Adsorption of Cr(III) and Mg(II) from Hydrogen Peroxide Aqueous Solution by Amberlite IR-120 Synthetic Resin

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ABSTRACT: *In concentration of hydrogen peroxide, first, the solution should be quite pure, and then, it concentrate with methods such as vacuum distillation and cooling crystallization, because impurities in the hydrogen peroxide solution in high concentrations are causing decomposition of this substance; that is very dangerous. The purpose of this article is separation of chromium and magnesium cations from 35wt% commercial hydrogen peroxide solution by ion exchange method with strong acid cation resin Amberlite IR-120 H^+ with styrene divinylbenzene copolymer network and sulfunic acid functional group. In separation of chromium and magnesium, we used batch system and tank equipped with mixer. Effect of the amount of resin and contact time on the separation of cation is investigated. The metal ion concentration in the original solution and the metal ions left unsorbed were determined by Inductively coupled plasma spectrometry (Varian Vista ICP–AES) technique. In determining the effect of the amount of resin and contact time on separation of cation, amount of chromium and magnesium in hydrogen peroxide solution was 0.1 mg/mL, 0.3 mg/mL and 0.5 mg/mL. Experimental results obtained from the separation of chromium and magnesium compared with Freundlich, Langmuir and Jovanovic adsorption isothermal models. Results show that these models only in a certain range of concentration, are consistent with experimental results.*

KEY WORDS: *Hydrogen peroxide, Ion exchange, Amberlite IR-120, Isothermal models.*

INTRODUCTION

Hydrogen peroxide, molecular wt 34.016, is a strong oxidizing agent commercially available in aqueous solution over a wide range of concentrations. It is a weak acidic, nearly colorless clear liquid that is miscible with water in all proportions [1].

Hydrogen peroxide is used in textile bleaching, disinfectants, paper industries, the microelectronics industry for cleaning IC and power supply for power plants. [2]. In high concentration, it is used as an oxidizer in rocket (bipropulsion and monopropellant systems
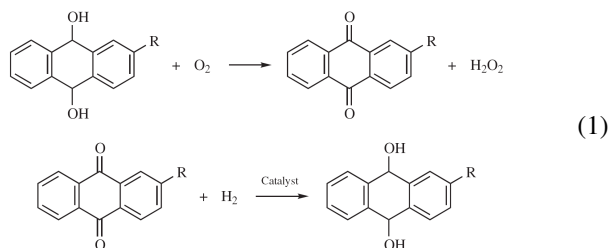
to correct orbit satellites, and submarine in the combustion chamber). Commercial hydrogen peroxide is usually produced technique antraquinine Reaction (1) it has many impurities including metallic cations [3].

$$(1)$$

Automatically, hydrogen peroxide decomposes into water and oxygen. Decomposition takes place in an basic environment fast and in an acid environment slow. Also at high temperatures, decomposition rate, is very fast (Table 1). In very high concentrations of hydrogen peroxide, decomposition was extremely dangerous and it may lead to explosion. Impurities in the hydrogen peroxide in high concentrations, act as catalyst and its decomposition rate increases.

The hydrogen peroxide decomposition Reaction (2) is:

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \qquad \Delta H_{dec} = 23.44 \frac{kcal}{mole} \qquad (2)$$

This decomposition process is irreversible [4]. Kinetic studying of this particular decomposition process can theoretically illustrate 10 to 20 intermediate reactions which may exist in hydrogen peroxide decomposition; however, the above equation is the effective result of these intermediate steps in the decomposition. Decomposition of hydrogen peroxide releases a lot of energy. Amount of oxygen produced was very high and it is suitable for combustion and oxidation reactions of organic compounds.

Many methods exist for separation of impurities from hydrogen peroxide solution, such as distillation, extraction, Reverse Osmosis (RO), adsorption and ion exchange. Ion exchange method by resin is a suitable and simple method with high efficiency [5-10]. Resin structure does not change during the separation process. Ions in solution penetrate quickly into the resin and the molecular network, where ion exchange takes place [11-13]. Ion exchange process includes five steps [14 , 15]: 1- ions penetrate the surface of the resin into solution (diffusion film), 2- ions penetrate into the gel particles (pore diffusion), 3-The exchange of ions with ion exchanger resins, 4- ions penetrate to the surface

Table 1: Shelf life of commercial H₂O₂ solutions.

