemical materials. It also produces a large amount of sludge. Efficiency of any method used to treat wastewater is dependent on its properties, current standards and receipt of water sources [4,5].

Wastewater treatment using electrochemical processing has been highly regarded during the last two decades. It can be used for hospital laundry wastewater pretreatment [6]; heavy metals removal such as zinc and copper [7]; cadmium from plating bath wastewater [8]; phenol removal [9, 10]; and textile wastewater treatment [11]. This method is also applied to removal of pollutants from gases, liquids and soil. Electrochemical technology has become a rapidly growing area of wastewater treatment due to environmental compatibility, safety, selective capacity and ability to remove impurities resistant to chemical and biological treatments. Additionally, the technique needs no any chemical or physical pretreatment process [12,13].

Electrochemical methods present a strong and innovative approach to in situ coagulation of dilute media by electro-oxidation of sacrificed electrode and destabilizing contaminants [3]. Electrocoagulation compared with other coagulation methods is environmentally compatible, less expensive, produces only small amounts of sludge and requires simple and reliable technology. In this approach, coagulants from sacrificed electrodes are released into the wastewater solution. Removal mechanisms in electrocoagulation include absorption, precipitation and flotation [14, 15]. The basic steps of an electrocoagulation process are: (i) electrolytic reactions at electrode surfaces, (ii) formation of OH^- ions and H_2 at the cathode, (iii) oxidation of generated metal ions and subsequent precipitation of metal hydroxides in aqueous phase, (iv) adsorption of pollutants at a metal hydroxide surface and charge neutralization, and (v) removal of pollutants by settling [16]. Clots formed in this process are similar to those in chemical coagulation except that clots are larger in size so they settle easier and faster [17,18].

Few studies have reported treatment of pulp and paper mill wastewater using the batch electrocoagulation process [19-22]. However, there has been no report to date on paper and pulp recycling plant wastewater treatment by electrocoagulation. Accordingly, this study aimed to set up electrochemical coagulation treatment using different electrodes including Al and Fe. Moreover the effect of initial pH and initial voltage has been studied to determine optimized conditions for maximum COD and color removal.

2. **Experiment**

Wastewater samples used in this study were prepared from the paper recycling plant of Bandaregaz in Iran. Chemical and physical properties of the samples were analyzed then determinations made for BOD, COD and TSS.

2.1. *Analysis*

For COD determination at first, 1.5 ml of digestion solution contains $K_2Cr_2O_7$, Ag_2SO_4 in sulfuric acid solution, 2.5 ml of sample and 3.5 ml of sulfuric acid indicator was mixed and incubated for 120 min in 150 °C. Then, COD was determined by measuring medium turbidity in 600 nm and comparing with obtained standard curve [23]. For BOD determination based on standard method for water and wastewater analysis, 2 ml of sample with Phosphate, $CaCl_2$, $FeCl_2$, $MgSO_4$ buffers was mixed and brought to 1 L volume. Then a bottle containing solution was aerated for 5 min. The bottle was incubated in 21 °C for 5 days prior to determination of BOD [23].

The color of wastewater was determined using UV-visible spectrophotometer. Total suspended solids (TSS) was measured using passed volume of sample through Whatman paper. Then filter cake contained Whatman paper was incubated in 105 °C. Finally, using Eq. (1) TSS was determined [23].

A, B and C represent initial weight of Whatman paper (mg), dry weight of filter cake contained Whatman paper (mg) and volume of sample (ml), respectively.

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2.2 *Electrochemical cell*

Electrochemical cell used in this study was a cubic glass tank made with dimension of 10 cm × 10 cm × 20 cm. Fe and Al plates were used as anode and cathode electrodes, respectively. The effective surface area of each electrode was 12.5 cm. To improve mass transfer, a magnetic stirrer was used constantly at 100 rpm to produce a uniform electrolyte solution. A regulated DC power source was used to supply external electricity current. The voltage was kept constant during each run. The set up was run in a batch mood and parameters include pH, COD, BOD, TSS and color were analyzed during the process. All experiments were performed in duplicate at 30°C. The initial pH of electrolyte in all solution was adjusted with 1 M NaOH and 1 M HCl.

