Sorption Kinetics of Aqueous Solutions of Copper and Cadmium Ions Using Radiation Grafted Poly Vinyl Chloride Films

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Summary. y-Radiation induced grafted polyvinyl chloride film (PVC), using N-vinyl-2-pyrolidone (NVP) and N-vinyl-2-pyrrolidone/itaconic acid (NVP/IA) as unitary and co-monomer mixture have been studied for separation and extraction of copper and cadmium ions from wastewater. The parameters affecting the grafting percentage such as monomer concentration, types of solvent and radiation dose were investigated. Characterization of the prepared grafted films (PVC-g-NVP and PVC-g-NVP/IA) using FTIR spectroscopic analysis was done. Swelling behavior of the prepared grafted copolymer was also investigated; it was found that the swelling process was monitored by the increase in the weight of copolymer as a function of time. The swelling isotherm consisted of an initial fast increase, which leveled off asymptotically to the equilibrium-swelling limit.

The isothermal data fit well with the Freundlich equation, and the adsorption capacity of PVC-g-NVP and PVC-g-NVP/IA films were determined. Sorption kinetics for Cu^{2+} and $Cd^{2}*$ ions on PVC-g-NVP/IA were studied and found to follow the first order kinetics. The calculated apparent activation energies for the adsorption of Cu^{2+} and $Cd^{2}*$ on PVC-g-NVP/IA film are 23.28 and 26.60 k J mol"[1] respectively, indicating that both copper and cadmium ions adsorb mainly physically on the grafted copolymer. and the adsorption process has a low potential barrier.

Introduction

The release of toxic substances and their dispersal in the environment have tragic effects. The discharge of industrial wastewater without adequate treatment has increased significantly in the last decade as a result of wide industrial expansion/[15] Toxic substances are more easily controlled when they are generated than after they are dispersed. Therefore, our aim of minimizing adverse effects depends largely on the development of processes that isolate and remove the contaminants at their sources. The presence of metals such as copper and cadmium is

known to cause severe health problems in animals and human beings. Cadmium is one of the most toxic metals, in plants, it inhibits root and shoot growth, affects nutrient uptake and frequently is accumulated by agriculturally important crops. Thus cadmium is consumed by animal and humans with their diet and can cause diseases Attempts have been made to relate the occurrence of certain cancers and cardiovascular disease to the presence of trace metals in drinking water Therefore, information on the release and removal of these metals from water and wastewater is becoming highly desirable.

Graft polymerization provides a general method for modification of chemical and physical properties of polymeric material. Radiation induced grafting copolymerization of monomers onto different polymers has been widely studied to produce films for various purposes such as separation processes and electrochemical applications y-Radiation induced graft co-polymerization is one of the most promising methods due to its rapid formation of active sites on the substrate surface and in the material matrix during the grafting process.

Polymeric films have a series of particular characteristics; they are hydrophilic, insoluble in water, soft and elastic, and they swell with water, keeping their shapes but increasing in volume until reaching a physical chemical equilibrium. The properties of the prepared grafting copolymer depend strongly on the degree of crosslinking, the chemical composition of the polymer chains, and the interactions of the network with the surrounding liquid. The properties of the prepared films as adsorbent materials can be changed with the pH and temperature. The ability of certain polymers to form polymer metal complexes may be applied to several areas, such as, hydrometallurgy and biochemistry. In recent years, there has been a great deal of interest in the applicability of polymers for the removal, separation and purification of metal ions from heavy metal contaminated water and solid waste.

This study was designed to investigate the efficiency of N-vinyl-2-pyrrolidone (NVP) and N-vinyl-2-pyrrolidone/itaconic acid (NVP/IA) grafted onto polyvinyl chloride film (PVC) for the removal of copper and cadmium from their wastes. Grafting percentage, swelling percentage, adsorption isotherm, adsorption kinetics, rate constants and activation energy of adsorption have been determined and discussed.

Experimental Materials

Polyvinyl chloride film (PVC) was supplied by Misr packing company Egypt and N-vinyl-2-pyrrolidone (NVP), Germany, with a purity of 99% was used without further purification. Itaconic acid (IA),

Merck was analytical pure grade, and chloride salts of copper and cadmium ions have been used.

