Removal of Nickel and Cadmium Ions from Wastewater by Sorptive Flotation: Single and Binary systems

Ahmed A. Mohammed
Assistant Professor
College of Engineering-University of Baghdad
E-mail: ahmed.abedm@yahoo.com

Farah Qasim Mohammed
College of Engineering / University of Baghdad
E-mail: eng_farahqassim@yahoo.com

ABSTARCT

The removal of heavy metal ions from wastewater by sorptive flotation using Amberlite IR120 as a resin, and flotation column, was investigated. A combined two-stage process is proposed as an alternative of the heavy metals removal from aqueous solutions. The first stage is the sorption of heavy metals onto Amberlite IR120 followed by dispersed-air flotation. The sorption of metal ions on the resin, depending on contact time, pH, resin dosage, and initial metal concentration was studied in batch method .Various parameters such as pH, air flow rate, and surfactant concentration were investigated in the flotation stage. Sodium lauryl sulfate (SLS) and Hexadecyltrimethyl ammonium bromide (HTAB) were used as anionic and cationic surfactant respectively. The sorption process, which is PH dependent, shows maximum removal of metal ions at pH 7. Langmuir and Freundlich isotherm expressions were found to give both a good fit to the experimental data. Kinetic data correlated well with Lagergren second order kinetic model, and flotation step enhanced the removal efficiency of nickel and cadmium from wastewater from about 75% to 94% and reduce turbidity so it can dispense with the filtering process, which is expensive technology. It is believed that flotation separation has great potential as a clean water and wastewater treatment technology.

Key words: heavy metals; sorption; flotation; kinetics; turbidity.

أزالة ايونات النيكل والكادميوم من المياه الملوثه بطريقه الامتزاز والتعويم:النظام الاحادي والثنائي

أ.م. د. احمد عبد محمد
كلية الهندسة / جامعة بغداد

فرح قاسم محمد
كلية الهندسة / جامعة بغداد

الخلاصة

تمت دراسة ازالة أيونات النيكل والكاديميوم من المياه بواسطة الامتزاز والعويم باستخدام راتنج, مثل الامبرلايت وعامود التعويم . تعتبر عملية دمج المرحلتين مرحلة الامتزاز ومرحلة التعويم طريقة فعالة لازالة ايونات المعادن الثقيلة من المياه . تبدأ العملية بمرحلة الامتزاز على راتنج الامبرلايت تتبعها عملية التعويم بواسطة الفقاعات المشتتة . تمت دراسة سلوك الامتزاز على الراتنجات بطريقة الدفعة و يعتمد على الوقت, الدالة الهيدروجينية, وزن الراتنج, و التركيز (الكمية المعدة). ومرحله التعويم ، والتي تعتمد على الدالة الهيدروجينية وسرعة جريان الهواء وتركيز مادة التعويم , كما تم استخدام نوعين من مواد التعويم وهي كبريتات لويل الصوديوم ،وثلاثي مثيل بروميد الامونيوم كمادتي تعويم موجبه وسالبه على الترتيب . و قد تم تحليل البيانات المختبرية بواسطة موديلات لانكمير و فريندلخ .وتم احتساب الثوابت الخاصة بهذه الموديلات ووجد ان تعبير لانكمير وتعبير

فريندلخ يمثلا ملائمة جيدة ومتقاربة في تمثيل هذه البيانات المختبرية .كما وتم اختبار البيانات الحركية من الدرجة الاولى و الثانية , تبين انها ملائمة مع الدرجة الثانية اكثر من ملائمتها مع الدرجة الاولى للنظامين الفردي والثنائي. النتائج تشير الى ان الامبرليايت (IR 120) يمكن استخدامه بكفاءة عالية لازالة المعادن الثقيلة من المياه . اما عملية التعويم فتعتبر خطوة مهمة لتعزيز كفاءة إزالة النيكل والكادميوم من مياه الصرف الصحي حوالي (75٪ إلى 94٪) وللحد من العكورة لذلك يمكن الاستغناء عن عملية الترشيح، والتي تعتبر تقنية مكلفة. كما وتحتل عملية الفصل بالامتزاز والتعويم مكانة كبيرة باعتبارها تقنية واعدة في تكنولوجيا المياه النظيفة و معالجة مياه الصرف الصحي.

الكلمات الاستدلالية : معادن ثقيلة , أمتزاز , تطويف , حركية ,عكوره.

1. INTRODUCTION

Heavy metals are generally considered to be those whose density exceeds 5 g/cm^3, **Nocito et al., 2007.** Removal of heavy metals from wastewater is of primary importance because they are not only causing contamination of water bodies and are also toxic to many life forms. Industrial processes generate wastewater containing heavy metal contaminants. Since most of heavy metals are non degradable into nontoxic end products, their concentrations must be reduced to acceptable levels before discharging them into environment. Otherwise these could pose threats to public health and/or affect the aesthetic quality of potable water, **Aslam, et al, 2004**.According to World Health Organization (WHO) the metals of most immediate concern are nickel, cadmium, chromium, copper, zinc, iron, mercury and lead, **WHO, 1984**.

Nickel ions represent a serious environmental problem since they are widely used in many industries and general applications. Among them are: industrial effluents, industrial fertilizers, catalysts, gears, magnets, airbag valves, electronics, tooth protects, exhaust smokes, stainless steels, etc, **Arsalani, et al., 2009**. Its removal is of major concern because nickel compounds are carcinogenic and also can cause asthma. Another common adverse health effect of Ni (II) is skin allergy, **Aslam, et al., 2010**. In addition to nickel, cadmium is consider one of the most toxic metals affecting the environment, the source of cadmium are mining and metallurgy of cadmium, cadmium electroplating, , is widely used in pigments, as heat stabilizers for plastics, for corrosion resistance of steel and cast iron, metal plating, phosphate fertilizer, mining, pigments, alloy industries, in soldering and brazing and in the battery industry (Ni - Cd batteries), and ceramic industries waste waters contain undesired amounts of Cd^{2+} ions is highly toxic and there is some evidence that it is carcinogenic, **Hiatt and Huff, 1975**. Sorptive flotation involves the preliminary abstraction or scavenging of metal ions using appropriate sorbents which exists in fine or ultrafine particle size range, subsequently he process was followed by a flotation stage for solid – liquid separation of the metal –loaded sorbent particles from the treated clean solution.

The aim of the present work is to study the removal of nickel, and cadmium ions from wastewater by sorptive flotation method using Amberlite IR120 and Amberlite CG50 as an exchanger resins and bubble column for flotation. In addition, investigate the parameters that influence the separation efficiency, such as contact time, pH, and dose of resin, and initial metal concentrations, air flow rate, surfactant type. Also this study aims at determining isotherm model and kinetic models for this system.

2. MATERIAL and EXPERIMENTAL PROCEDURE

2.1 Materials

Analytical grade reagents were used in experimental studies. Nickel nitrate Hexahaydrate $N_2NiO_6.6H_2O$ and Cadmium nitrate tetrahydrate Cd $(NO_3)_2.4H_2O$ were used for preparing synthetic solutions. pH adjustments were carried out by using 0.1N HNO_3 and 0.1N NaOH. Amberlite IR120 strong acid cation exchange resin from (Rohm and Hass) and Amberlite CG50 resin from (Hopkin and Williams Company, UK) was used, its physical and chemical properties are given in **Tables 1 and 2** respectively. Sodium lauryl sulfate $C_{12}H_{25}NaO_4S$ (SLS) and Hexadecyl trimethyl ammonium bromides (HTAB) as anionic and cationic surfactants, respectively.

Table1. Properties of Amberlite IR120.

Matrix	Styrene
Functional group	Sulfunic acid (strong acid)
Particle size(mm)	0.3-1.2
Maximum temperature °C	120
pH range	0-14
Total capacity(equiv/l)	1.8

Table 2. Properties of Amberlite CG50.