Temperature (°C)	Decomposition rate
20	<2%/year
70	<2%/week
95	<5%/24h

Table 2: Physical and chemical properties of the cation exchange resin Amberlite IR-120.

Data	Amberlite IR-120
Matrix	Styrene divinylbenzene copolymer
Functional group	Sulfunic acid
Ionic form as shipped	H^+
Screen grading(wet)	16-50 (US std screens)
Maximum temperature(°F)	250
pH range	0-14
Total capacity(eq/L)	2
Shipping weight(lb/ft³)	52

exchange resin, 5- The influence of ions into the solution [5]. In ion exchange method often used polymeric resins [16], Some of the resins used to cation separation by ion exchange, are Amberlite IR-120, Amberlite XAD-2, Amberlite XAD-4, Dowex 50, Doulite C-25, DIAION PK224, DIAION PK228 and Nalcite HCR.

High concentration of hydrogen peroxide, is very valuable. However in concentration of hydrogen peroxide, first, the solution should be perform separation of impurities (such as chromium and magnesium) from this solution, and then, it can be concentrated by cooling crystallization and vacuum distillation techniques [3].

The purpose of this article is evaluation of chromium and magnesium cations separation by Amberlite IR-120 resin in different conditions. Metal cation in concentration hydrogen peroxide is extremely dangerous and may act as a catalyst and hydrogen peroxide can cause decomposition. Finally, the suitability of Freundlich, Langmuir and Jovanovic adsorption models were investigated for Cr and Mg.

EXPERIMENTAL SECTION
Materials
Synthetic Amberlite IR-120 in H^+ form was obtained from Rohm and Haas Co. The properties of Amberlite IR-120 are given in Table 2. For activation of the resin, initially 24 hours was placed into the hydrochloric acid 7% solution and then several times was washed with deionized water; Finally, the resin was dried at 45 °C [17,18].
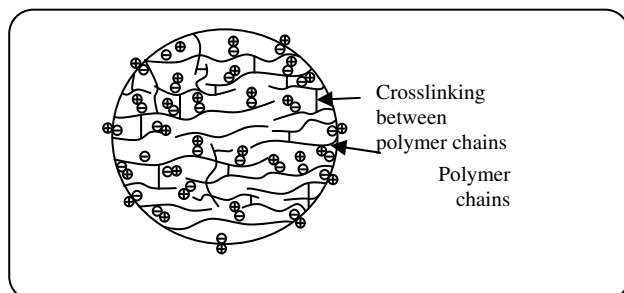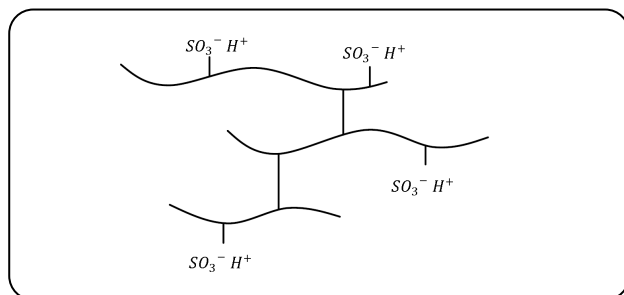
Fig. 1: Cation exchanger.

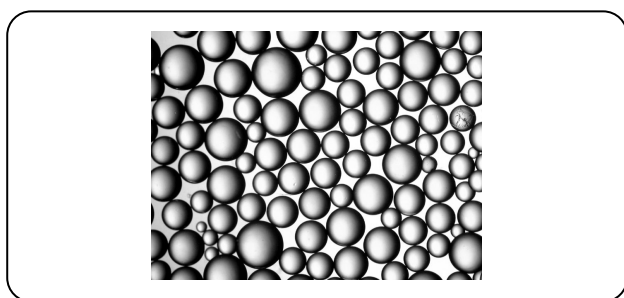*Fig. 2: Strong acid cation exchanger.*

Fig. 3: Resin picture.

For resin recovery solution HCl with concentration of 4 to 10% or H_2SO_4 with concentration of 1 to 5% was used experiments were performed with 35wt% hydrogen peroxide solution.

Apparatus

Measuring amounts of chromium and magnesium cations in solution of hydrogen peroxide, has been done by method of Inductively Coupled Plasma (ICP) spectrometry, Varian-VistaPro model.