Graft Copolymerization

The grafting polymerization process of N-vinyl-2-pyrrolidone (NVP) and vinyl-2-pyrrolidone/itaconic acid onto polyvinyl chloride film is schematically show in Figure (1).
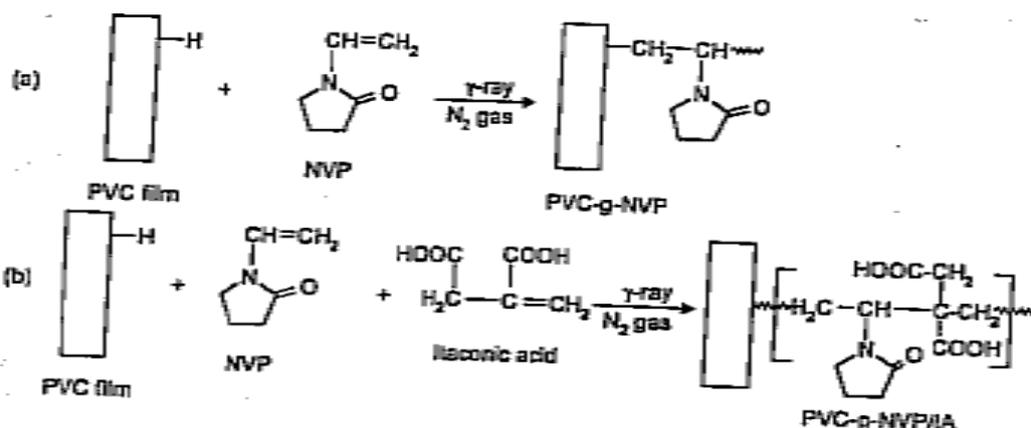

Figure 1. Schematic representation of the grafting process of:

(a) NVP onto PVC film using y-radiation under nitrogen gas. ...

(b) NVP/itaconic acid onto PVC film using y-radiation under nitrogen gas.

The grafted films were taken out and washed in boiling distilled water for 8hr and dried in an oven at 50°C and weighed.

Measurement of grafting percentage

The grafting percentage of modified PVC film can be determined gravimetrically.

FUR Spectroscopy

Fourier Transform Spectra of blank and grafted PVC samples were measured using (Mattson 5000, unicam) spectrometer .

Swelling measurements

A clean, dried film of a known weight was immersed in distilled water at room: temperature. The grafted film was removed from water after various time intervals and the excess water on the surface was

removed, blotted with absorbent paper, quickly weighed and then returned to the distilled water until equilibrium was reached (24h). Alkaline treatment of the prepared films.

The alkaline treatment of PVC-g-NVP and PVC-g-NVP/IA was carried out through refluxing with aqueous solution of NaOH (2 M) for 6 h. The films were then washed with hot distilled water for the removal of occluded NaOH and then dried in an oven at 40-50°C and quickly weighed to calculate swelling percentage.

Adsorption measurements

Adsorption of Cu2+ and $Cd2^+$ ions on either PVC-g-NVP or PVC-g-NVP/IA was carried out by a batch technique at ambient temperature (25°C+1) except otherwise specified. Known weight (0.1 g) of either PVC-g-NVP or PVC-g-NVP/IA was mixed with a certain volume of different metal ion concentrations in the range from 10^{-5} to 10^{-2} M at pH 4.5 for 4h. to allow the attainment of equilibrium. The supernatant solution was analyzed by atomic absorption spectrometer(AAS vario6 analytikjeno, Germany) to determine the remained ion concentration in the bulk solution.

Kinetic measurements

Adsorption kinetics of $Cu2^+$ and $Cd2^+$ ions on PVC-g-NVP/IA was investigated by taking 0.1 g of the grafted film with 50 ml of the metal ions at a desired concentration and at pH 4.5. The supernatant solution was separated at different time intervals (10-120 mints.), at different temperatures (15-55DC) and detected by atomic absorption spectrometer.

Results and Discussion

Graft co polymerization of NVP and NVP/IA onto PVC film Graft co polymerization of hydrophilic or functional monomers was reported as a useful method for the modification of film surface to increase the surface hydrophilicity as well as special properties required for different applications.