Matrix	Macroporous crosslinked methacrylate
Functional groups	-COO
Physical form	Dry fine powder
Ionic form as supplied	H+ week acid
Total exchange capacity	10 meq/g min
Moisture content	10% max
Particle size	Nominally 100 to 200 mesh (US Std) 75 to 150 μm

2.2. Apparatus

Batch experiments were carried out in Lap Mixer (Cole Parmer, USA). WTW series ion lab pH-meter used for pH measurements. GBC 933 plus Atomic Absorption Spectrometer AAS was used to measure concentrations of soluble nickel and cadmium ions.

2.3. Equilibrium studies

Batch equilibrium experiments have been carried out to find the optimum PH, time, and equilibrium isotherms. The procedure involved filling the flask with 1L of heavy metal ions solution of 25-200 ppm. About 1 g of adsorbent was added into flask. Resins and solution dumped into a flask and after mixing at 400 rpm, the solution and the resin allowed for equilibrium for 50 min in the mixer. The adsorbent and the solution were separated through filter paper. The effect of pH for heavy metal ions removal using ion exchangers was studied in pH range of 3-8 amount of resin o.25- 3 g, concentration of heavy metal ions 25-200 ppm. Sorption isotherm studies were carried out with different initial concentrations of metal ions while maintaining the resin dosage at constant level. For pH effects, 25-200 mg/l of metal ions and ion exchange resins amberlite IR120 dose 1000 mg/1L were used. Kinetic experiments were conducted by using a known weight of resin dosage and optimum metal ion concentration. After regular intervals of time, suitable aliquots were analyzed for metal ions concentrations and recorded. The rate constants were calculated by using the conventional rate expression. After the sorption stage the solution was placed in the flotation column. The flotation tests were carried out in a bubble column (acrylic) of 6 cm inside diameter and 120 cm in height. **Fig.1** shows a schematic diagram of experimental apparatus. Air supplied by the compressor was fed to the column through a pre – calibrated rotameter. Air entered the column was dispersed as bubbles into liquid. Feed inter with different metal concentration was poured gently at the top of the column. At the same time, the column was pressurized so as not to weep the liquid through the holes. Perforated plate of the air distributer was used which has 25 holes with 0.05 cm diameter. The holes are arranges in the equilateral triangular pitch through the whole area which are located inside the column. The column was operated at batch mode as far as the liquid phase and continuous flow with respect to air. This column contains six taps of 0.2 cm inside diameter, these taps arranged at interval of 15 cm and used to draw samples from the column , samples were taken at preset time intervals as 2 , 5, 10 and 15 min, samples were withdrawn slowly to minimize entrainment of air bubbles. Between experiments, the column was cleaned using HNO_3, and then rinsed three times with double distilled water. Metal contents of solution were analyzed by AAS.

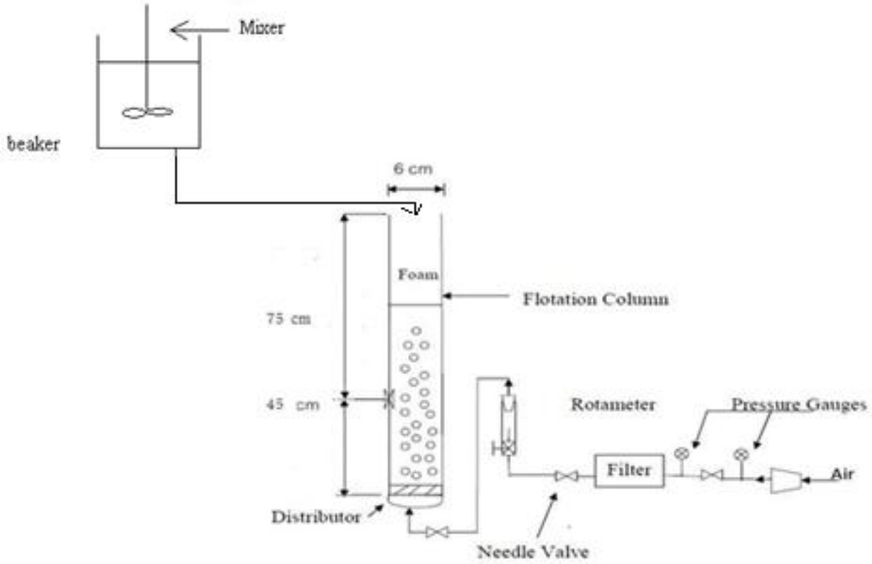

Figure 1. Schematic diagram of the experimental set-up.

3. RESULTS and DISCUSSION

3.1. Effect of Resin Type

Two types of Resin were used in this study to find out the most efficient resin

1- weak acid ion exchange resin (Amberlite CG50)

2- Strong acid ion exchange resin (Amberlite IR120)

Fig.2 shows the effect of resin type on the removal efficiency of Cd^{2+} and Ni^{2+} ions, respectively, from these figures it can be seen that the strong ion exchange resin (Amberlite IR120) is more efficient than week acid ion exchange resin (Amberlite CG50), were the removal efficiency when using 2 g dose of amberlite IR120 reaches about 98.8% and 99.4% for nickel and cadmium respectively, while for the same dose of CG50 it reaches 23% and 47% for nickel and cadmium respectively, and this is because of the ability of the sulfuric acid group to exchange cations or split neutral salts also because the strong acid ion exchange resin useful across the entire pH range, **Wheaton and Lefevre, 2000**, so the decision towards use strong acid ion exchange resin Amberlite IR 120.

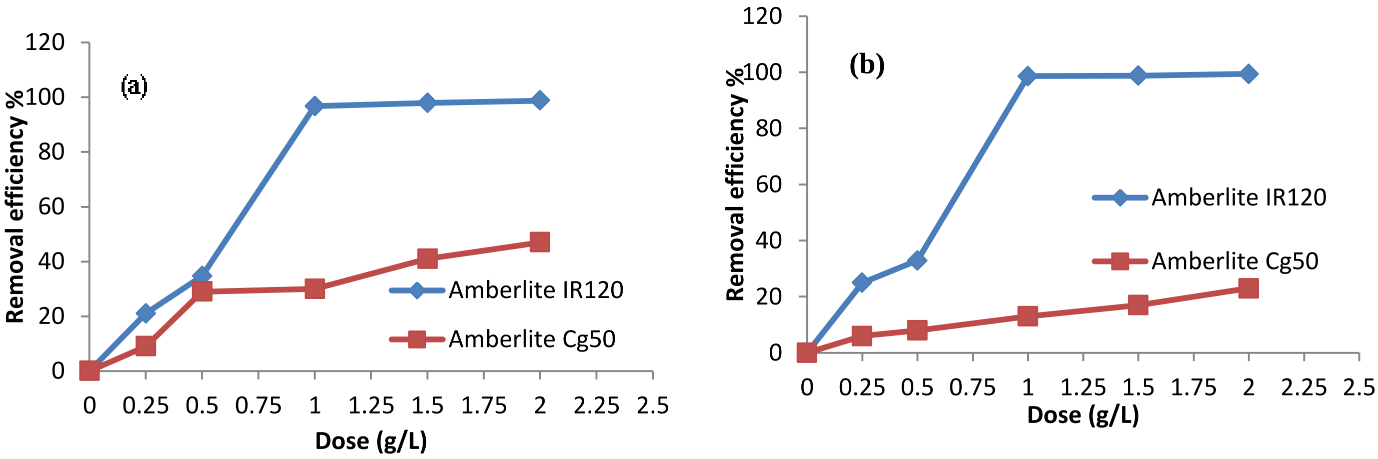

Figure 2. Effect of resin type on removal of (a) Cd^{2+} (b) Ni^{2+} with different dosages at (t,120min ; PH, 7; mixing rate 400 rpm; initial metal concentration 100 mg/L).