3. **Results and discussion**

In this section, the first step was to determine the initial properties of the used wastewater, results are shown in Table 1. Then, the effect of electrode type was evaluated on efficiency of the process. Finally, conditions were optimized using the experiment set up considered to have the best electrode.

(1)

Table 1: Initial properties of wastewater used in this study

Parameter	Value*
COD	1600
BOD	1100
TSS	950
pH	7

* All parameter are in mg/l except pH

3.1. *Effect of pH*

Effect of initial pH value was studied in three levels; 5, 7 and 9. Figures 1 and 2 show the effect of pH on COD and color removal in Fe and Al electrodes. As it can be seen, in both cases removal efficiency increased with time. The maximum removal in both cases was in pH value 7. Efficiency percentages for COD and color removal for the Fe electrode were 73% and 92%, respectively and for the Al electrode these were 63% and 91%, respectively. It must be mentioned that these experiments were performed at the constant voltage of 20 v and temperature 30 °C. Additionally, maximum BOD and TSS removal for Fe electrode were 63% and 75%, and for Al electrode were 83% and 99%, respectively.

Electrolitic dissolution of Al electrode resulted in production of Al ions (Al^{+3}) which involves hydrolysis reactions and forms monomeric species such as Al^{+3}, $Al(OH^{)+2}$, $Al(OH)_2^{+}$, $Al_2(OH)_3$. Therfore, the polymeric form of hydrolysis products of Al is also generated [2,24,25]. The presence of this species is dependent on pH value of the system. These species create a gelatinous structure. The gelatinous structure allows absorption mechanisms that have an important role in the removal of particulate solids from wastewater. Therefore, pH value has an important role in efficiency of an electrochemical wastewater treatment system [9, 26].