In this study different solvents (methanol, ethanol, toluene, benzene, DMF and H_2O) were examined for the grafting of NVP and NVP/IA onto PVC fi]m J find the suitable solvent which can enhance both the diffusion of the reaction mixture into the interior region of the film and the grafting process. It was observed that H_2O is the best solvent since the prepared grafted films were highly transparent and the grafting process was homogenous in presence of H2O as a solvent, while the use

of other solvents mentioned above produced rigid, shrinked, brittle and hardly extracted films.

The influence of monomer (NVP) concentration on the grafting percentage was studied, and the results indicate that the grafting percentage increases as the monomer^ concentration increases and the maximum grafting percentage was observed at 30 wt% monomer. This may be due to the increase of monomer difrusibility onto polymer. film After 30% monomer, the polymer film is hardly extracted and the grafting process leveled off.

The effect of radiation dose on the grafting percentage is shown in Figure (2) The data reveals that the grafting percentage could be greatly increased as the radiation dose increased and reached 85% when the radiation dose was 20 kGy. Increasing radiation dose more than 20 kGy decreases the grafting percentage. This may be due to the "recombination of free radicals which greatly reduces the amount of active sites for the graft polymerization and results in the decline of grafting percentage.
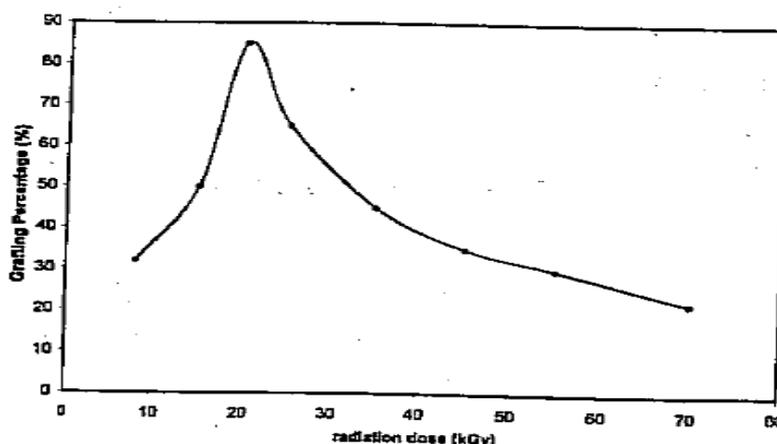

Figure 2. Effect of radiation dose on the grafting percentage of NVP on PVC film; 30% monomer and 70% solvent (H_2O)

itaconic acid is introduced to the grafting system to enhance the hydrophilcity and ionizable property more than neutral monomer NVP. Figure (3) indicates that the percentage increases and reaches its maximum value at (0.4 wt%) of the total co monomer concentration. Itaconic acid was grafted and polymerized by random radical polymerization reaction due to the hydrogen obstruction and double bond containing diprotic carboxylic groups producing graft copolymer structure, increasing itaconic acid percentage in the reaction mixture decreases the grafting percentage of copolymer NVP/IA onto PVC film. This may be attributed to the transfer of the grafted chain agent on the NVP homopolymer. This in turn may restrict the co monomer diffusion

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through the interior part of PVC film and mask the free active sites onto PVC film. Accordingly the grafting percentage is reduced as a whole.
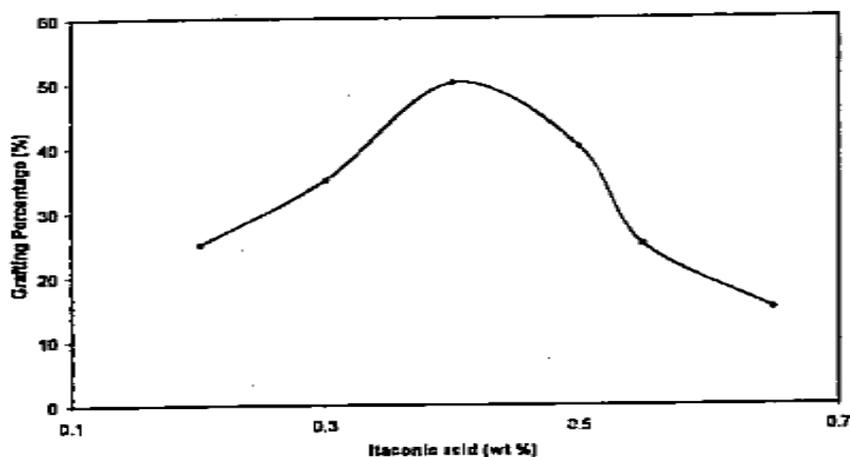

Figure 3. Effect of itaconic acid concentration on the grafting percentage of NVP/IA; monomer concentration 30 wt %, radiation dose 20 kGy and 70 wt. % solvent.