3.2. Effect of Contact Time

The effect of contact time on the sorption of metal ions by Amberlite IR120 was studied by adding 1 g /L of resin to 100 mg/L of contaminated solution. The solution was mixed for different time intervals. **Fig.3** shows the effect of contact time on the sorption of nickel, and cadmium. From this figure it can be seen that the percentage of metal removal increased with increasing time and it reached the plateau value at 2 hr for nickel and cadmium ions. The same behavior were noticed by **Onundi et al., 2010**, also the results shows that within the first 30 min uptake metal ions removal by the resin were relatively fast, which is 72.7% for nickel and 70.4% for cadmium, a few progressive increase between 30 to 60 min and after 60 min the percentage of removal efficiency reached 96.8% and 98.6% for nickel and cadmium respectively. The initial sorption rate was very fast due to the existence of greater number of resin sites available for the sorption of metal ions. As the remaining vacant surface sites decreasing, the adsorption rate slowed down due to formation of repulsive forces between the metals on the solid surface and in the liquid phase. The decreasing of Mass transfer leads to increase the uptake of metal ions with contact time. This is a critical parameter for best removal of metal ions in the waste water. The ion exchange rate and the equilibrium removal efficiency of cadmium was faster than nickel while in binary system a decreasing in removal efficiencies are noted because of the competition between two metal in the solution the results are plotted in **Fig. 4** ,the same behavior were noticed by **El-Sayed et al., 2010**.

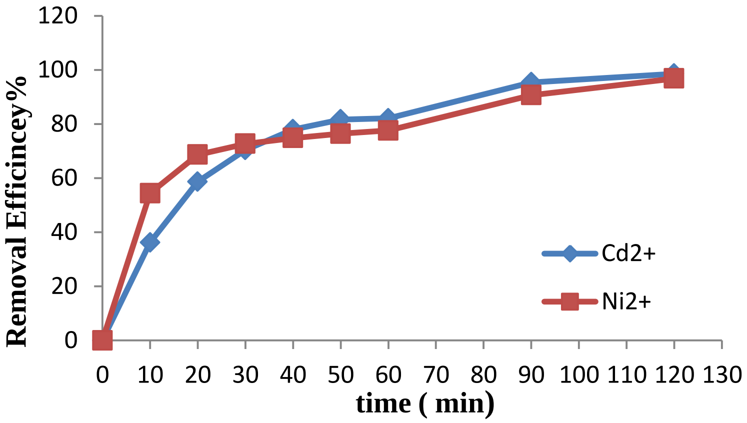

Figure 3. Effect of contact time on removal of Ni^{2+} & Cd^{2+} ions (pH 7; amount of resin 1g/l; mixing rate 400 rpm; initial metal concentration 100 mg/L; single system).

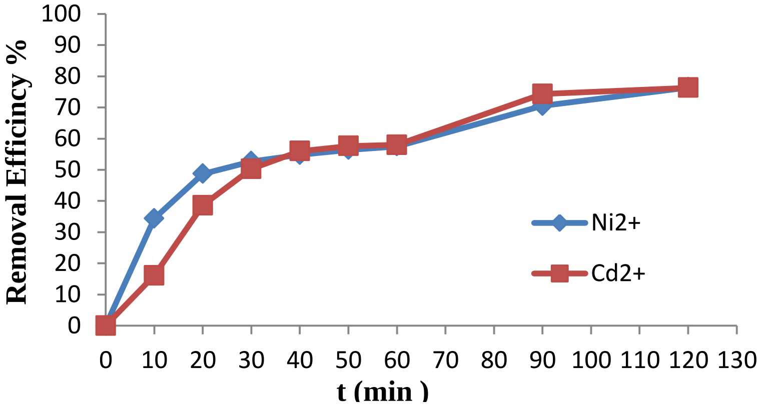

Figure 4. Effect of contact time on removal of Ni^{2+} & Cd^{2+} ions (pH 7; amount of resi 1g/L; mixing rate 400 rpm; initial metal concentration 100 mg/L, binary system).

3.3. Effect of pH

The effect of pH was examined by adjusting the pH in range of 2-8. Hydronium ion concentration is a parameter affecting the ion exchange process. This is partly because hydrogen ions themselves are strongly competing adsorbate and the solution pH influences the ionization of surface function group.; 100 mg/L metal solution was used. Resin amounts of 1 g/L were added to the beaker and solution were mixed at 400 rpm at temperature 25°C. The sorption of metal ions increases with an increase in pH. Up to pH 5, the increase in sorption is gradual, which however, increase drastically at pH > 5. At higher pH ≥ 7.0, Cd^{2+} and Ni^{2+} ions sorption become nearly constant, the amount of sorbate was found to decrease because the surface area of the sorbent were more Protonated and competitive sorption occurred between H^+ protons and free metal ions toward the fixation sited, **Onundi, et al., 2010**. Therefore, H^+ ions react with ionic functional groups on the surface of the sorbent and result in restriction of the number of the binding sites favorable for the sorption of metal ions; pH affects both the surface charge of adsorbent and the degree of ionization of heavy metals in solution. The results are plotted in **Figs. 5 and 6** for single and binary systems, respectively. From these figures it can be seen that the removal efficiency reached 98.4% and 96.7% for nickel and cadmium ions, respectively, for single system while for binary system it reaches 75.5% and 73.8% for nickel and cadmium, respectively.

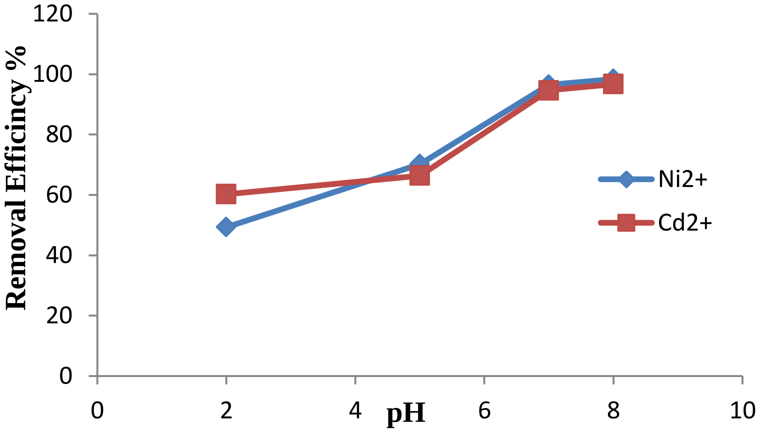

Figure 5. Effect of pH on removal of Ni^{2+} & Cd^{2+} ions (contact time 2 hr; amount of resin 1g/L; mixing rate 400 rpm; initial metal concentration 100 mg/L; single system).

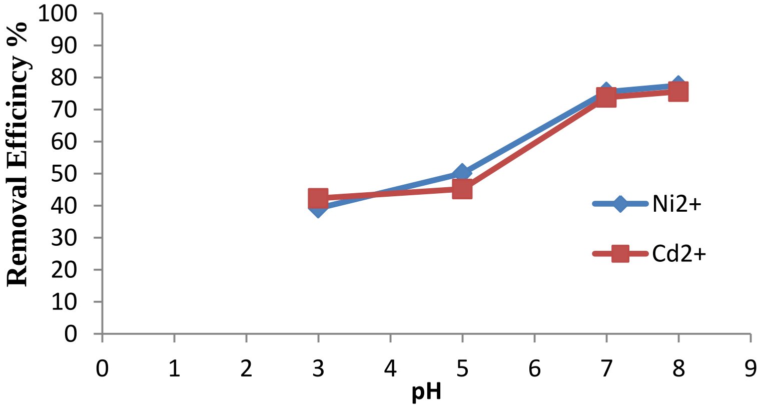

Figure 6. Effect of pH on removal of Ni^{2+} & Cd^{2+} ions (contact time 2 hr; amount of resin 1g/L; mixing rate 400 rpm; initial metal concentration 100 mg/L; binary system).

3.4. Effect of Resin Dose:

The resin amount also one of the important parameters to obtain the quantities uptake of metal ion. The dependence of metal sorption on resin amount was studied by varying the quantity of Amberlite IR120 0.25, 0.5, 1, 2 and 3 g/L in 100 mg/L of metal solution, pH 7 and contact time 2 hr. The mixing speed of 400 rpm remained constant and temperature was maintained at 25°C. The results are plotted in **Figs. 7 and 8**. These figures reveals that the removal of metal ions increase with increases in resin dosage from 0.25 to 1 g/L, the removal remain unchanged above 1 g/L of Amberlite IR120 , Obviously that by increasing the resin amount, the sorption density, and the amount of adsorbed metal ion per unit mass increases, **Rafati, et al., 2010**. A small increase in the removal efficiency can be noticed when the amount of resin increased from 1 to 3 g/L because 1g/L was enough to adsorb nearly all metals existing in the solution and reach very high removal efficiencies. The increasing in the resin amount resulted in a decrease in the contact time required to reach equilibrium. The results were expected because for a fixed initial metal concentration, increasing sorbent amount provides greater surface area or ion exchange sites or adsorption site, **Gupta and Bhatta, 2009**.

