Flotation Method for Selective Separation of Lead and Zinc from Simulated Wastewater

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ABSTRACT

In this paper flotation method experiments were performed to investigate the removal of lead and zinc. Various parameters such as pH, air flow rate, collector concentrations, collector type and initial metal concentrations were tested in a bubble column of 6 cm inside diameter. High recoveries of the two metals have been obtained by applying the foam flotation process, and at relatively short time 45 minutes . The results show that the best removal of lead about 95% was achieved at pH value of 8 and the best removal of zinc about 93% was achieved at pH value of 10 by using 100 mg/l of Sodium dodecylsulfate (SDS) as a collector and 1% ethanol as a frother. The results show that the removal efficiency increased with increasing initial metal concentrations in the alkaline conditions while it decreased in the acidic condition. Increasing air flow rate up to 1000 ml/min enhanced the separation efficiency. Selective flotation experiments were also conducted in the presence of metal ion mixture solutions. It was possible to separate lead and zinc under suitable condition, successful removals reached about 84% and 81% for lead and zinc respectively . It was observed that the first order equation fitted the data as good and better than any of the other equations.

KEY WORDS: - Flotation, heavy metals, wastewater

طريقة التعويم للفصل الانتقائي لعنصري الرصاص والخارصين من المياه الملوثه

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الخلاصه

طريقه التعويم انجزت لتحقيق فصل عنصري الخارصين والرصاص من المياه الملوثه ولقد تم دراسه العوامل التي تؤثرعلى عمليه الازاله وبالتالي كفاءه الفصل هذه العوامل تتضمن الداله الحامضيه ،تصريف الهواء، تركيز الخارصين، تركيز الرصاص، تركيزالماده الخافضه للشد السطحي ونوعها وايضا تاثير اضافه ملح الطعام. ولقد تم الحصول على كفاءات عاليه في استرجاع العنصرين باستخدام طريقه التعويم وبوقت قصيرنسبيا 45 دقيقه. النتائج اعطت 95% استرجاع لعنصرالرصاص في داله حامضيه مقدارها8 و93% استرجاع لعنصرالخارصين تم في داله حامضيه مقدارها 10 باستعمال SDS كماده خافضه للشد السطحي واستخدام 1%ايثانول كعامل مساعد. النتائج بينت ان زياده التركيز الاولي للعناصر يزيد كفاءه الازاله في الوسط القاعدي ويقللها في الوسط الحامضي .وقد وجد ان زياده تصريف الهواء الى 1000 ml/min يزيد كفاءه الازاله .

تجارب التعويم للفصل الانتقائي ايضا تم مناقشتها بوجود محاليل خليط ايونات المعادن حيث من الممكن فصل الرصاص والخارصين تحت ظروف ملائمه بكفاءات 84% و81% للرصاص والزنك على التوالي .وقد وجد ان معدل ثابت الانتقال من الدرجه الاولى.

كلمات رئيسيه :- التعويم، العناصر الثقيله، المياه الملوثه

INTRODUCTION

Water pollution is nowadays a matter of deep apprehension. Many industrial wastewaters contain numerous toxic metals, such as chromium, zinc, cadmium, lead and copper which must be removed before reuse of the water or its discharge to the environment (Zhang and Jing, 2009). In order to reduce the pollution problem in environment that is caused by these heavy metals, their concentrations must be reduced before discharging to obey the wastewater standards So, an effective treatment process must be applied. Among the evaluated processes flotation method is proved to be one of the most effective method as a separation process due to its simplicity, rapidity, economy, good and high separation yields(R>95%), large possibility of application for species having different nature and structure and production of more concentrated sludge, occupying smaller volumes .It is believed that this process will be soon incorporated as a clean technology to treat water and wastewater (Ghazy et. al.,2008). Therefore, flotation technique was selected for this investigation. The technique of ion flotation provides a simple physical method for removing and concentrating the ions present in very dilute solutions. The method is classified as a foam separation process, which relies on the direct