Characterization of the grafting polymerization of NVP and NVP/IA onto PVC film

To detect the occurrence of grafting onto PVC film, Fourier Transform Infrared spectroscopy (FITR) of both PVC film itself and grafted, films with monomer NVP and co monomer NVP/IA in the range of 400-4000 cm"1 was carried out and recorded in Figure (5). FTIR spectra of PVC film as shown from Figure (4a) show good confirmation to that described in the literature/191 The characteristic peaks appear at 744cm^{-1}, 1429cm^{-1} and 2871cm^{-1} corresponding to -CH2- asymmetric stretching, rocking and binding respectively. The peaks at 1250 cm^{-1} and at 1665cm^{-1} may be d to the chlorine atom and to C-Cl stretching respectively. The FUR spectra of PVc NVP (Figure 5b) show characteristic peaks at 1660 cm^{-1} and 3440 cm^{-1} which may due to C=O and N-H stretching of NVP. Figure (5c) shows a characteristic peak 1 750 cm^{-1} that may be due to carboxylic groups of itaconic acid.
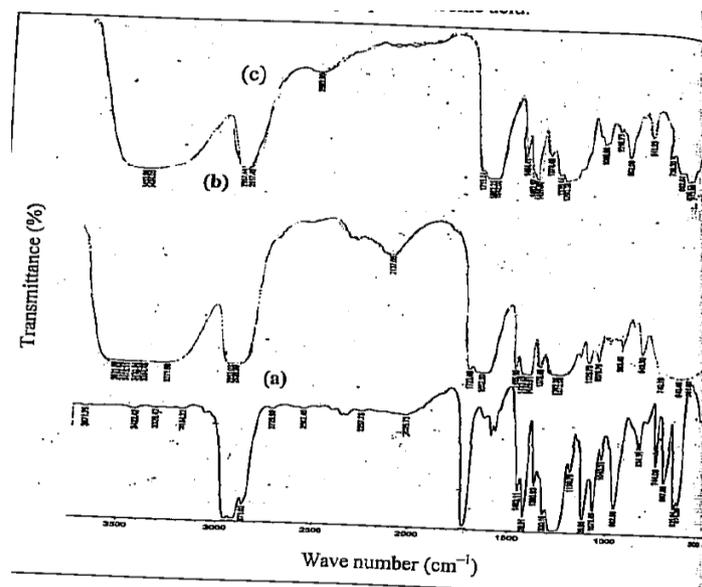
Figure 4. FTIR spectra for (a) blank PVC, (b) PVC-g-NVP (G% 50%) and (c) PVC-g-NVP/IA (G% 26%).

Swelling is one of the most important parameters affecting the characteristic properties of grafting copolymer and therefore, determining their applicability for practical use. The influence of the swelling time on swelling percentage was investigated for PVC-g-NVP and PVC-g-NVP/tA films as shown in Figure (5). As the swelling time of treatment increases the hydration degree increases sharply at the beginning reaching 550% and 650% in the first 8h for PVC-g-NVP and PVC-g-nVTA respectively. At this time water has already diffused through the whole discs, become soft and elastic. Later, swelling increases slowly to reach an asymptote at equilibrium. Also it was noticed that the swelling percentage of PVC-g-NVP/LA was higher than that of PVC-g-NVP film due to the diprotic character of carboxyl per chain length of itaconic acid. Therefore, the observed behavior is a consequence of me higher number of ionizable groups on the polymer, which enhance repulsive forces of -COOH groups with the neighboring chains. The electrostatic repulsion is responsible for the network swelling with the expected reduction of the hydrostatic pressure inside the network.