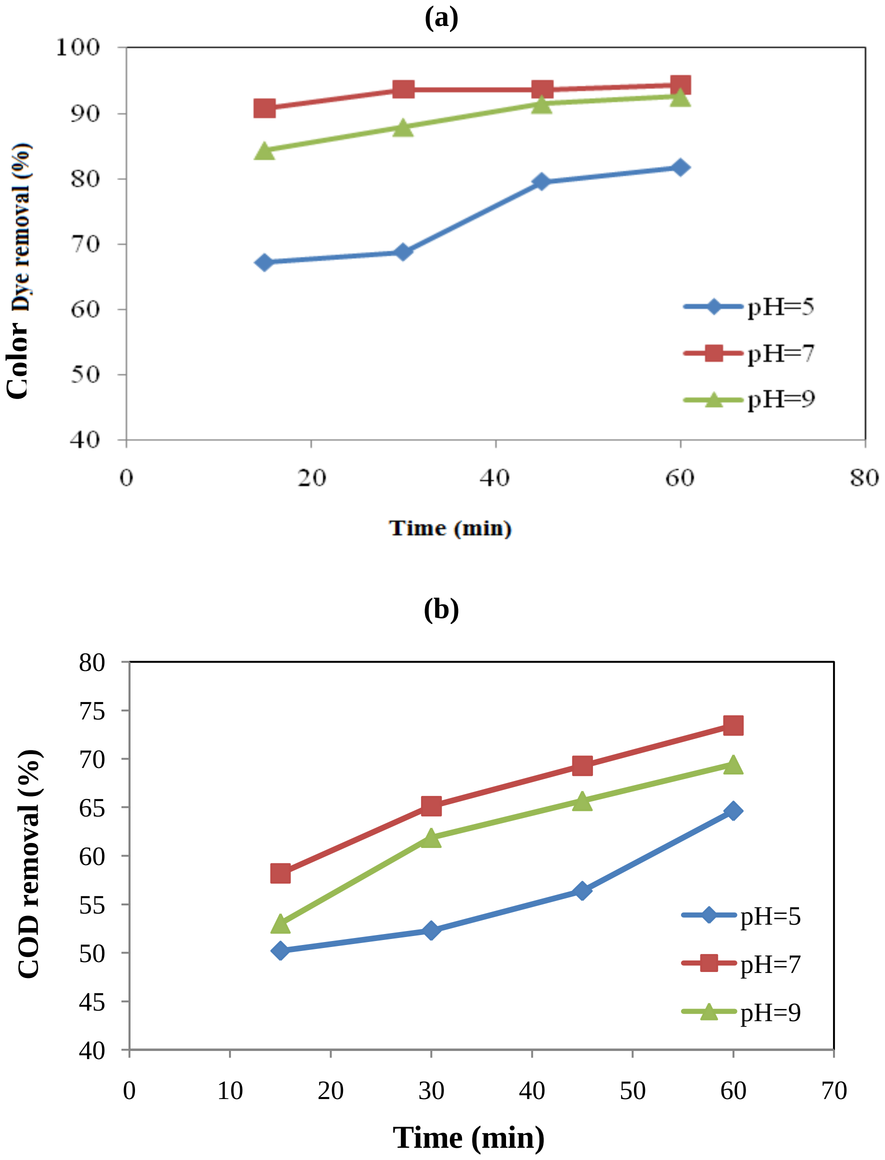


Fig 1: Removal efficiency of Fe electrode in different pH. a: Color removal, b: COD removal.

Ssacrificial Fe electrodes generate Fe^{2+} and OH^{-} ions according to Faraday's law. Sacrificial electrochemical degradation is a complicated and time-dependent process, which is completed in several steps; hydrolysis, polymerization and precipitation [27-29]. During these steps, three classes of product of different species are involved, these are (a) low molecular weight iron hydroxides $Fe(OH)^{2+}$, $Fe(OH)_2^{+}$, $Fe(OH2)^{4+}$ etc.; (b) hydrolytic iron polymer $(Fe_n(OH)_m(H2O)_x^{(3n-m)+}$, or $Fe_mO_n(OH)_x^{(3m-2n-x)+}$; and (c) precipitated oxides (amorphous(am)-$Fe(OH)_3$, FeOOH and Fe_2O_3. Fe^{3+} ions may undergo hydration depending on pH of the solution.

For pH ≤ 5, at least four different Fe(III) ions coexist: Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^{+}$ and $Fe_2(OH)_2^{4+}$. In the range of pH ≥ 5, $Fe\ (OH)_6^{-}$, $Fe(OH)_4^{-}$ and other species may also be formed [20,30]. Following anode and cathode reactions that take place in an electrocoagulation reactor having iron electrodes, over a pH range of 6-9 [31]:

Anode:

$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2e^{-}$ (2)

$\mathrm{Fe} \rightarrow \mathrm{Fe}^{3+} + 3e^{-}$ (3)

Iron undergoes hydrolysis by following reactions:

$\mathrm{Fe} + 6\mathrm{H_2O} \rightarrow \mathrm{Fe(H_2O)_4(OH)_2(aq)} + 2\mathrm{H}^{+} + 2e^{-}$ (4)

$\mathrm{Fe} + 6\mathrm{H_2O} \rightarrow \mathrm{Fe(H_2O)_3(OH)_3(aq)} + 3\mathrm{H}^{+} + 3e^{-}$ (5)

$\mathrm{Fe(H_2O)_3(OH)_3(aq)} \rightarrow \mathrm{Fe(H_2O)_3(OH)_3(s)}$ (6)

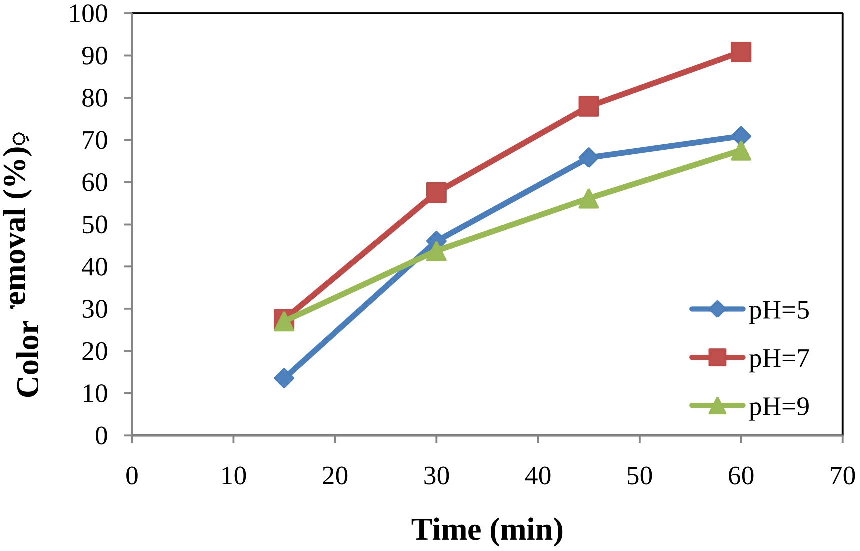
$\mathrm{Fe(H_2O)_4(OH)_2(aq)} \rightarrow \mathrm{Fe(H_2O)_4(OH)_2(s)}$ (7)