Interaction between an ionic surfactant and an oppositely charged metal ion (either simple or complex). If the ions to be removed are not surface active, they can be made so through union with or adsorption of surface-active agents (Nicol et. al.,1992). With the aid of suitable surfactants the metal ions are rendered hydrophobic giving origin to metal-collector complexes known as "sublate". When rising bubbles are introduced into the system, the sublate adsorbs on the bubble-water interface and are carried upwards producing a foam layer at the top of the bulk solution. This layer can then be physically separated from the bulk solution (Scorzelli et. al.,1999). The size of the air bubbles in flotation cell should be fine in the order of a few hundred micrometers to present sufficient surface area for collection. The reagents which control the size of the bubbles by reducing the air/water interfacial tension are called frothers. As opposed to the classical flotation process where the valuable mineral species are floated and removed with the froth, ion flotation is selectively concentrating the metal ions in froth phase. A successful removal of metal ions should correspond to a large metal ion/water ratio in the froth phase (Polat and Erdogan, 2007). The scope of this study was to investigate the efficiency of bubble column for the removal of zinc and lead from waste water analyzing the flotation kinetics in term of pH, air flow rate, anionic and cationic surfactant, initial metals concentration and ionic strength.

EXPERIMENTAL WORK

Materials

two types of surfactants, Sodium dodecyl sulfate (SDS; MW=288 g/mol) and Hexadecyltrimethyl ammonium bromides (HTAB; MW=364.5 g/mol) from Fisher Scientific were used as anionic and cationic collectors, respectively. The first type is a white powder material with a chemical structure of ($C_{12}H_{25}OSO_3Na$).The second type is a white powder material with a chemical structure of ($C_{12}H_{42}BrN$). Ethanol (C_2H_5OH) from Lancaster Synthesis was used as frother. Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2o$, assay (complexometric)= 98.5-102% and MW=297.51 g/mole) made in the European Union and Lead nitrate ($Pb(NO_3)_2$; Minimum assay =99.5% and MW=331.21 g/mole) made by (BPH) chemical LTd poole England were used as the colligend. Sodium chloride (NaCl, purity=99.5% wt) from Fisher Scientific were used as the ionic strength adjuster. Nitric acid (HNO_3) and caustic soda (NaOH) were used for pH adjustments. Air was the gas used in the present study (compressed at 1 bar up to 7 bars) and supplied by a compressor.

Method

The foam flotation tests were carried out in a bubble column (acrylic) of 6 cm inside diameter and 120 cm in height. 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 enter with different metal concentration (25 ,50 ,and 100 ppm) was poured gently at the top of the column. Perforated plate of the air distributor was used which has 25 holes with 0.05 cm diameter. 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, arranged at interval of 15cm and used to draw samples from the column.

Preparation of Solution

Synthetic polluted water samples with desired concentration of Zinc and Lead were prepared by dissolving ($Zn(NO_3)_2.6H_2O$, and $Pb(NO_3)_2$) in distilled water. Surfactants and ethanol were added to the synthetic polluted water. Foam samples were taken at preset time intervals as 3, 5, 10, 15, 20, 25, 30, 40 and 55 minutes. A port 0.45 m above the base was used for periodic sampling. The required mass of $Zn(NO_3)_2.6H_2O$ or $Pb(NO_3)_2$ was calculated as follows:

$$W = V \times C_i \times \frac{M.wt}{At.wt} \quad (1)$$

Where W: Weight of $Zn(NO_3)_2.6H_2O$ or $Pb(NO_3)_2$ (mg); V: Volume of solution (l); C_i: Initial concentration of zinc or lead ions in solution (mg/l); MW: Molecular weight of $Zn(NO_3)_2.6H_2O$ or $Pb(NO_3)_2$ (g/mol); At.wt: Atomic weight of zinc or lead (g/mole).