The alkaline treatment of PVC-g-NVP and PVC-g-NVP/IA resulted in a very pronounced increase in their swelling Figure (5). This was probably due to the conversion of free -COOH groups of itaconic acid into the sodium salt, which is possessed more easily ionizable and electrolytic groups, having much higher hydrophilic properties.
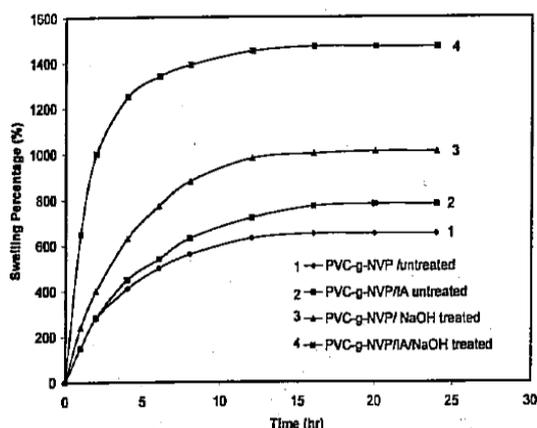
Figure 5. Swelling isotherms for untreated and NaOH treated of PVC-g-NVP and PVC-g-NVP/IA films.

Adsorption studies

This study was designed to investigate the efficiency of the prepared grafted films, including PVC-g-NVP and PVC-g-NVP/IA in the removal of copper and cadmium ions from their wastes. Among the factors affecting the treatment processes of such metal ions from their wastes with the prepared films are the treatment time an the metal ion concentration.

Effect of the treatment time

From an economical point of view, the time of treatment is an important factor since, the efficiency of the prepared grafted films in waste treatment can he determined from the time required to adsorb the maximum capacity of metal ions by chelation or complexation with the functional group of the grafted copolymer.

Table (1) shows the metal uptake as a function of time for both $Cu2^+$ and $Cd2^+$ ions using the prepared grafted films of PVC-g-NVP and PVC-g-NVP/IA. The data show that metal uptake increases with time and reaches its maximum value after almost 4hr. for the two metal ions investigated. Cd^{+2} ions record higher metal uptake than Cu^{2+} ions which accounts for the dependence of the initial rate of chelated metal ions and the maximum uptake value on the type of metal ion, its coordination and stability constant and the steric effect of these copolymer complexes.^' This can be explained by considering the diffusion of these metals through the porous films which is mainly-dependent on their polarity, electronic configuration, ionic radii and on the nature of the interaction with the functional groups of the prepared grafted films. Furthermore, maximum metal uptake was higher on PVC-g-NVP/IA than on PVC-g-NVP due to higher tendency of itaconic acid to metal chelation.

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Time (min)	Cu^{2+}		Cd^{2+}	
	PVC-g-NVP	PVC-g-NVP/IA	PVC-g-NVP	PVC-g-NVP/IA
30	6.99	106.70	16.86	134.88
60	12.71	189.20	33.72	236.00
90	17.79	265.32	47.20	365.30
120	22.81	355.41	56.20	438.36
240	25.42	362.15	62.94	443.98
360	26.69	368.10	67.44	449.60

Effect of the metal ion concentration

In exploring the applicability of the prepared sorbent film, it is informative to obtain knowledge of their sorption capacity toward different metal ions. This was done by the equilibration of a fixed weight (0.1 g) of both the two sorbent films (PVC-g-NVP and PVC-g-NVP/IA) with a series of initial metal ion concentration ranging from 10^{-2} to 10^{-5} M at pH 4.5 and at 25°C. The supernatant solution was removed when the chelating sites of the sorbent were saturated.

The results of concentration dependence study have been fitted to the classical Freundlich equation.

$$\log (W/m) = (1/n) \log C_e + \log K_F$$

Where W/m is the amount adsorbed at equilibrium, (m mol/g) C_e is the equilibrium bulk concentration and K_F and $1/n$ are the Freundlich constants characteristic of the system indicators of the adsorption capacity and adsorption intensity, respectively. Plots of log (W/m) versus log C_e for the adsorption of Cu^{2+} and Cd^{2+} ions on PVC-g-NVP and PVC-g-NVP/IA. This linear relation supports the applicability of the Freundlich adsorption isotherm in the present study. It is valid for physical adsorption and usually for an adsorbent with a heterogeneous surface. The values of $(1/n)$, (K_F) and the correlation coefficients (r2) are given in Table (2).

