KINETIC STUDIES OF URANYL ION ADSORPTION ON ACRYLONITRILE (AN)/ POLYETHYLENE GLYCOL (PEG) INTERPENETRATING NETWORKS (IPN)

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ABSTRACT

The kinetics of the adsorption of uranyl ions on amidoximated acrylonitrile (AN) / polyethylene glycol (PEG) interpenetrating network (IPNS) from aqueous solutions was studied as a function of time and temperature. Adsorption analyses were performed for definite uranyl ion concentrations of $1x10^{-2}$m and at four different temperatures as 290K, 298K, 308K and 318K. Adsorption time was increased from zero to 48 hours. Adsorption capacities of uranyl ions by PEG/AN IPNS were determined by gamma spectrometer. The results indicate that adsorption capacity increases linearly with increasing temperature. The max adsorption capacity was found as 602 mgu/g IPN at 308K. Adsorption rate was evaluated from the curve plotted of adsorption capacity versus time, for each temperature. Rate constants for uranyl ions adsorption on amidoximated ipns were calculated for 290K, 298K, 308K and 318K at the solution concentration of $1x10^{-2}$m. The results showed that as the temperature increases the rate constant increases exponentially too. The mean activation energy of uranyl ions adsorption was found as 34,6 kJ/mole by using arrhenius equation.

INTRODUCTION

Adsorption is an effective and convenient technique in the separation of elements. The greatest advantage of adsorption is the possibility of separating of all amounts of substances from a very large volume of solution. Uranium adsorption from aqueous systems on various adsorbents is important from the purification, environmental and radioactive waste disposal viewpoints. The adsorption of uranyl ions on inorganic and organic adsorbents from wastewater and seawater has been studied by numerous scientists (1-14). Many types of organic adsorbents containing various functional groups were synthesized and used for highly selective and of high capacity removal/recovery for uranyl ions. Chelating resins, which were studied for the recovery of uranium from waste-and seawaters, has become increasingly more important in recent years. The polymers containing amidoxime groups are one of the most used chelating systems. Amidoxime groups have a selective behaviour toward uranyl ions, forming a chelate with uranyl ions. Although interests in the adsorption of uranyl ions onto polymeric and copolymeric adsorbents containing amidoxime functional groups has increased manifold in recent years (15-18), none of them addressed adsorption kinetics.

Interpenetrating networks consisting of poly ethylene glycol (PEG) and acrylonitrile (AN) were prepared, characterized and adsorption capacities of these amidoximated IPNs were investigated in our previous work (18).

In this study the adsorption kinetics of uranyl ions from aqueous solutions on AN/PEG IPN has been studied. The effects of concentration of uranyl ions, contact time and temperature on the adsorption were investigated. Experimental data were used to determine the degree and rate constants of adsorption reaction for 290K, 298K, 308K and 318K at the solution concentration of $1x10^{-2}$m. Activation energy was also calculated consecutively.

EXPERIMENTAL

Preparation of IPNs: IPNs were obtained by mixing PEG (35000) and AN in ratio of 1g of PEG / 3ml of AN, and the solutions were placed in glass tubes (10mm outer-diameter, 8,3mm inner diameter). Then the solutions were irradiated in Co-60 gamma source under 2,09 kGy/h dose rate, totally 14,1 kGy doses. This is the dose value required for maximum IPN formation (18). After formation IPNs were cut into pieces 16-20 mesh of chips. These chips were used in amidoximation and adsorption procedures.

Amidoximation of IPNs: In order to change CN groups of PEG/AN IPNs into amidoxime ($HONCNH_2$) groups, 16-20 mesh of IPNs at a molar ratio of $NH_2/CN=1,5$ were immersed into deionised water for 24 hours and then mixed with neutralized hydroxylamine solution by using 120 rpm of rotary evaporator at 338K for 3,5 hours. The amidoximated IPNs were put into deionised water for 24 hours and then dried at 313K to constant mass. The degree of amidoximation ratio was investigated by FTIR spectrometer of amidoximated and non-amidoximated IPN chips formed into discs by using KBr.