RESULTS AND DISCUSSION

Effect of pH

Solution pH is a significant factor for determining the form and the charge of the metal present in solution, so, the initial flotation tests were conducted as a function of pH to observe the response of the zinc and lead towards the collectors used. The experiments with anionic SDS (100 mg/l) were carried out at pH values of 3, 6, 8, and 10 for lead and zinc and the results are presented in Figures 1 and 2. These Figures show that the concentration ratios decreases suddenly at the beginning of the run then the ratios began to decrease slowly with time due to consumption of surfactant with time. From the figure the highest removal of lead was a chieved when the pH of the solution was 8. And the highest removal of zinc was achieved when the pH of the solution was 10. According to (Ghazy et. al.,2008) the dominant species for lead are positively charged Pb^+, $PbOH^+$ recovery for pH value of 8. The removal of lead ions at pH=8 was rapid and virtually complete within a relatively short time than the removal of lead at any other pH. Similar observations can also be made for Zn at pH value of 10. At pH 10 where zinc hydroxide precipitation take place the removal of zinc ions was more efficient (Zouboulis et. al., 2003).

Effect of initial metal concentration

The effect of initial metal concentration was also tested. The results were presented in Figures 3 and 4, when the initial metals concentrations was increased to 100 mg/l in the presence of 100 mg/l SDS and 1% ethanol at pH 8 for lead and pH 10 for zinc, the recovery decreased. According to (Shakir and Ahmed, 2010) the decreasing in removal rate due to large surfactant:metal ion ratio which cause competition for bubble surface, between the metal-collector product and free collector ions.

Effect of surfactant concentration

Similar flotation tests were also conducted as a function of SDS at pH value of 8 for lead and 10 for zinc, the results were presented in Figures 5 and 6. From these figures, it was found that surfactant concentrations have a much greater effect on removal efficiency at acidic conditions than basic conditions. This result was similar to (Lemlich, 1972) he suggested that the metal ions are completely soluble at low pH and the removal rates are strongly dependent on collector concentration requiring higher collector concentration for at pH values less than 8, and they are negatively charged $Pb(OH)^-_3$ and $Pb(OH)^-_4$ at pH values greater than 8. At pH value of 8, precipitation takes place that explain the higher complete removal and at high pH the metal ions are insoluble and the removal rates are considerably less affected by collecter concentration.

Effect of surfactant type

The removal rate of metals ions from water was studied at two different types of surfactant (sodium dodecyl sulfate and Hexadecyltrimethyl ammonium bromide) in order to show the effect of adding anionic and cationic surfactant on the removal rate of metals. The effect are shown in Figures 7 and 8. From these figures, it can be seen that the anionic surfactant (SDS) is more efficient than the cationic surfactant (HTAB), and at pH 8 for (lead, zinc) there is no significant removal rate was obtained by using (HTAB) and the removal rate increases for pH 10 for lead. This result was similar to Polat and Erdogan (2007) they suggested that the increasing removal rate for more alkaline pH solutions was explained by the appearance of negatively charged metal species.

Effect of air flow rate

The effect of air flow rate (250,500 and 1000 ml/min) at fixed SDS and ethanol concentration was also tested. The data presented in Figures 9 and 10 indicate that the removal efficiency of metals was highly affected by the gas flow rate. According to (Sulaymon and Mohammed, 2010) as gas flow rate increased, the removal efficiency 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. However, higher gas flow rate of 1000 ml/min results in decreasing the removal efficiency from the maximum due to the redispersion of some of the metal collector–precipitate product back in to the bulk solution.

Selective flotation of metals

In the selective flotation of lead and zinc, metal ions were floated selectively when they are present together. The foregoing discussion implies that selective separation of ionic constituents in a solution can be achieved through pH adjustment (Lu et. al. 2005). Different flotation experiments were performed. The influence of the pH on the selectivity of metal ions were examined, for Lead-Zinc system, the best separation of lead was achieved at pH 8 where the lead in precipitate form $pb(OH)_2$ whereas zinc is in positive form.The results are presented in Figures 12 these results simply show that SDS has much more affinity towards the available lead species at this pH than it has towards the zinc species. And the best separation of zinc was achieved at pH 10 where the zinc in precipitate form $Zn(OH)_2$ whereas lead is in negative form.

The effect of adding NaCl to the (Zinc-Lead) system at pH value of 8 was shown in Figures 11 From this figure the removal rate decreases with NaCl concentration. This decrease can be explained by the competition between Na^+ ions with Zn^+ and Pb^+ ions so the metals cannot find enough sulfate molecules to attach to (Choi et. al.,1998).