Procedures
Water Washing of Resin

H^+ form of the ion exchange resin was washed with deionized water to remove all the excess acid. It was then dried and the dried material was used for further experimental work.

Equilibrium Study

For equilibrium studies, 1g resin Amberlite IR-120 H^+ form was used, so that the resin is mixed with 20 mL of 35wt% by weight hydrogen peroxide solution into a flask. For suspending the resin in solution a 180 rpm mixer was used. Tests were performed at 298 K and 2 hours. After end of the experiments, the amount of 5 mL of hydrogen peroxide solution was sent for ICP analysis. The results of this analysis show that the balance has happened over the same period.

RESULTS AND DISCUSSION
Effect of Contact Time

In determining of the effect of contact time on separation of chromium and magnesium cations that values in solution are 0.1 mg/mL, 0.3 mg/mL and 0.5 mg/mL, the amount of cations that remaining in hydrogen peroxide solution was measured at times 1, 2, 4, 6, 8, 10 , 12, 14, 16, 18 and 20 minutes. Experiments were performed with 1 g of dry resin in 20 mL of 35wt% hydrogen peroxide solution at 298 K. This solution was stirred with 180 rpm. The results are given in Figs. 4 and 5 [19].

Fig. 4 shows that adsorption of Cr increased with increasing contact time to equilibrium point. Equilibrium point decreases with increasing chromium cation in 35wt% hydrogen peroxide solution.

Results of the Figs. 4 and 5 show that with increasing contact time, the removal percentage of chromium and magnesium to equilibrium point increases; For a solution containing 0.1 mg/mL of the chromium, Contact time is about 15 minutes, cation removal percent is about 100%, and a solution containing 0.3 mg/mL of the chromium, contact time about 16 minutes, cation removal percent is about 100%, and a solution containing 0.5 mg/mL of the chromium, contact time about 16 minutes, cation removal percent is about 97%. For a solution containing 0.1 mg/mL of the magnesium, contact time about 10 minutes, cation removal percent is about 100%, and a solution containing 0.3 mg/mL of the magnesium, Contact time about 14 minutes, cation removal percent is about 100%, and a solution containing 0.5 mg/mL of the magnesium, contact time about 16 minutes, cation removal percent is 97.2%. The ion exchange rate of Mg was faster than that of Cr. The maximum removal of 0.5 mg/mL for Cr and Mg is not 100%.
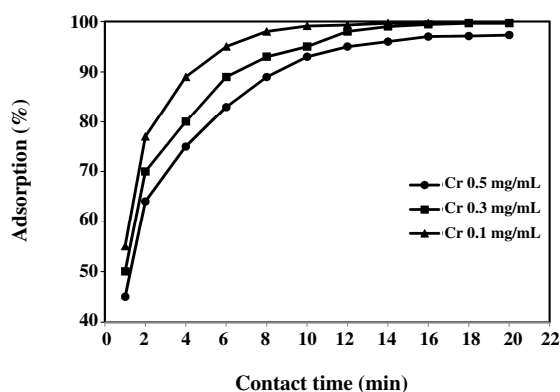
Fig. 4: Effect of contact time on the separation of Cr from hydrogen peroxide solution.
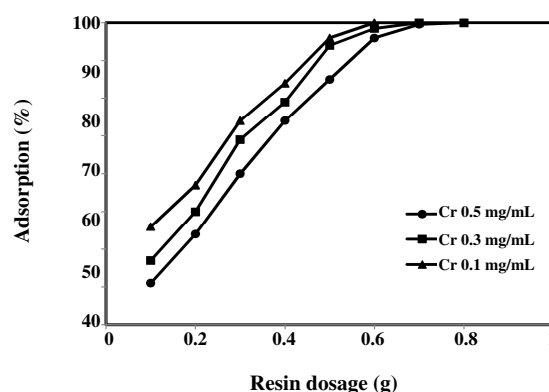

Fig. 5: Effect of contact time on the separation of Mg from hydrogen peroxide solution.