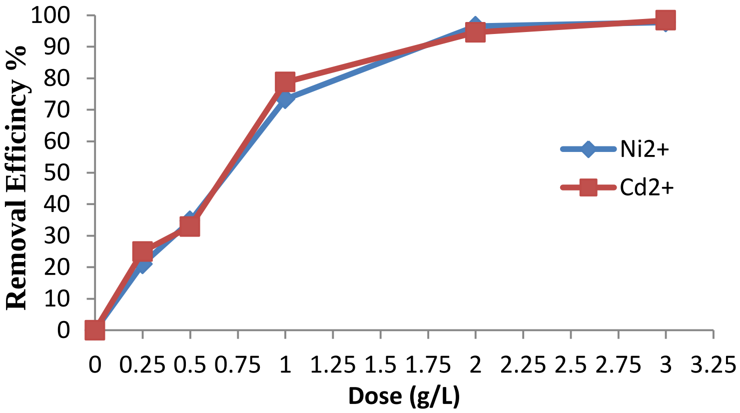

Figure 7. Effect of resin dose removal of Ni^{2+} & Cd^{2+} ions on Amberlite IR120 on (pH 7; Time 120 min; mixing rate 400 rpm; initial metal concentration 100 mg/L; single system).

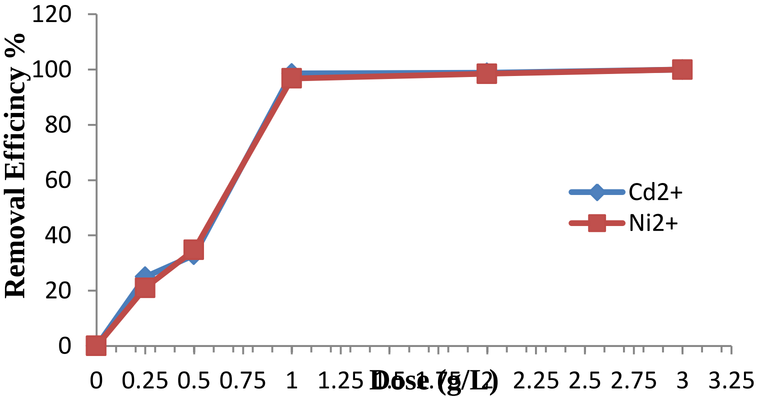

Figure 8. Effect of resin dose removal of Ni^{2+} & Cd^{2+} ions on Amberlite IR120 on (pH7; Time 120 min; mixing rate 400 rpm; initial metal concentration 100 mg/L; binary system).

3.5. Effect of Initial Concentration

Experiments were done by using 1 g/L of resin, pH 7, contact time 120 min, and constant shaking speed, 400 rpm with different initial metal concentrations 25, 50, 100, 200 mg/L for Ni^{2+} and Cd^{2+} ions. **Fig.9** shows the effect of varying metal concentrations on the sorption under the best conditions. The results show that the increase in initial metal ion concentration decreases the sorption percentage removal. This behavior due to that 1 g of resin may contain enough exchangeable sites for the concentration range 25-50 mg/L, but when the concentration increases to 100 and 200 mg/L the exchangeable sites in 1 g will not be enough to accumulate these concentrations so that the depletion in percentage removal was obvious. The maximum cation exchange resin percent was obtained as 95.7% and 91.6% for Ni^{2+} and Cd^{2+} for single system while it reaches 57.6% and 67.4% for Ni^{2+} and Cd^{2+} for binary system, respectively. This decrease in the removal efficiency is due to competition between metals Ni^{2+} and Cd^{2+} for binding sites presented in the resin. The adsorption phenomena depend on the charge density of cations. The charges of metal ions are the same (+2); therefore Cd^{2+} (biggest diameter) have minimum sorption while Ni^{2+} (least diameter) have maximum sorption.

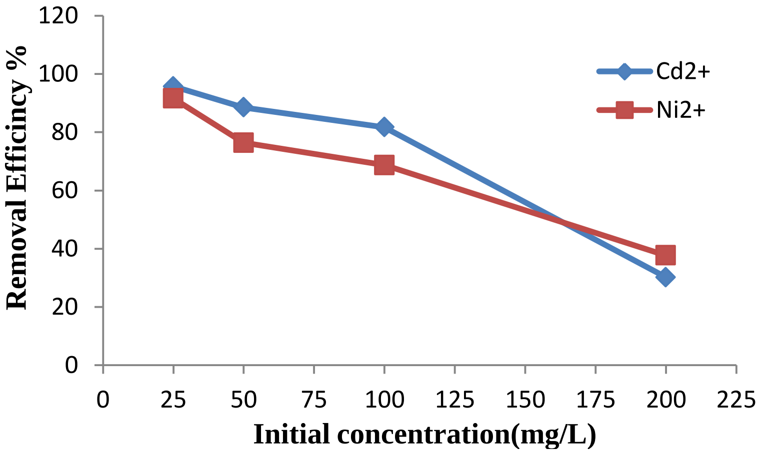

Figure 9. Effect of initial metal concentration on removal of Ni^{2+} & Cd^{2+} ions on Amberlite IR120 (pH 7; amount of resin 1g/L; Time 120 min; mixing rate 400 rpm; single system).

3.6. Sorption Isotherms

Sorption isotherms are very powerful tools for the analysis of sorption process. Sorption isotherms establish the relationship between the equilibrium pressure or concentration and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature, **Sevgi, 2007**. Langmuir and Freundlich isotherm models are widely used to investigate the sorption process.

3.6.1 Langmuir Isotherm Model

Langmuir sorption isotherm models the monolayer coverage of sorption surfaces and assumes that sorption occurs on a structurally homogenous adsorbent and all the sorption sites are energetically identical. The saturated monolayer curve can be represented by the expression, **Rao, et al., 2006**:

$$q_e = \frac{q_{max}\, bC_e}{1+bC_e} \qquad (1)$$

A linear form of this equation is:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{2}$$

Where:

b = is constant related to the affinity of the binding site (L mg^{-1}).

q_e = the sorbed metal ions on the biomass (mg g^{-1}).

C_e = metal ions concentration in the solution at equilibrium (mg L^{-1}).

q_m = maximum sorption capacity for a monolayer coverage (mg g^{-1}). The linear Langmuir plots are obtained by plotting C_e/q_e vs. C_e (**Fig. 10**).

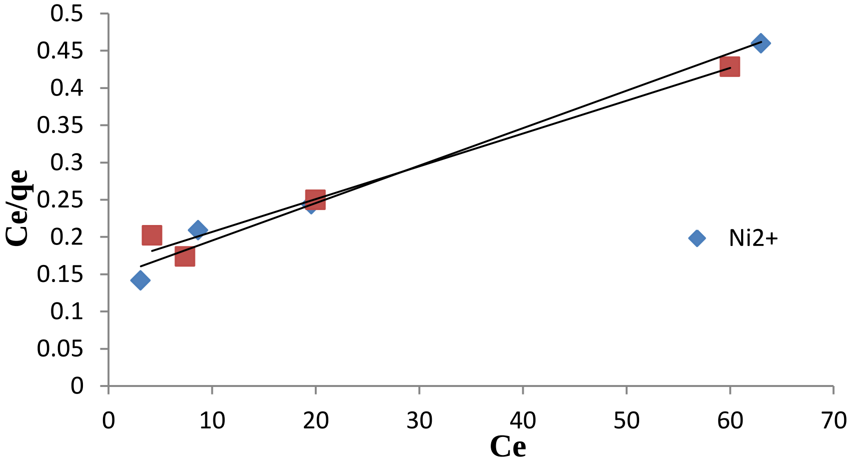

Figure 10. Langmuir isotherm for ion exchange of Ni^{2+} & Cd^{2+} ions on Amberlite IR120 (concentration 100 mg/l, amount of resin 1g/l ;Time 120 min ; mixing rate 400 rpm).