CONCLUSIONS

1. High recoveries of metals from dilute aqueous solutions containing SDS have been obtained by applying the foam flotation process, and at relatively short time. The results show that the best removal of lead
2. about 95% was achieved at pH value of 8 when lead concentration 100 mg/l, SDS concentration 100mg/l, ethanol 1% and gas flow rate 500 ml/min and the best removal of zinc about 93% was achieved at pH value of 10 when zinc concentration 100 mg/l, SDS concentration 100mg/l, ethanol 1% and gas flow rate 500 ml/min.
3. Flotation studies were conducted to investigate the selectively removing metals, high recoveries from mixture solutions containing SDS have been obtained. The results show that for lead the best removal about 84% was achieved at pH value of 8 and for zinc the maximum removal efficiency about 82% was achieved at pH value of 10, when zinc concentration 100 mg/l, lead concentration 100 mg/l, SDS concentration 100 mg/l, ethanol 1% and gas flow rate 500 ml/min.

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l; SDS=100 mg/l; Q =500 ml/min;
Ethanol=1%)

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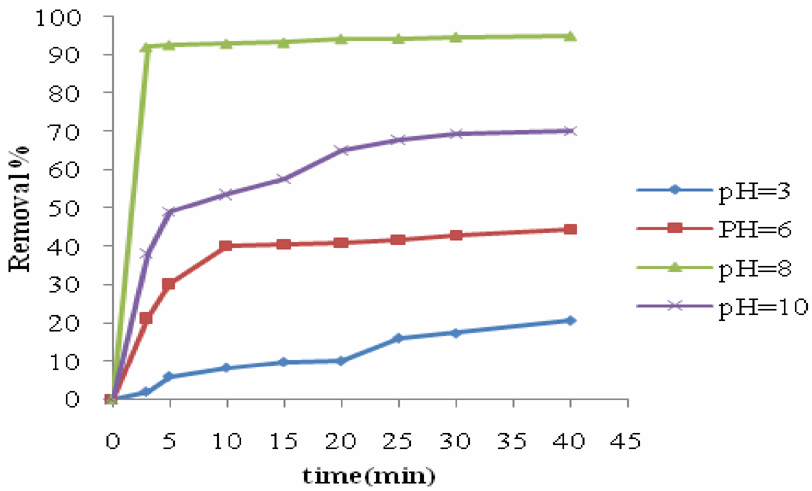

Fig. 1 Effect of pH on the removal efficiency of lead ions (C_o = 100 mg/l; SDS=100 mg/l; Q =500 ml/min; Ethano1=1%).

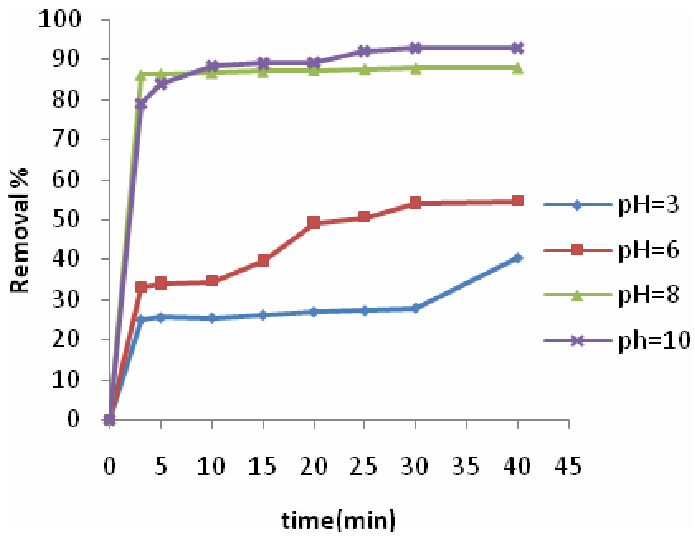

Fig. 2 Effect of pH on the removal efficiency of zinc ions (C_o = 100 mg/l; SDS=100 mg/l; Q =500 ml/min; Ethanol=1%).