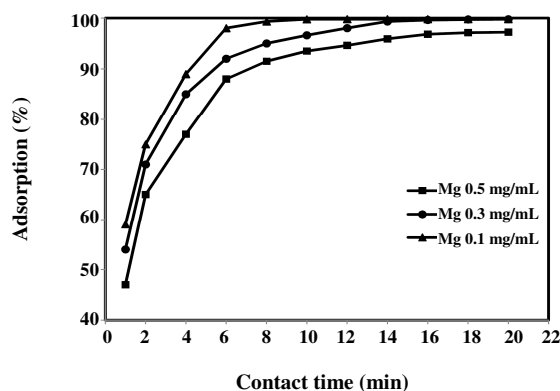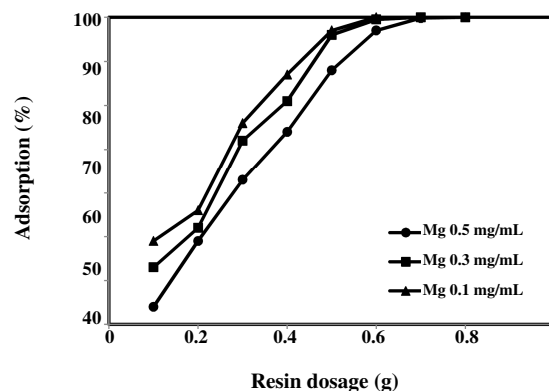**Fig. 6: Effect of resin dosage on the separation of Cr from hydrogen peroxide solution.**

Fig. 7: Effect of resin dosage on the separation of Mg from hydrogen peroxide solution.

Effect of Resin Dosage

In determining the amounts of resin on percentage removal of chromium and magnesium cations were 0.1 mg/mL, 0.3 mg/mL and 0.5 mg/mL, resin capacity calculated. Testing was done with values of 0.1, 0.2, 0.3, 0.4 and 0.5 g (2 to 10 g per liter of resin) resin. Experiments were performed with 1 g of dry resin in 20 mL of 35wt% hydrogen peroxide solution at 298 K. This solution was stirred with 180 rpm for optimum contact time (Figs. 6 and 7) [19].

Figs. 6 and 7 show that adsorption of Cr and Mg increased with increasing resin dosage to equilibrium point and also increase in amount of Cr and Mg in initial solution has shown negligible effect towards increase in removal percentage of Cr and Mg from hydrogen peroxide solution. So that for a solution containing 0.1 mg/mL of the chromium and magnesium, amount of

the resin was 0.6 g, cation removal percent was 100% and for a solution containing 0.3 mg/mL of chromium and magnesium, with 0.66 g and 0.62 g resin, respectively, cation removal percent was 100% and for a solution containing 0.5 mg/mL of chromium and magnesium, with amounts of 0.7 g resin and 0.72g, respectively, cation removal percent was 100%.

Adsorption Isotherm

Models of Freundlich, Langmuir and Jovanovic, are common isotherm models in ion exchange relations between solid and liquid phases. [20-23].

Non-linear Freundlich isotherm relation is as Eq. (1).

$$Q_e = K_F C_e^n \quad (\text{non-linear form}) \tag{1}$$

Form a linear Freundlich equation, according to Eq. (2).

$$\log Q_e = \log K_F + n \log C_e \quad (\text{linear form}) \tag{2}$$

Table 3: Constants and correlation coefficients of Freundlich, Langmuir and Jovanovic isotherm for adsorption of Cr.

Resin	Concentration of Cr in HP(mg/mL)	Freundlich isotherm			Langmuir isotherm		Jovanovic isotherm	
		n	K	R^2	K	R^2	K	R^2
Amberlite IR-120	0.1	0.168	11.6	0.896	198	0.991	-	-
	0.3	0.178	27.99	0.985	300.3	0.908	0.115	0.882

Table 4. Constants and correlation coefficients of Freundlich, Langmuir and Jovanovic isotherm for adsorption of Mg.

Resin	Concentration of Mg in HP(mg/mL)	Freundlich isotherm			Langmuir isotherm		Jovanovic isotherm	
		n	K	R^2	K	R^2	K	R^2
Amberlite IR-120	0.1	0.210	12	0.840	198.4	0.993	-	-
	0.3	0.229	28.05	0.996	450.45	0.921	9.253	0.976