Cathode:

$2\mathrm{H}^{+} + 2e^{-} \rightarrow \mathrm{H_2(g)}$ (8)

The pH for minimum solubility of $\mathrm{Fe(OH)_n}$ is in the range of 7-8 that is like the obtained result in this study.

(a)



(b)

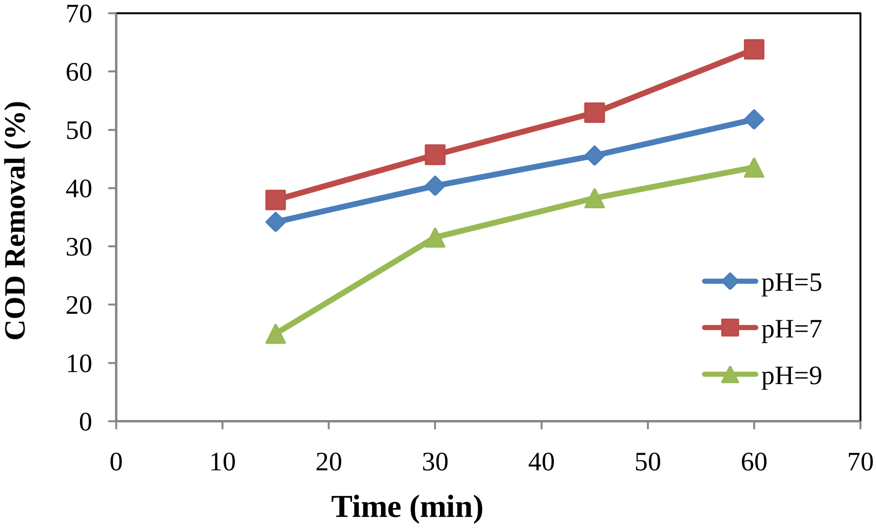


Fig 2: Removal efficiency of Al electrode in different pH. a: Color removal, b: COD removal

3.2. *Effect of Voltage*

Figures 3 and 4 indicate the effect of applied voltage on removal efficiency using Fe and Al electrodes. Effect of applied voltage was evaluated in three levels; 20, 40 and 60 v under initial pH of 7 and 30 °C. As depicted in Figures 3 and 4, process efficiency increased with time and maximum COD and color removal for Fe electrode were 90% and 100%, respectively. Maximum values for COD and color removal efficiency for the Al electrode were 87% and 99%, respectively. BOD and TSS removal efficiency for Fe electrode were 63% and 75%, respectively and those of the Al electrode were 99% and 98 %, respectively.

Figures 3 and 4 show that efficiency of the process increased at higher voltage and increased production of the coagulant. In accordance with Faraday's law, the theoretical value of electrode dissolution was directly related to time and applied voltage. Increasing the voltage resulted in an increase of the released complex of $Al(OH)_3$ and electrons in the medium that then improved efficiency of the process. The electrode in an electrocoagulation system is connected to the DC current power supply. Therefore, the amount of metal ions dissolved or deposited is dependent on the amount of electricity passed through the electrolyte solution.

Oxygen and hydrogen bubbles produced in the electrodes caused the coagulant material to float. Bubble size produced at the electrodes had a positive effect on success of the electrocoagulation process. Smaller bubbles have a larger surface area per volume available for attachment of particles in the electrolyte, which results in better separation and flotation of coagulants. On the other hand, bigger bubbles result in quick flotation of the coagulant [26]. Results indicate that magnet stirrer speed rate of 100 rpm was enough to provide efficient turbulence in the electrolyte solution and to activate O_2 and H_2 bubbles on the surface of the electrode. Combined high applied voltage and stirred cell guaranty efficiency of electrocoagulation process. Used electrolysis current increased with electrode gap. Therefore, low electrode gap used in this study decreased the amount of electricity power used in the treatment.