Adsorption of uranyl ions on amidoximated IPNs: Certain amounts of amidoximated IPNs (about 10 mg) put into 20 ml of 0,01M uranyl nitrate solution at four different temperatures (290K, 298K, 308K and 318K) for a known period of time for adsorption kinetics. After adsorption, the adsorbent was separated by decantation, rinsed with deionised water and dried at 313K to constant mass. The amount of adsorbed uranium to the IPNs was determined by gamma measurements by using peak areas determined for 63,3 and 92,5 keV energies of uranium.

RESULTS AND DISCUSSION

Amidoximation of IPNs: By examining the FTIR spectra of amidoximated and non-amidoximated IPNs the characteristic stretching bands of C≡N, C=N, N-O, OH^- and N-H groups, it was realized that the amidoximation reaction was achieved but the conversion was not entirely completed.

Optimum mass determination: The effect of IPNs mass on the adsorption of uranyl ions was presented in Fig.1. As it can be seen, the amount of adsorbed uranium decreased with increasing mass of IPNs. The adsorption of uranium (mgU/g IPNs) reached maximum reasonable value at about 10 mg of IPNs mass. As a result, 10 mg of IPNs and 20ml of 0,01M uranyl nitrate solution were used in adsorption kinetics studies.

Adsorption of uranyl ions on amidoximated IPNs: In order to characterize the binding mechanism, FTIR spectra of AN/PEG IPN before and after the uranyl ion adsorption were analysed, Fig.2. When FTIR spectra of uranyl ion adsorbed and not adsorbed IPNs are compared, as can be seen from the difference FTIR spectra and known the literature, the adsorption can be well realized.

Adsorption kinetics of uranyl ions on amidoximated IPNs: Amidoximated IPNs, contacted with uranyl ions in periods changed from 2 minutes to 48 hours at different temperature, were analysed by gamma spectrometric methods.

The studies of the effect of contact time on the adsorption of uranyl ions showed an increase in the amount of adsorbed uranyl ions with increasing the contact time which reaches plateau, as seen in Fig.3. It was shown that the half times for the adsorption curves were about 240 minutes. The adsorption of uranium reached a considerable value almost first two hours after mixing and then it remains almost constant after 1500 minutes.

By increasing the temperature, the amount of adsorbed uranyl ions increased per unit weight of IPNs, and reached a plateau. The period of reaching to the plateau is independent from the temperature and the adsorption reached to maximum value (plateau) almost after 24 hours at all four temperatures. This indicates that the rate of uptake of uranyl ions increases with increasing temperature. Therefore, the increasing rate of adsorption ($\Delta q/\Delta t$) follows a linear way without temperature dependence. Plot of adsorbed uranyl ions (q mgU/gIPN) versus for different

temperatures was shown in Fig.4. The maximum adsorption capacity of IPNs (q) obtained in this work was found to be 421 mgU/gIPNs at 298K. The adsorption of uranyl ion solution onto IPNs was carried out in a thermostated bath with and without shaking at 298K. The maximum uranyl ion adsorption capacity of IPNs was found higher in shaking bath than in stagnant bath, due to transportation of solute in the solution is usually rapid because of mixing. However, the adsorption of uranyl ion in shaking bath increases in parallel with the adsorption in stagnant bath within first 24 hours. After 24 hour the rate of adsorption increased much higher in shaking bath than in stagnant bath. That may be because of the desorption of uranyl ions in stagnant bath after a certain period.

Adsorption rate: The plots of q (mgU/gIPNs) for different adsorption periods are shown in Fig.3. As it is seen, the experimental points are almost on the straight lines until 240 minutes. Because the rate of uranyl ion adsorption by IPN tends to follow zero order rate reaction, the adsorption rate was equal to the adsorption rate constants. Therefore, the adsorption rate constants were found easily to be 0,2952; 0,3966; 0,6347; 1,03 min^{-1} at 290K, 298K, 308K and 318K respectively.

The activation energy (E_a) of uranyl ions adsorption on IPN, calculated using the Arrhenius equation by plotting rate constant in logarithmic scale (lnk) versus 1/T K degrees temperatures, was found to be 34,6 kJ/mole.