Fig. 8: Plot for Freundlich isotherms for adsorption of Cr by the resin Amberlite IR-120.
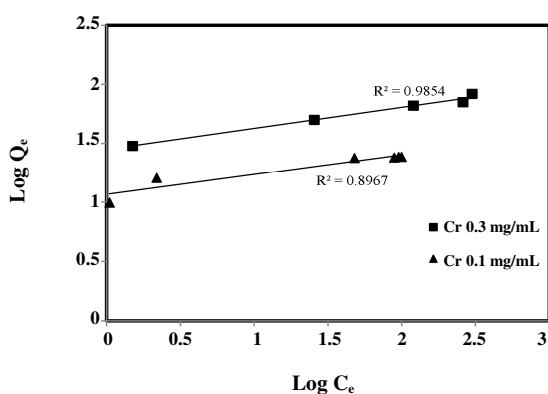

Fig. 9: Plot for Langmuir adsorption isotherms for Cr by the resin Amberlite IR-120.

C_e is equilibrium concentration of metal in solution; Q_e is amount of metal adsorbed on resin weight unit; K_F and n are constant, depends on the absorption capacity and intensity respectively.

Langmuir isotherm is non-linear relation according to Eq. (3).

$$Q_e = \frac{K_L Q_m C_e}{1 + K_L C_e} \quad \left(\text{non} - \text{linear form}\right) \qquad (3)$$

Langmuir equation as a linear form is given by Eq. (4).

$$\frac{1}{Q_e} = \left[\left(\frac{1}{K_L Q_m}\right)\left(\frac{1}{C_e}\right)\right] + \left(\frac{1}{Q_m}\right) \quad \left(\text{linear form}\right) \qquad (4)$$

Q_m is the resin capacity (maximum possible amount of metallic ion adsorbed per unit mass of adsorbent) and K_L is equilibrium constant related to the affinity of the binding sites for the metals or the Langmuir constant.
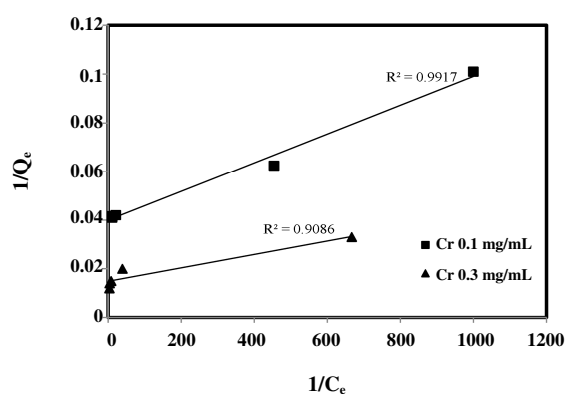
non-linear Jovanovic relation is according to Eq. (5) [24].

$$Q_e = Q_m \left(1 - \exp\left(-K_J C_e\right)\right) \quad \left(\text{non} - \text{linear form}\right) \qquad (5)$$

Linear form of Jovanovic equation is according to Eq. (6).

$$-\ln\left(1 - \frac{Q_e}{Q_m}\right) = K_J C_e \qquad \left(\text{linear form}\right) \qquad (6)$$

In equations of Jovanovic, K_J and n are constant.

Constants of adsorption isotherm equations and correlation coefficients (R^2) listed in Tables 3 and 4. The plots for Freundlich, Langmuir and Jovanovic isotherms with correlation coefficient are presented in Figs. 8-13.

Data presented in Table 3 and Table 4 showed that the Freundlich equation for the amount of 0.3 mg / mL of the chromium and magnesium is valid and for the amount of 0.1 mg / mL of the chromium and magnesium, is not valid; But the Langmuir equation in both the amount of
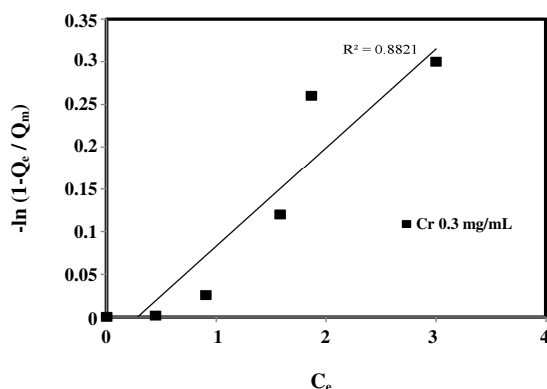
Fig. 10: Plot for Jovanovic adsorption isotherm for 0.3 mg/mL Cr by Amberlite IR-120 resin.
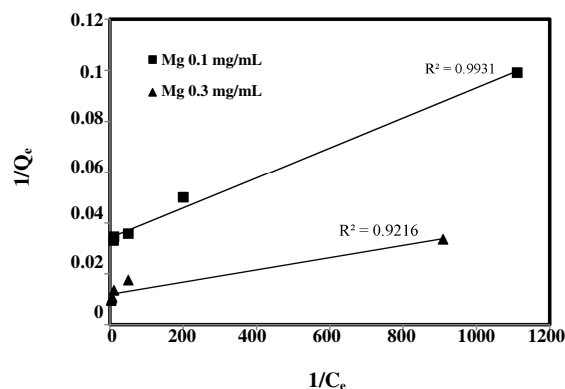