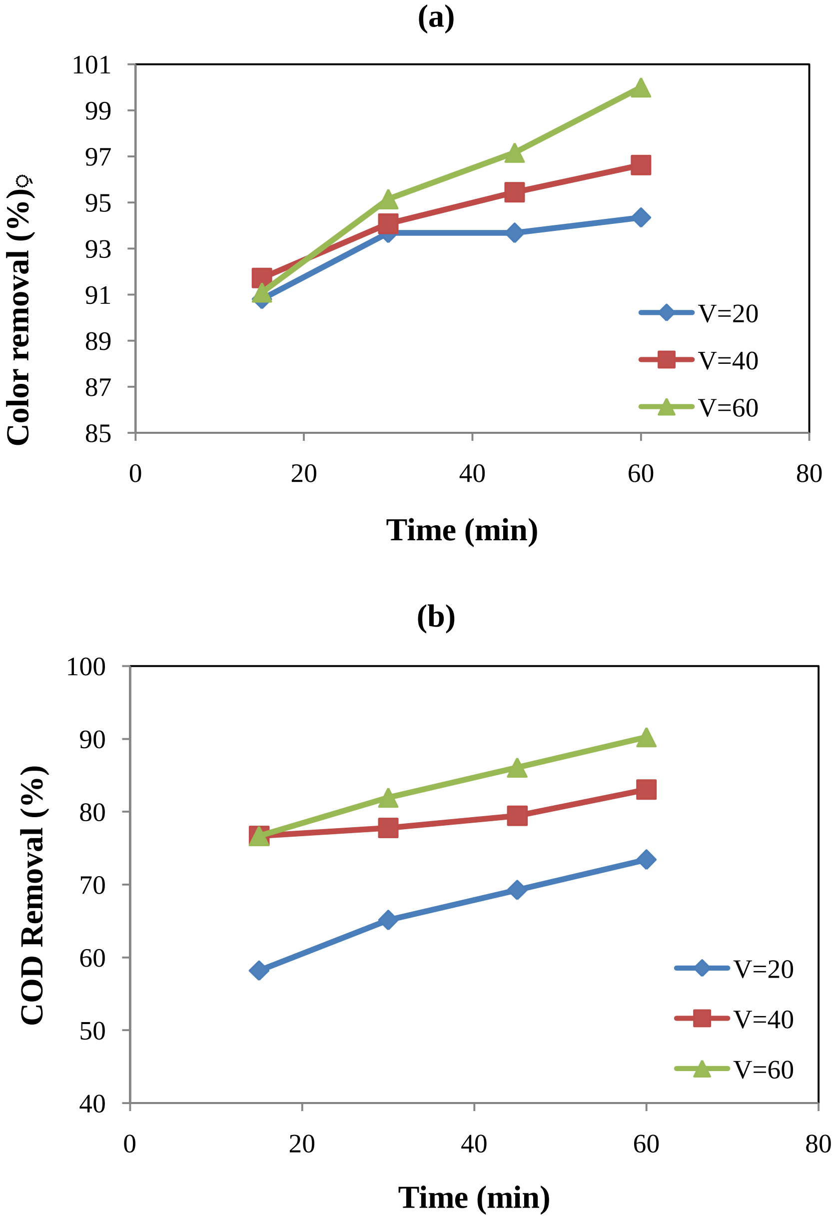


Fig 3: Removal efficiency of Fe electrode in different voltage. a: COD removal, b: color removal efficiency.