Table 2. Freundlich isotherm constants for the adsorption of Cu^{2+} and Cd^{2+} ion on PVC-g-NVP and PVC-g-NVP/IA films

Films	Cu^{2+}			Cd^{2+}		
	$1/n$	K_F m.mol.g^{-1}	r^2	$1/n$	K_F m.mol.g^{-1}	r^2
PVC-g-NVP	0.32	1.90	0.996	0.25	3.98	0.996
PVC-g-NVP/IA	0.18	7.07	0.995	0.16	10.00	0.998

It can be seen from Table 2 that the values of the correlation coefficients demonstrate almost perfect agreement of the experimental data with the Freundlich model. This, however, is indicative of the heterogeneity of the adsorption sites on both grafted copolymers.

The values of the Freundlich constants K_F increased from 1.90 to 7.07 for Cu^{2+} ions and from 3.98 to 10.00 for Cd^{2+} ions when PVC is modified from PVC-g-NVP to PVC-g-NVP/IA. In addition, the other Freundlich constant $(1/n)$ is smaller than 1 reflecting favorable adsorption, and thus new adsorption sites occur.

Kinetic Studies

A simple kinetic analysis for the adsorption of Cu^{2+} and Cd2+ ions on PVC-g-NVP/IA was carried out in the temperature range 15-55°C and at pH 4.5. The data obtained were plotted as shown in Figure (7). The plots show that the relation between $\log (Q_e-Q_t)$ and time is a straight line according to the Lagergren equation:

$$\log (Q_e-Q_t) = \log Q_e - (k/2.303)t \qquad (2)$$

Where Q_e and Q_t are the amounts adsorbed at equilibrium and after time t, respectively and k is the adsorption rate constant. These linear relations reveal that the adsorption of Cu^{2+} and Cd^{2+} ions on PVC-g-NVP/IA follows the Lagergren first order kinetics. The adsorption rate constants have been estimated from the slopes of these straight lines and their values at different temperatures are recorded in Table (3).
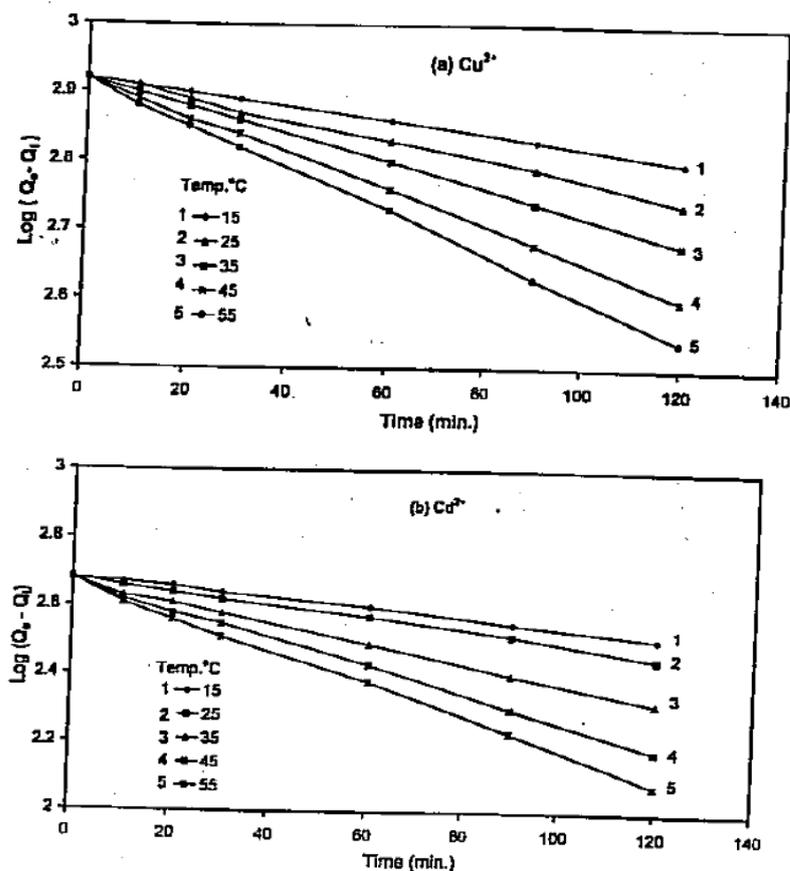
Figure 6. Plots of log $(Q_e - Q_t)$ vs. time for the adsorption of (a) Cu^{2+} ions and (b) Cd^{+2} ions on PVC-g-NVP/IA at various temperatures