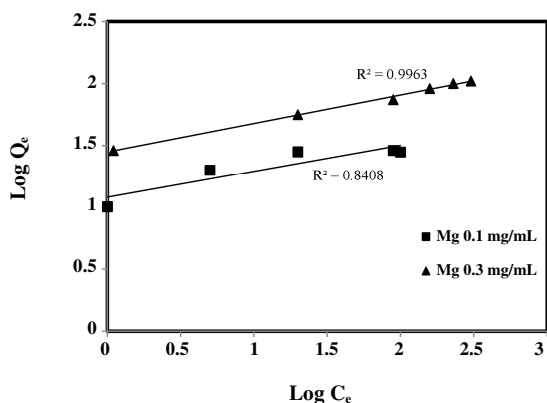**Fig. 12: Plot for Langmuir adsorption isotherms for Mg by the Amberlite IR-120 resin.**

Fig. 11: Plot for Freundlich isotherms for adsorption of Mg by the Amberlite IR-120 resin.
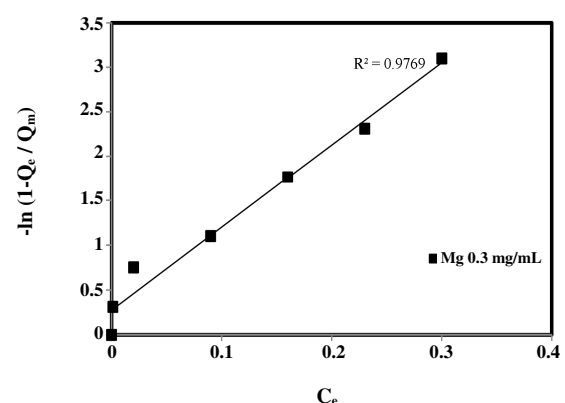

Fig. 13: Plot for Jovanovic adsorption isotherm for 0.3 mg/mL Mg by Amberlite IR-120 resin.

approximately 0.1 mg / mL and 0.3 mg / mL for chromium and magnesium cations is valid and Jovanovic equation, only for the amount of 0.3 mg / mL of the magnesium is valid and for other values, is not valid.

CONCLUTIONS

The results showed that Amberlite IR120 resin is suitable for the separation of Cr and Mg from hydrogen peroxide solution. In this study, the effect of resin dose and contact time on removal of Cr and Mg have been investigated. The results show that the removal percentage of Cr and Mg increased with increasing contact time to equilibrium that the equilibrium point depends on the amount of cations in hydrogen peroxide solution and with decreasing cation concentration in solution, contact time is reduced. Increase in adsorption of Cr and Mg with increase in resin

dose as available sites increases with higher quantity of resin. Increase in resin dose as available sites or surface area increases with higher quantity of resin. An increase in surface area of resin automatically enhances the rate of adsorption.

Increasing temperature will cause decomposition of hydrogen peroxide. The equilibrium distribution of Cr and Mg ions was modeled by Freundlich, Langmuir and Jovanovic isotherm equations. It was found that equilibrium data can be fitted by these models at higher concentration (0.3 mg/mL) however Langmuir isotherm is valid with experimental results at lower concentration (0.1 mg/mL).

REFERENCES

[1] "Ullmann's Encyclopedia of Industrial Chemistry". 6th. ed.,Wiley VCH, (1998).

[2] Lin Q., Jiang Y., Geng J., Qian Y., Removal of Organic Impurities with Activated Carbons for Ultra-Pure Hydrogen Peroxide Preparation, *Chemical Engineering Journal* **139**, p. 264 (2008).

[3] Kirk-Othmer, "Encyclopedia of Chemical Technology", 5th. ed., John Wiley & Sons, (2008).