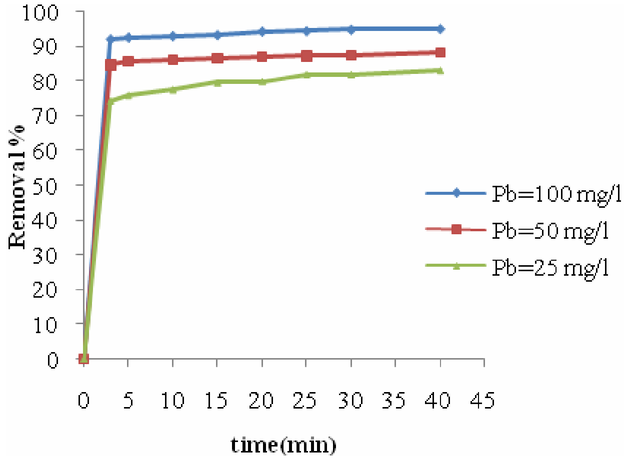

Fig. 3 Effect of lead concentration on the removal rate (pH=8; SDS= 100mg/l; Q=500 ml/min)

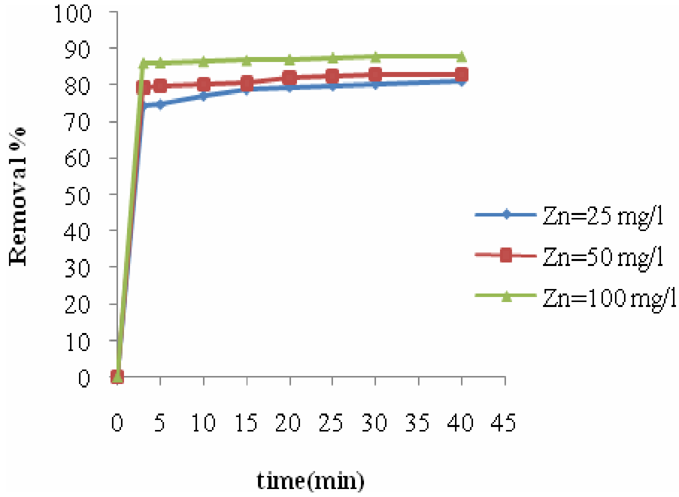

Fig. 4 Effect of zinc concentration on the removal rate (pH=8; SDS= 100 mg/l; Q =500 ml/min)

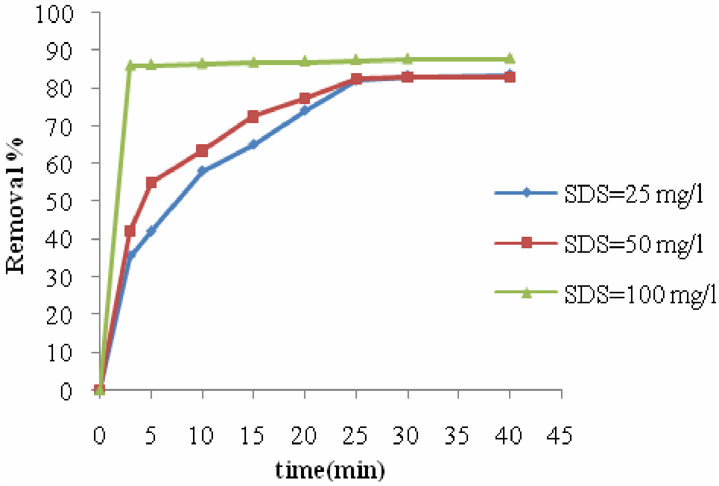

Fig.5 Effect of surfactant conc. on the removal of zinc that (pH = 8; Co = 100 mg/l; Q = 500ml/min)