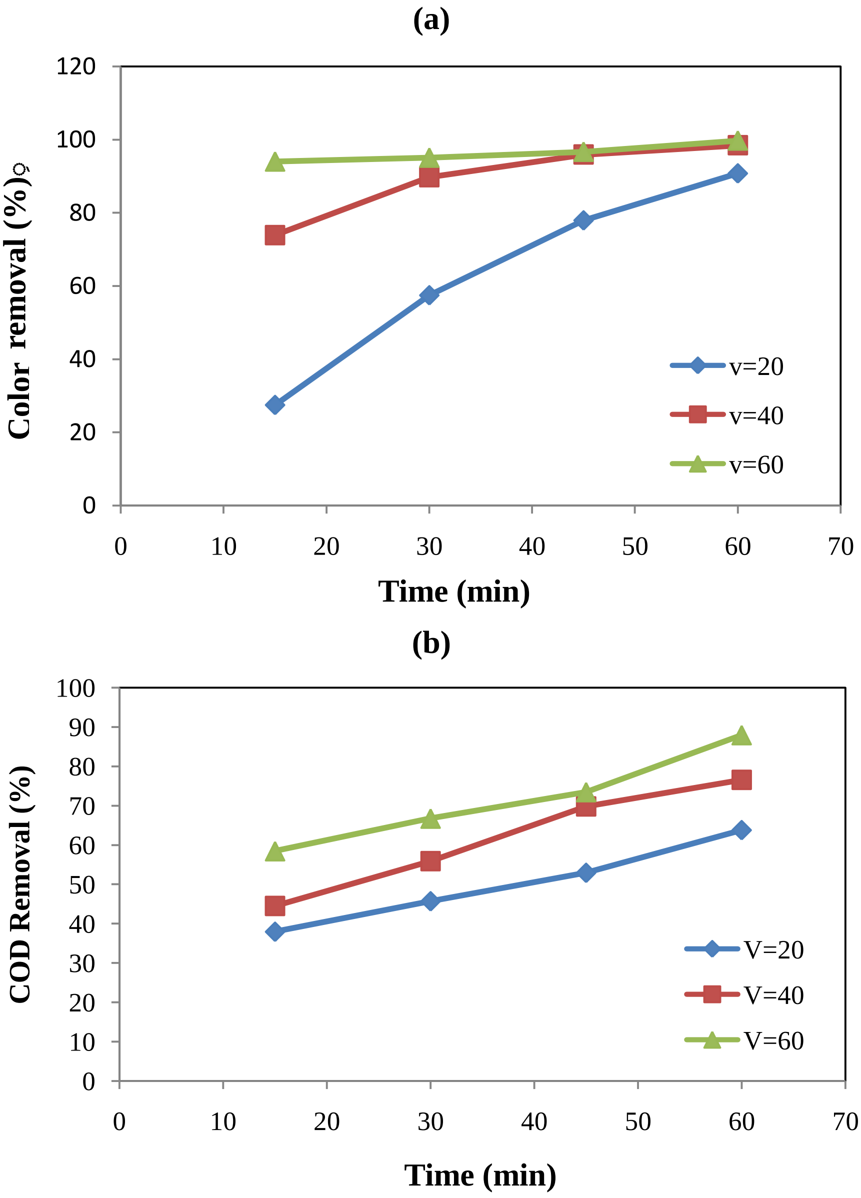


Fig 4: Removal efficiency of Al electrode in different voltage and constant pH of 7. a: Color removal b: COD removal.

3.3. *Effect of Electode type*

Electrode type is one of the most important factors in an electrocoagulation process. In this section the effect of Fe and Al electrode type on the process in different initial pH values and applied levels of voltage were investigated. These experiments were done with application of one factor at a time. In summary, maximum removal of COD and color were 87% and 99% for aluminum electrode, respectively. Also maximum removal of COD and color were 92% and 100% for iron electrode, respectively.

Conclusion

This study examined treatment of wastewater from a paper recycling plant by electrocoagulation. Effects of Al and Fe as electrodes in the electrocoagulation process were studied and results showed that efficiency of both electrodes in COD and color removal were approximately similar. This study concludes that efficiency of the process increased with initial pH, duration time and applied voltage.

Acknowledgments-The authors would like to express their thanks to the laboratory staff of the Department of Environmental Health engineering , Faculty of Health, especially Eng Yahya Esfandiary for their collaboration; to the Health Sciences Research Center and the Research Deputy of Mazandaran University of Medical Sciences for the financial support of this study (Project No:1156). It should be mentioned that this article is part of the MSc thesis of Ms Malihe Ahmadi.

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(2017) ; http://www.jmaterenvironsci.com