3.6.2 Freundlich Isotherm Model

Freundlich equation is derived to model the multilayer sorption and for the sorption on heterogeneous surfaces. The Freundlich isotherm theory says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations, **Rao, et al., 2006**. The Freundlich equation is:

$$q_e = K_f\, C_e^{1/n} \tag{3}$$

Where: K_f and n = the Freundlich constants

A linear form of equation 3 is:

$$Log\, q_e = (1/n) \log C_e + \log K_f \tag{4}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), Ce is the equilibrium concentration of solute in the bulk solution (mg/L), K_f is a constant indicative of the relative adsorption capacity of the adsorbent (mg/g), 1/n is a constant indicative of the intensity of the adsorption. The linear Freundlich plots are obtained by plotting log q_e versus log Ce from which the adsorption coefficients could be evaluated (**Fig. 11**). All constants determined from Langmuir and Freundlich isotherms are given in **Tables 3 and 4** for single and binary system.

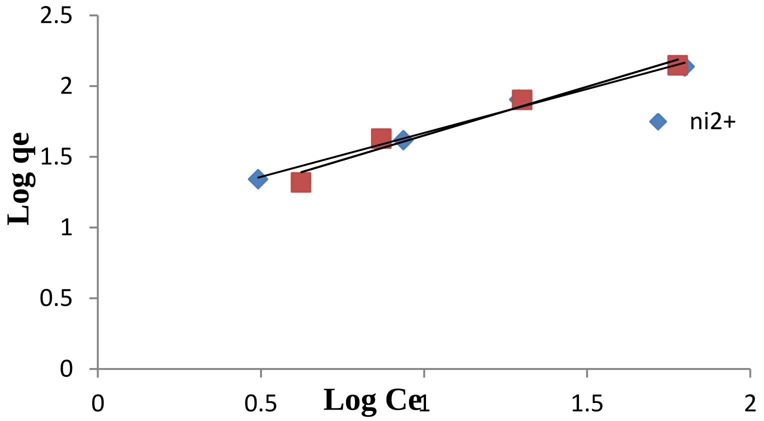

Figure 11: Freundlich isotherm of Ni^{2+} & Cd^{2+} ions on Amberlite IR 120 (pH7, concentration 100 mg/l; amount of resin 1g/L; Time 120 min; mixing rate 400 rpm).

Table 3. Parameters of Langmuir and Freundlich isotherms for ion exchange of Ni^{2+} & Cd^{2+} ions on Amberlite IR120 (single system).

Model	Parameters	Ni^{2+}	Cd^{2+}	Model	Parameters	Ni^{2+}	Cd^{2+}
Langmuir equation	qm(mg/g)	227.27	200	Freundlich equation	K_f(mg/g)	11.155	9.143
	b (l/mg)	0.0270	0.0345		1/n	0.621	0.689
	R^2	0.9771	0.986		R^2	0.9884	0.961

Table 4. Parameters of Langmuir and Freundlich isotherms for ion exchange of Ni^{2+} & Cd^{2+} ions on Amberlite IR120 (binary system).

Model	Parameters	Ni^{2+}	Cd^{2+}	Model	Parameters	Ni^{2+}	Cd^{2+}
Langmuir equation	qm(mg/g)	140.84	243.9	Freundlich equation	K_f (mg/g)	3.634	1.438
	b (l/mg)	0.0126	0.004		1/n	0.6718	0.8438
	R^2	0.9937	0.9925		R^2	0.9946	0.9981

3.7. Kinetics of Sorption

The study of sorption kinetics of heavy metal removal from waste water is significant as it provides valuable insights into the reaction pathways and into the mechanism of sorption reaction. Monitoring a kinetic experiment helps to study how the sorption system is affected by process variables and to understand the step which limit sorption. In addition the sorption kinetics describes the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid – solution interface .Therefore it is important to predict the rate at which sorbate is removed from aqueous solutions in order to design appropriate treatment processes. Kinetic studies were performed by using 100 mg/L concentration, pH was adjusted to 7, resin mass was 1 g and 400 rpm for 120 min.

3.7.1. Pseudo-First Order Reaction Kinetic

Simple linear equation for Pseudo-first order reaction kinetic is, **Lagergren, 1989**.

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad (5)$$

where k_1 is the rate constant of the first-order adsorption, q_t is the amount of heavy metal adsorbed at time t (mg/g) and qe is the amount of heavy metal adsorbed at saturation (mg/g). Plot of ln (q_e-q_t) versus t allows calculation of the rate constant k_1 and q_e.

3.7.2. Pseudo-Second Order Reaction Kinetic

Pseudo-second order reaction kinetic can be expressed as, **Ho and Mckay, 1999**:

$$\frac{t}{q_t} = \frac{1}{h} + (\frac{1}{q_e})t \qquad (6)$$

$h=k_2q_e^2$ that can be regarded as the initial sorption rate as $t \longrightarrow 0$. Under such circumstances, the plot of t/q_t vs. t should give a linear relationship, which allows the computation of q_e, K_2 and b. A comparison of sorption rate constants, experimental and calculated q_e values for the pseudo- first and pseudo second order reaction kinetics of removal of Ni^{2+} and Cd^{2+} for single and binary systems are tabulated in **Tables 5 and 6**, respectively.

Table 5. Comparison of sorption rate constants, experimental and calculated q_e values for the pseudo-first- and –second-order reaction kinetics of removal of Ni^{2+} & Cd^{2+} ions by Amberlite IR120 for single component systems.

Metal	q_e *experimental mg/g*	Pseudo-first-order			Pseudo-second-order		
		$k_1 * 10^3 min^{-1}$	q_e *calculated mg/g*	R^2	$k_2 * 10^{-3}$ *g/mg h*	q_e *calculated mg/g*	R^2
Ni^{2+}	98.3	0.0375	66.254	0.9848	$1.408*10^{-3}$	102.04	0.9942
Cd^{2+}	98.6	0.0365	76.624	0.9689	$7.14*10^{-4}$	107.52	0.9796

Table 6. Comparison of sorption rate constants, experimental and calculated q_e values for the pseudo-first- and –second-order reaction kinetics of removal of Ni^{2+} & Cd^{2+} ions by Amberlite IR120 for binary component systems.

Metal	q_e *experimental mg/g*	Pseudo-first-order			Pseudo-second-order		
		$k_1 * 10^3 min^{-1}$	q_e *calculated mg/g*	R^2	$k_2 * 10^{-3}$ *g/mg h*	q_e *calculated mg/g*	R^2
Ni^{2+}	38.2	0.0361	29.189	0.9662	$9.08*10^{-4}$	45.66	0.9945
Cd^{2+}	39.15	0.0375	25.888	0.935	$1.235*10^{-3}$	42.918	0.9911

4. FLOTATION

After the completion of the sorption stage, the solution transferred to the second stage (flotation stage), and study removal efficiency for different time intervals 2,5,10,15 min at different pH value 3,5,7 and 8 with two types of surfactant, Sodium Lauryl Sulphate (SLS) and Hexadecyltrimethyl ammonium bromides (HTAB) as cation and anion surfactant respectively with different surfactant concentration 100 , 200 and 300 mg/L.

4.1 Effect of pH

Several works related to the foam separation techniques point out that pH plays an important role in flotation. Depending on pH, different interfacial properties and reaction routes may be found, **Matis and Mavros, 1991**. The effect of pH on the removal of nickel & cadmium ions by bubble column are shown in **Figs. 12 and 13** by plotting the removal ratios versus time at various pH values .As shown in these figures the removal ratios increase after approximately 5 minute from the beginning of the run. It was found that the highest removal achieved when the pH of the solution was between 7-8, this result was similar to **Turtureanu, et al., 2008**. They suggested that the flotation of nickel and cadmium ions, has significantly values of removal efficiency at pH 7 -8 because at pH higher than 8 the metals will precipitates as hydroxide and flotation is a precipitate flotation process.