[4] Romero A., Santos A., Vicente F., Rodriguez S., Lafuente A.L., In Situ Oxidation Remediation Technologies: Kinetic of Hydrogen Peroxide Decomposition on Soil Organic Matter, *J. Hazard. Mater.*, **170**, p. 627 (2009).

[5] Elliot R.B., Yan P., Young J.H., Purification of Hydrogen Peroxide, *USP 3297404*, (1957).

[6] Watanabe S., Ohura O.,Process for Preparing High Purity Hydrogen Peroxide, *USP 5055286*, (1988).

[7] Kirksey K., Purification of Hydrogen Peroxide, *USP 4985228*, (1990).

[8] Morris G.W., Feasey N.D., Purification of Hydrogen Peroxide, *USP 5262058*, (1990).

[9] Bianchi U.P., Leone U., Lucci M., Process for the Industrial Production of High Purity Hydrogen Peroxide, *USP 6333018*, (2001).

[10] Tanaka F., Sugawara I., Adachi T., Mine K., Process for Producing a Purified Aqueous Hydrogen Peroxide Solution, *USP 6896867*, (2005).

[11] Cavaco S.A., Fernandes S., Augusto C.M., Quina M.J., Gando-Ferreira L.M., Evalution of Chelating Ion-exchange Resins for Separating Cr(III) from Industrial Effluent, *J. Hazard. Mater.*, **169**, p. 516 (2009).

[12] Rengaraj S., Yeon J.-W., Kim Y., Jung Y.,.Haa Y.K., Kima W.H., Adsorption Characteristics of Cu(II) onto Ion Exchange Rresins 252H and 1500H: Kinetics, Isotherms and Error Analysis, *J. Hazard. Mater.*, **B 143**, p. 469 (2007).

[13] Hamdaoui O., Removal of Copper (II) from Aqueous Phase by Purolite C100-MB Cation Exchange Resin in Fixed Bed Columns: Modeling, *J. Hazard. Mater.*, **161**, p. 737 (2009).

[14] Abo-Farha S.A., Abdel-Aal A.Y., Ashour I.A., Garamon S.E., Removal of Some Heavy Metal Cations by Synthetic Resin Purolite C100, *J. Hazard. Mater.*, **169**, p. 190 (2009).

[15] Demirbas A., Pehlivan E., Gode F., Altun T., Arslan G., Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), Cd(II) from Aqueous Solution on Amberlite IR-120 Synthetic Resin, *J. Colloid Interface Sci.*, **282**, p. 20 (2005).

[16] Demirbas A., Heavy Metal Adsorption Onto Agro-Based Waste Materials: A Review, *J. Hazard. Mater.*, **157**, p. 220 (2008).

[17] Alguacil F.S., Alonso M., Lozano L.J., Chromium(III) Recovery from Waste Acid Solution by Ion Exchange Processing Using Amberlite IR-120 Resin: Batch and Continuous Ion Exchange Modeling, *Chemosphere*, **57**, p. 789 (2004).

[18] Kocaoba S., Comparation of Amberlite IR120 and Dolomite's Performances for Removal of Heavy Metals, *J. Hazard. Mater.*, **147**, p. 488 (2007).

[19] Alipour M., "B.Sc. Thesis", Iran University of Science and Technology (2010).

[20] Do D.D., "Adsorption Analysis: Equilibria and Kinetics", Imperial College Press, London, (1998).

[21] Bayat B., Comparative Study of Adsorption Properties of Turkish Fly Ashes. I.The Case of Nickel(II), Copper(II) and Zinc(II), *J. Hazard. Mater.*, **95**, p. 251 (2002).

[22] Langmuir I., The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum, *J. Am. Chem. Soc.*, **40**(9), p. 1361 (1918).

[23] Kumar Jha M., Van Nguyen N., Lee J., Jeong J., Yoo J., Adsorption of Copper from Sulphate Solution of Low Copper Contents Using the Cationic Resin Amberlite IR120, *J. Hazard. Mater.*, **164**, p. 948 (2009).

[24] Oancea A.M.S., Drinkal C., Holl W.H., Evaluation of Exchange Equilibria on Strongly Acidic Ion Exchangers with Gel-Type, Macroporous and Macronet Structure, *Reactive & Functional Polymers*, **68**, p. 492 (2008).