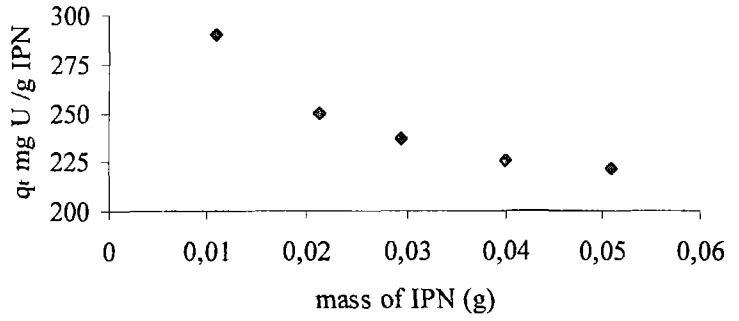

Fig.1. The adsorption of uranyl ion (mgU/g IPNs) on different mass of IPNs.

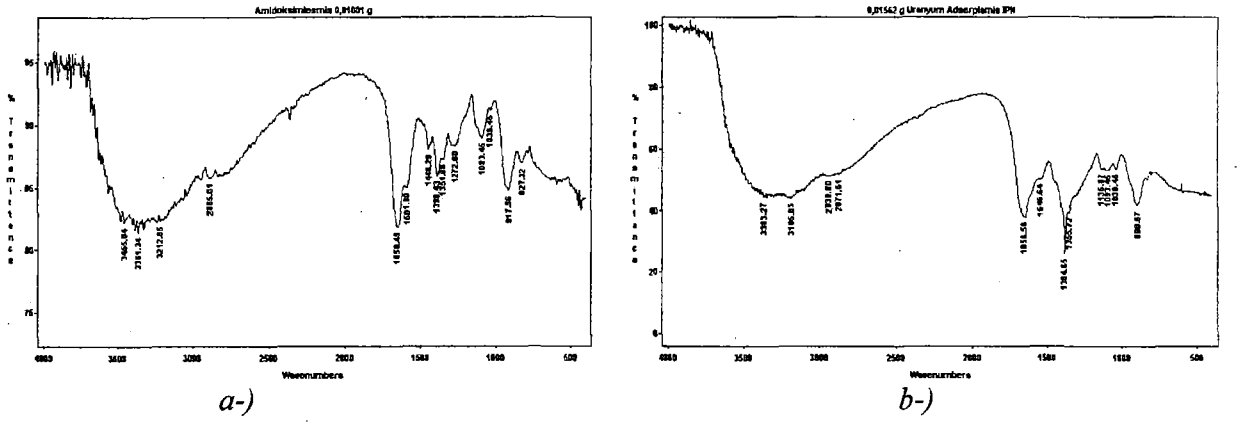

Fig.2. FTIR spectra of amidoximated IPNs (a) before, (b) and after the uranyl ion adsorption

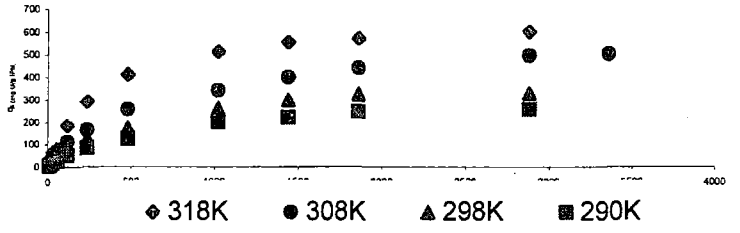

Fig.3. The dependence of the adsorption of uranyl ions on contact time.

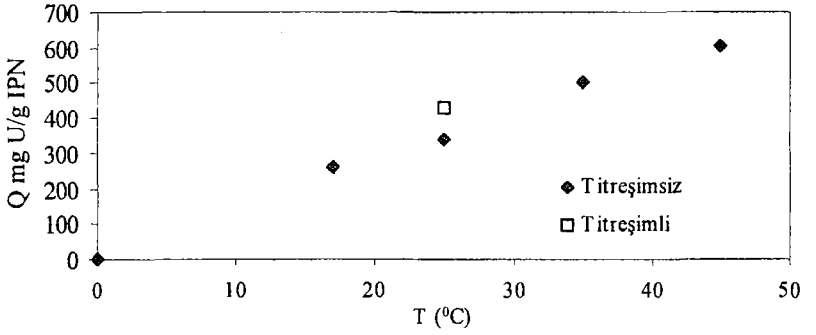

Fig.4. The temperature effect on the adsorption of uranyl ion on IPNs.

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