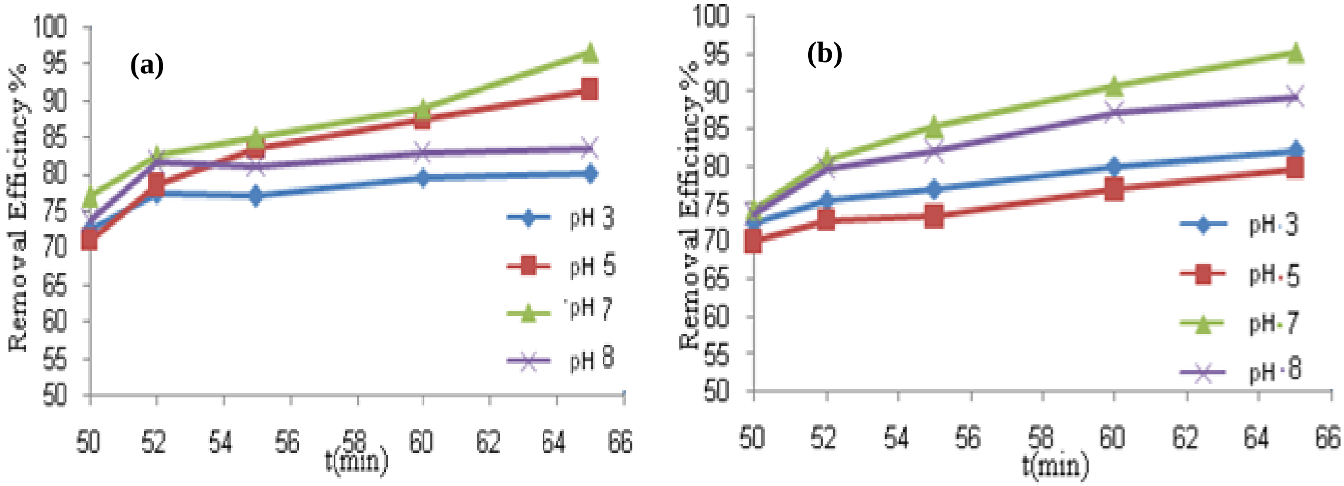

Figure 12. Effect of pH on the removal efficiency of (a) Cd^{2+} (b) Ni^{2+} (concentration 100 mg/L; Q=500 ml/min; SLS=100 mg/L; single system).

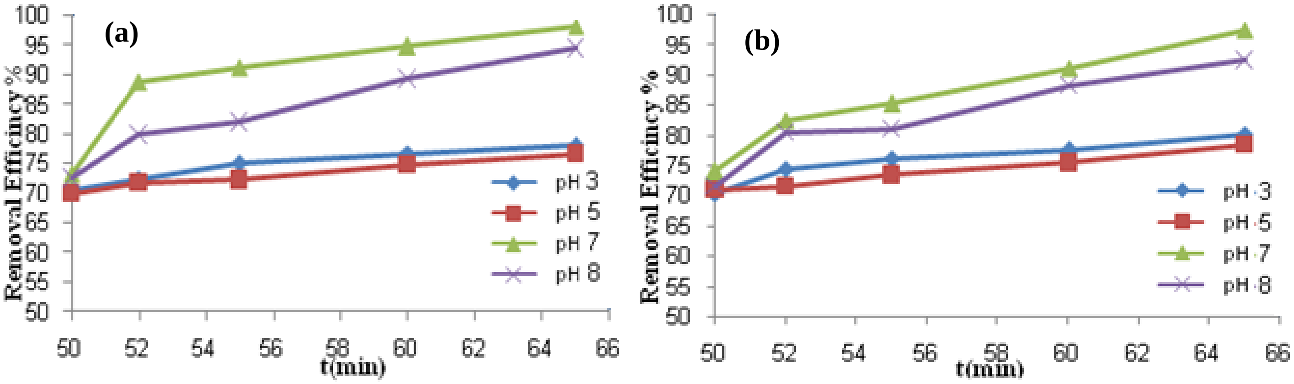

Figure 13. Effect of pH on the removal efficiency of (a) Ni^{2+} (b) Cd^{2+} (concentration 100 mg/L; Q=500 ml/min; SLS=100 mg/L; binary system).

4.2 Effect of Surfactant Type

The type of surfactant plays a significant role in foam flotation. The type of collector needed depends on the pH of the solution. In general, anionic collectors are needed at pH 1-7 because the metal ions are in cationic forms. at very high pH, cationic collectors would be needed if the metal ions were present as anions, **Zoubolis and Matis, 1987**. The removal rate of Ni^{2+} and Cd^{2+} ions from water was studied at two different types of surfactant (sodium lauryl sulfate and Hexadecyltrimethyl ammonium bromide) in order to show the effect of adding anionic and cationic surfactant on the removal rate of metal ions. The effects are shown in **Figs. 14 and 15** by plotting the (R %) versus time. From these figures, it can be seen that the anionic surfactant (SLS) at pH 7 is more efficient than the cationic surfactant (HTAB) at the same pH, no significant removal rate was obtained using (HTAB), **Al-Obaidi, 2011**.

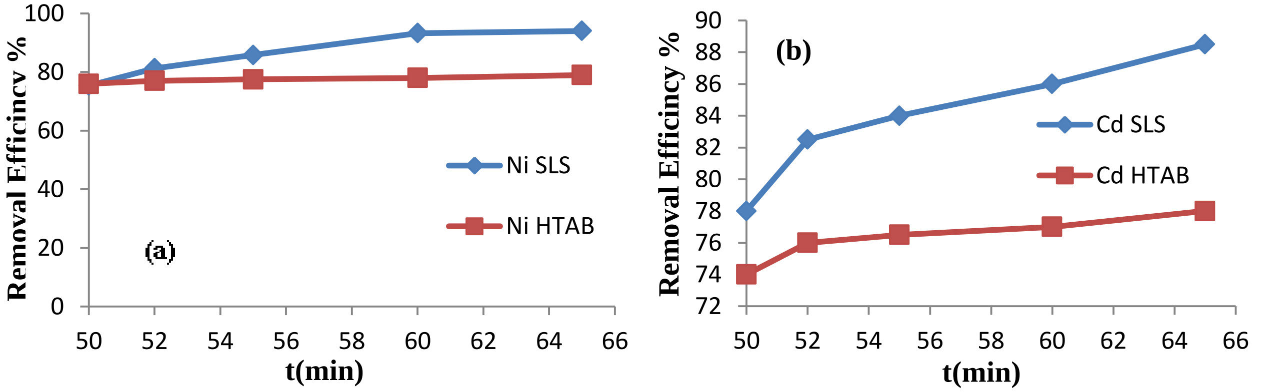

Figure 14. Effect of surfactant type on the removal ratio of (a) Ni^{2+} (b) Cd^{2+} (concentration 100 mg/L; Q=500 ml/min; SLS=100 mg/L; HTAB=100 mg/L; single system).

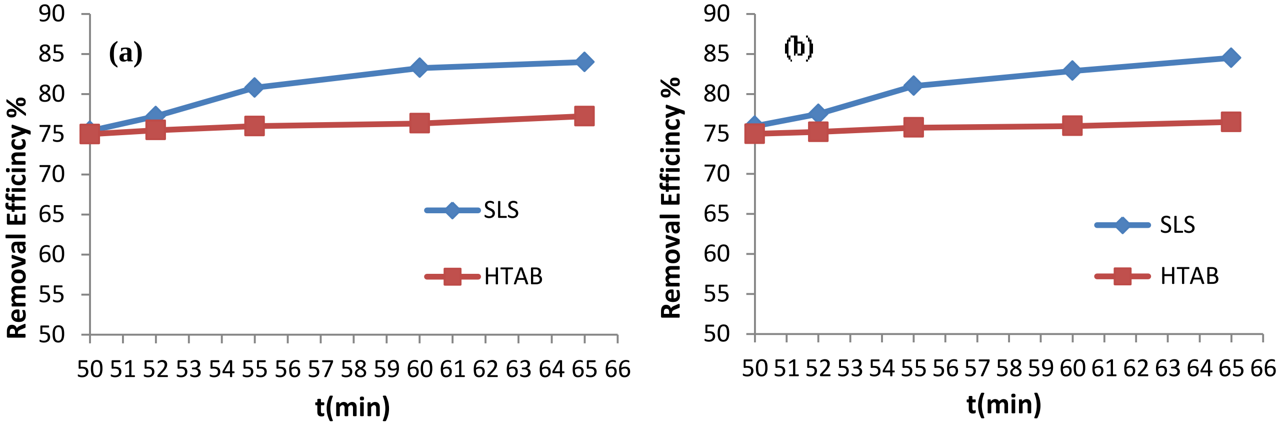

Figure 15. Effect of surfactant type on the removal of (a) Ni^{2+} (b) Cd^{2+} (concentration 100 mg/L; Q=500 ml/min; SLS=100 mg/L; HTAB=100 mg/L; binary system).