Table 3. Kinetic data for the adsorption of Cu^{2+} and Cd^{2+} ion on PVC-g-NVP/IA at different temperatures

Temp. (°C)	$K \times 10^3$ (min^{-1})	
	Cu^{2+}	Cd^{2+}
15	1.11	1.66
25	1.30	2.33
35	2.00	3.33
45	2.40	4.33
55	3.07	5.40

Figure (7) shows the effect of temperature on the adsorption rate constant for Cu^{2+} and Cd^{2+} ion on PVC-g-NVP/IA. The adsorption rate constant shows a steady increase with temperature for the graft copolymer investigated. The values of adsorption rate constants were found to increase from 1.11 to 3.07 x 10-3 min^{-1} for Cu^{2+} and from 1.66 to 5.40 x 10-3 min"1 for Cd^{2+} with an increase in the solution temperatures from 15

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to 55°C. This is attributed to the increase in the kinetic energy of metal ions with the temperature, and increase of the flexibility of the graft copolymer as well. In conventional physisorption systems, increasing temperature usually increases the rate of approach to equilibrium, but decreases the equilibrium adsorption capacity.
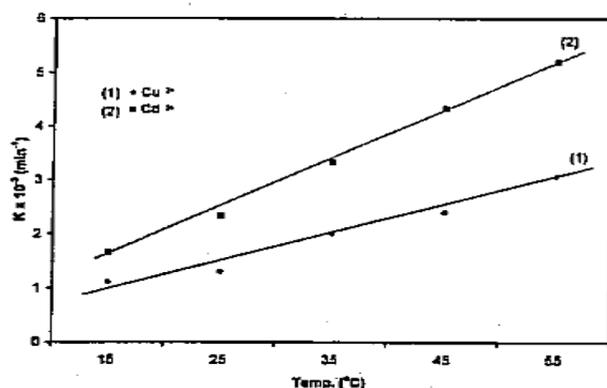

Figure 7. Effect of temperatures on the adsorption rate constant for Cu^{2+} and Cd^{2+} ions on PVC-g-NVP/IA film

The adsorption rate constant for both Cu^{2+} and Cd^{2+} is expressed as a function of temperature by the Arrhenius type relationship

$$= in\ k = In\ A - Ea/RT \qquad (3)$$

Where E_a is the Arrhenius activation energy of sorption representing the minimum, energy that the reaction must have to proceed, A is the Arrhenius factor, R is the gas constant and T is the absolute solution temperature. When In k is plotted versus 1/T (Figure 8), a straight line with slope (-Ea/R) is obtained.
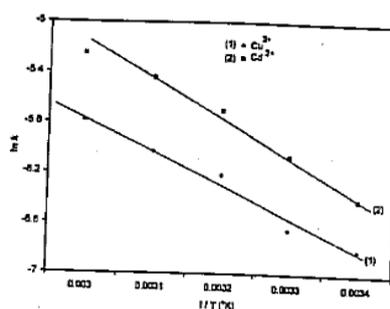

Figure 8. Arrhenius plots for the adsorption of Cu^{2+} and Cd^{2+} on PVC-g-NVP/IA film.

The activation energy values were found to be 23.26 and 26.60 kj mol^{-1} for Cu^{2+} and Cd2^{+} on PVC-g-NVP/IA film, respectively. Considering that these values are in the typical activation energy range for physisorption one can conclude that the adsorption of Cu^{2+} and Cd^{2+} ions on graft copolymer is mainly physically.

Conclusion

The results of the present investigation indicate that the two grafted copolymers PVC-g-NVP and PVC-g-NVP/IA obtained from low cost PVC film have suitable adsorption capacity for the removal of Cu^{2+} and Cd^{2+} ions from wastewater. PVC-g-NVP/IA showed a higher adsorption capacity' toward the two metal ions than PVC-g-NVP. However, there is a higher tendency for adsorption toward Cd^{2+} ions than Cu^{2+} ions. Isothermal data were represented well by the Freundlich model and kinetic data of adsorption were fitted well by first order kinetic model. The activation energy of adsorption was determined and discussed.

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