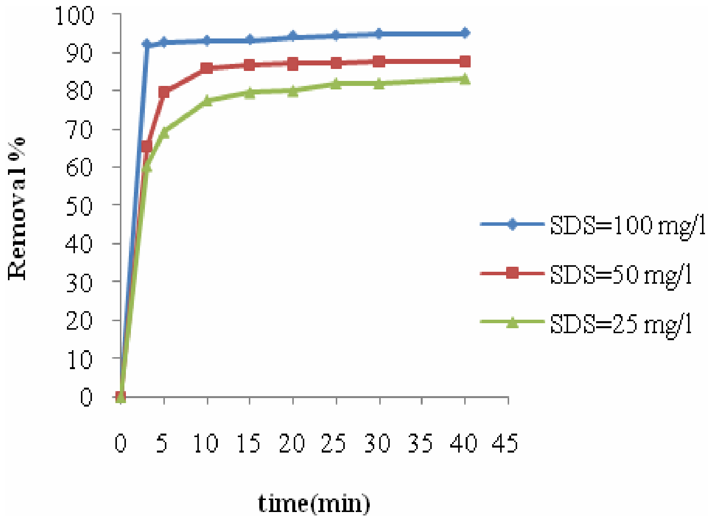

Fig. 6 Effect of surfactant conc. on the removal rate of lead (pH=8; Co=100mg/l; Q=500ml/min)

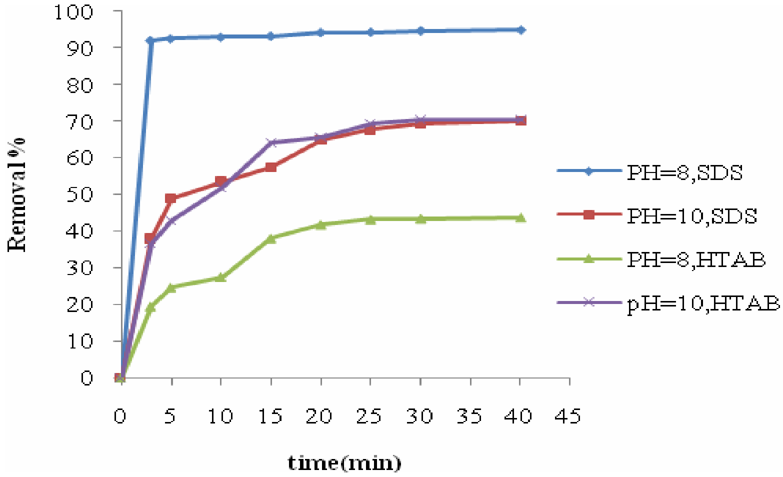

Fig.7 Effect of surfactant type on the removal rate of lead (SDS=100mg/l; HTAB=100mg/l; Pb=100 mg/l; Q=500ml/min)

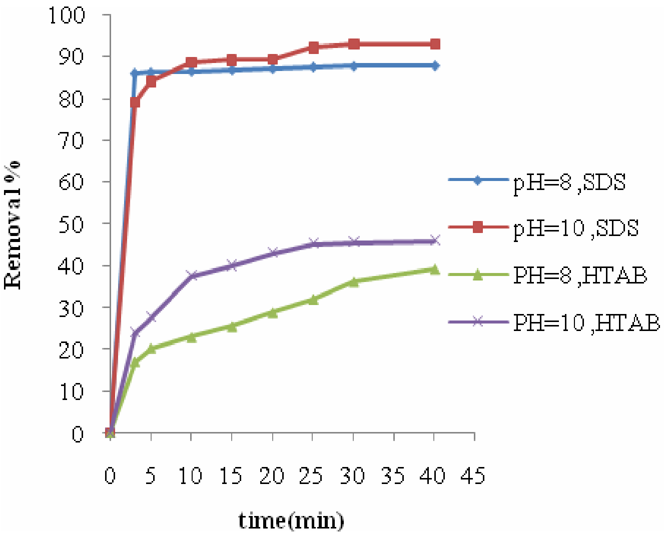

Fig. 8 Effect of surfactant type on the removal rate of zinc (SDS=100mg/l; HTAB=100mg/l; Zn=100mg/l; Q=500ml/min)

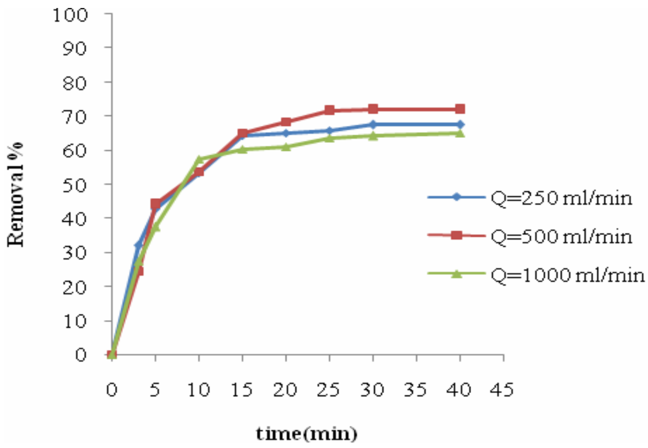

Fig. 9 Effect of gas flow rate on the removal of lead (pH=8; Pb=100 mg/l; SDS=100 mg/l;Ethanol=1%)