4.3 Effect of Surfactant Concentration

The key to floatability (or non floatability) of chemical species is hydrophobicity. Substances are rendered hydrophobic by addition of the appropriate collector, in which the polar groups are eliminated by adsorption leaving non-polar groups exposed to solution. An important factor relates to the ratio of collector to metal ion. Usually a small excess of collector is added to guarantee maximum removal of the metallic ions in solution. Excessive collector should be avoided, not only due to higher cost, but also because of other negative effects, such as large foam losses, micelle formation, competition between the metal-collector complex and free collector ions for bubble surface sites and the potential toxicity of residuals amounts of collector in the effluent, **Scorzelli, et al., 1999**. The ions are completely soluble at pH 7 and the removal rates are strongly dependent on collector concentration requiring higher collector concentration for complete removal and at high pH the ions are insoluble, the effect of different SLS concentrations on the Ni^{2+} and Cd^{2+} removal efficiency at pH=7 are presented in **Figs. 17 and 18** respectively. From these figures, it can be seen that at low surfactant concentration 50 mg/L low removal was obtained, this may be attributed to the presence of insufficient amounts of surfactant required for complete flotation, **Ghazy, et al., 2008**.The separation efficiency improves with increasing surfactant concentrations up to 200 mg/L. Further increasing in surfactant concentration up to 300 mg/L results in decreasing in the removal efficiency. The decreasing in the metal removal for raised collector concentration can be due to competition between collagen collector complex and free ion collectors for a place in the surface of the bubble, **Medina, et al., 2005, Mohammed, et al., 2014**.

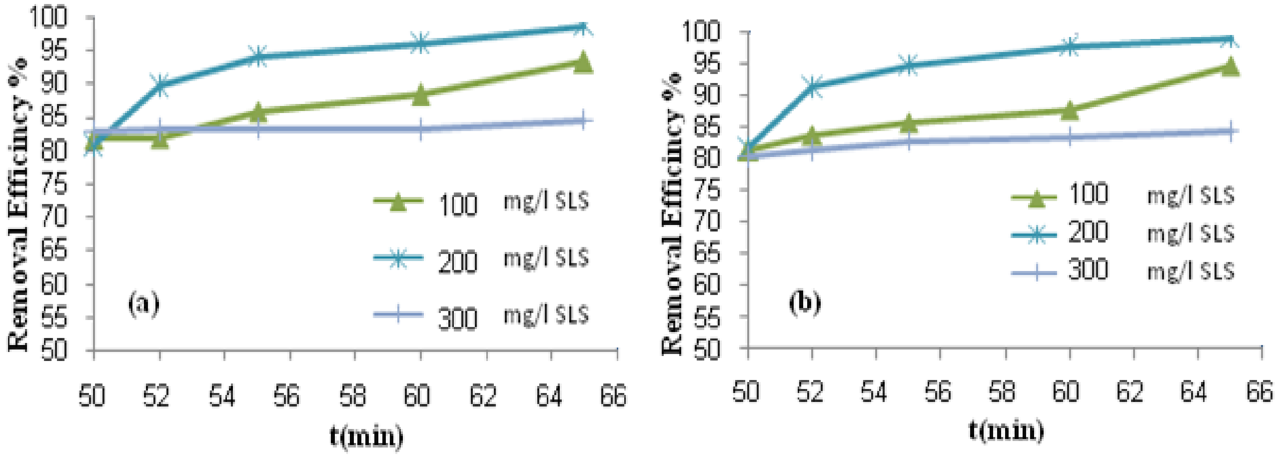

Figure 16. Effect of surfactant concentration on the removal efficiency of (a) Ni^{2+} (b) Cd^{2+} (concentration 100 mg/L; Q=500 ml/min; SLS=100 mg/L; single system).

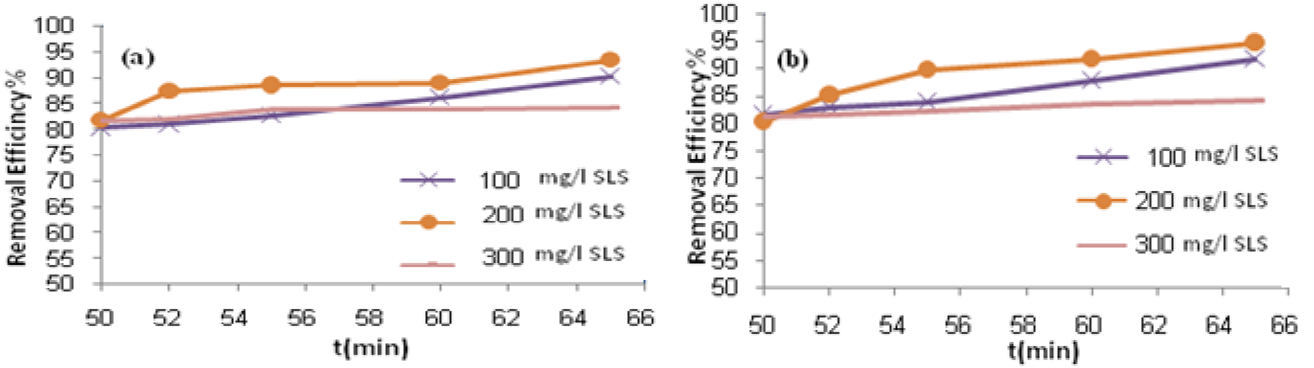

Figure 17. Effect of surfactant concentration on the removal efficiency of (a) Ni^{2+} (b) Cd^{2+} (concentration 100 mg/L; Q=500 ml/min; SLS=100 mg/L; binary system).

4.4 Effect of Air Flow Rate

The effect of gas flow rate 500, 1000 and 1500 ml/min on the removal efficiency of Ni^{2+} and Cd^{2+} in the bubble column was investigated. The results are shown in **Figs. 18 and 19** for pH=7 as gas flow rate increased, the removal ratio increased, This is because increased gas flow rate causes early bubble detachment, large fluid activities (stress) at the bottom section and bubble coalescence and (mostly) break up, **Sulaymon and Mohammed, 2010**. This results in a large number of small bubbles which leads to increasing surface area available for adsorption metal-collector.

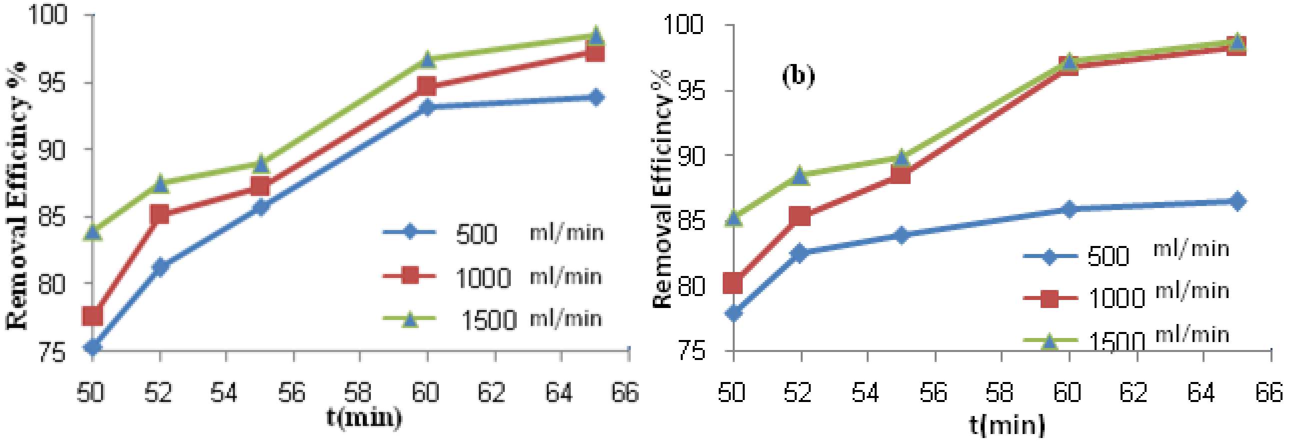

Figure 18. Effect of Air flow rate on the removal ratio of (a) Ni^{2+} (b) Cd^{2+} (concentration 100 mg/L; SLS=100 mg/L; single system.