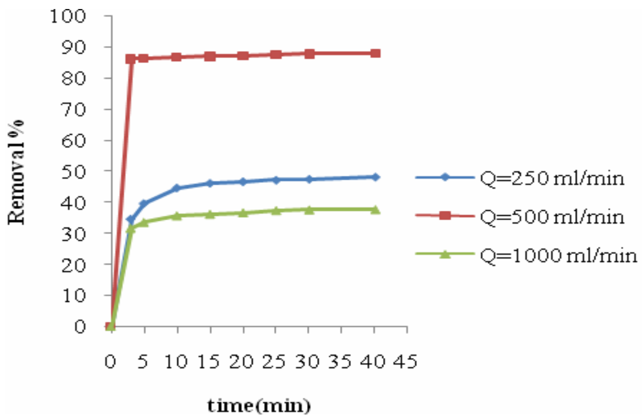

Fig. 10 Effect of gas flow rate on the removal of Zinc (pH=8;Zn=100mg/l; SDS=100mg/l;Ethanol =1%)

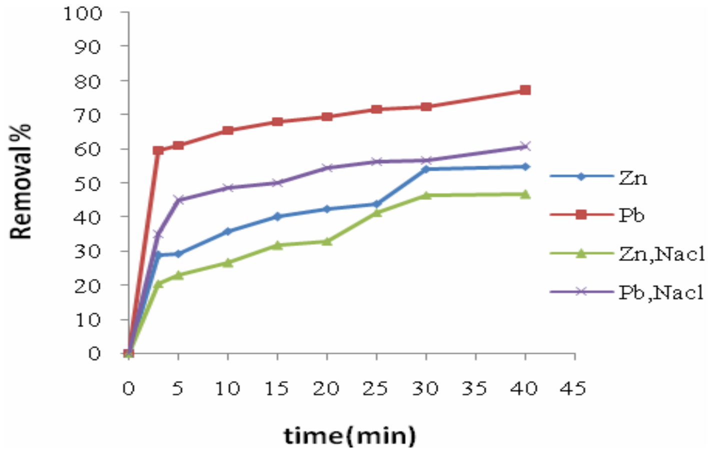

Fig.11 Effect of NaCl on the removal rate of metals(pH=8;SDS=100mg/l; NaCl=50mg/l Zn=100mg/l; Pb=100mg/l; Q=500 ml/min)

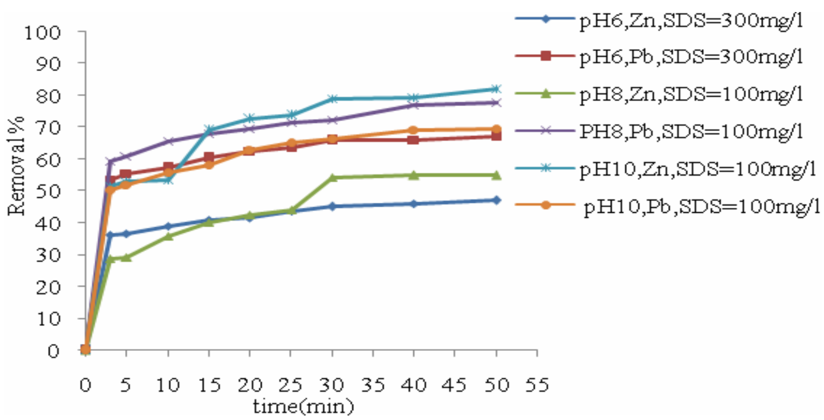

Fig. 12 Effect of pH on the removal of zinc and Lead (Zn=100 mg/l; Pb=100 mg/l; SDS=100mg/l; Q=500 ml/min)