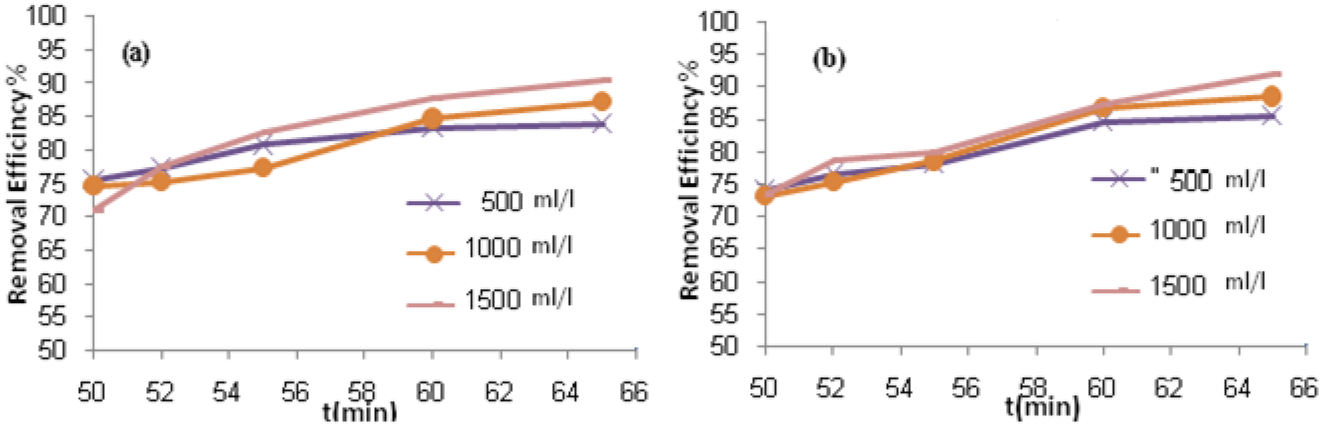

Figure 19. Effect of Air flow rate on the removal ratio of (a) Ni^{2+} (b) Cd^{2+} (concentration 100 mg/L; SLS=100 mg/L; binary system.

5. TURBIDITY

Turbidity is the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample, **Asano, 2007**. In our case turbidity caused by 3 different things (Amberlite IR120 resin, Ni^{2+} and Cd^{2+} ions, and SLS as a surfactant). The practical benefit of sorptive flotation process include turbidity decreasing from the wastewater , and by flotation process we will not need the filtering process, which is a complex and expensive one compared to the process of flotation. There is now interest in the technology as a pretreatment step in Ultrafiltration membrane plants and in desalination reverses osmosis plants, **Edzwald, 2010**, and by reducing turbidity the process of removing heavy metals from wastewater completed and here we fine the benefit of sorptive flotation.

5.1 Turbidity with Different Surfactant Concentration

From **Fig. 20** obviously turbidity rate dropped during the flotation process with different surfactant concentration. In the beginning of flotation process the contaminated water include three different contaminants metals and resin from the sorption stage and surfactant that added after sorption stage, the initial turbidity increase with increasing surfactant concentration. From this figure it can be noticed that starting the flotation process the turbidity decrease immediately in the first 2 min and almost fades after 15 min. the turbidity reduction efficiency reaches 90%, 85.3% and 78% for 100 mg/L, 200 mg/L and 300 mg/L SLS concentration, respectively. From these result we realized the fact that the flotation process is very useful and conceders to be very effective process to remove turbidity, and also we find out that with increasing of the surfactant concentration will decrease the turbidity removal efficiency.

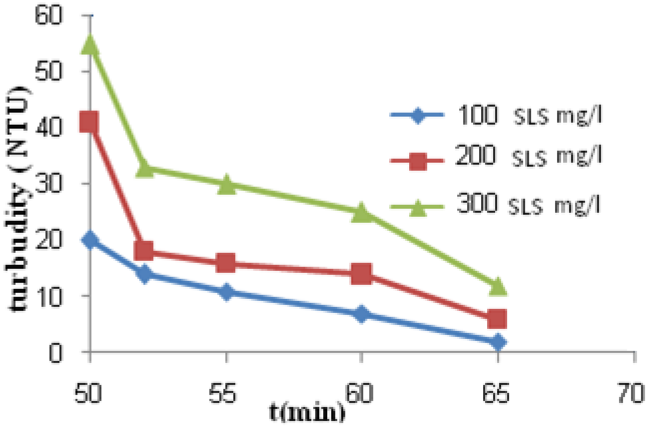

Figure 20. Turbidity with different surfactant concentration (resin dose 1g/L; Q=500 ml/L).

5.2 Turbidity with Different Flow Rates

Water flow rate has a significant influence in reducing turbidity due to increasing the bubble rise velocity .The effect of air flow rate on the turbidity removal is shown in **Fig. 21**. The experimental results showed that at 500 ml/min the turbidity decrease about 90 % while in 1500 ml/min the removal efficiency of turbidity is about 100%.

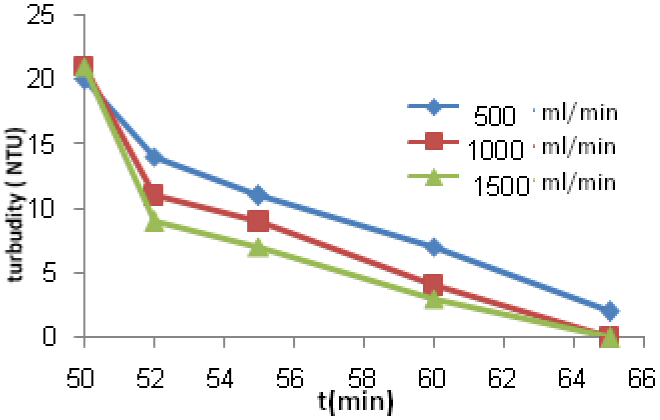

Figure 21. Effect of Air flow rate on the removal of turbidity (resin dose 1g/L; concentration=100 mg/L; SLS=100 mg/L).

4. CONCLUSION

The following conclusions are exacted from the present study:

1- Amberlite IR120 strong acid cation exchange resin is a better alternative to Amberlite CG50 weak acid cation resin for the removal of nickel and cadmium ions from wastewater.
2- The optimum pH for metal ions sorption on to Amberlite IR120 is about 7.
3- The linear Langmuir and Freundlich, isotherms were used to represent the experimental data. Langmuir and Freundlich both results good fitting to the experimental data for the two metals.
4- The monolayer adsorption capacity of nickel and cadmium calculated from Langmuir model was obtained 227.27, 200 mg/g for nickel and cadmium respectively.
5- By applying the kinetic models to the experimental data, it was found that the adsorption of nickel and cadmium ions on Amberlite IR120 resin followed second order kinetics.
6- The anionic surfactant SLS was found to be more efficient than HTAB. Removal efficiency increase with increasing SLS concentration up to 200 g/l for both metals while above this concentration the removal efficiency decrease due to the competition between colligend collector complex and free ion collectors for a place in the surface of the bubble.
7- Removal efficiency increase with increasing air flow rate , because of the large number of small bubbles which leads to increasing surface area available for adsorption metal-collector
8- Flotation process very effective in reducing turbidity so it can dispense with the filtering process, which is expensive technology by the flotation process.

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