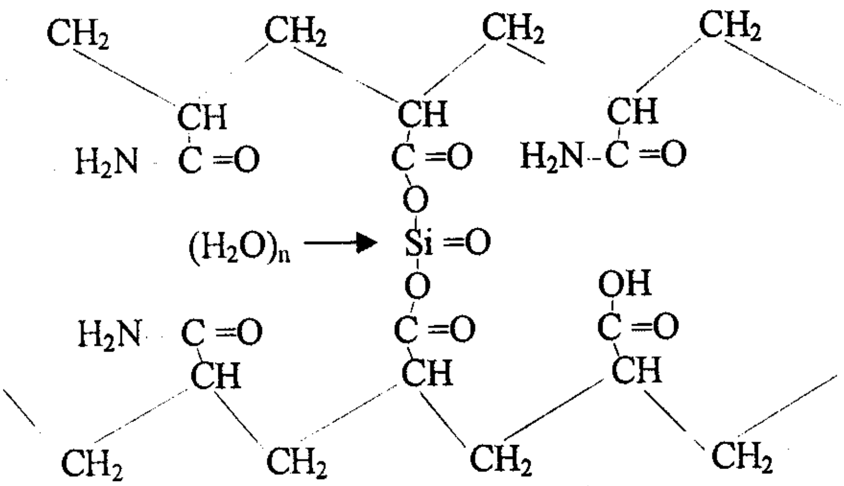
3. RESULTS AND DISCUSSION

3.1. Preparation of Poly(Acrylamide-Acrylic Acid)-Silicon Titanate {P(AM-AA)-SiTi}

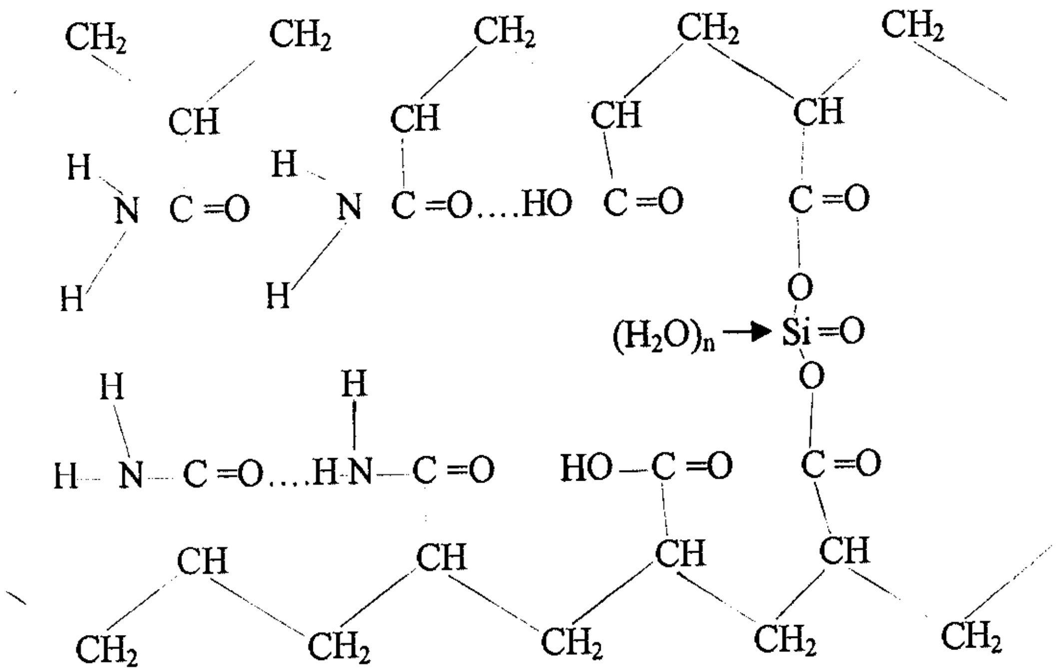
Poly(acrylamide–acrylic acid)- silicon titanate {P(AM-AA)-SiTi} was prepared by gamma radiation initiated polymerization of acrylic acid in the presence of a mixture of poly acrylamide and sodium metasilicate as a template added polymer using a template polymerization technique[119]. In gamma radiation initiated the template polymerization polymer complex was formed which may be attributed to the possible steps;

a- Preparation of the monomer by the generated radicals from the monomer, the polymer and the solvent, and

b- The propagation of the monomer associated with the polymer by the free radicals generated in the system [120-123]. The suggested reaction mechanism can be represented as shown in structures 1 and 2, respectively;

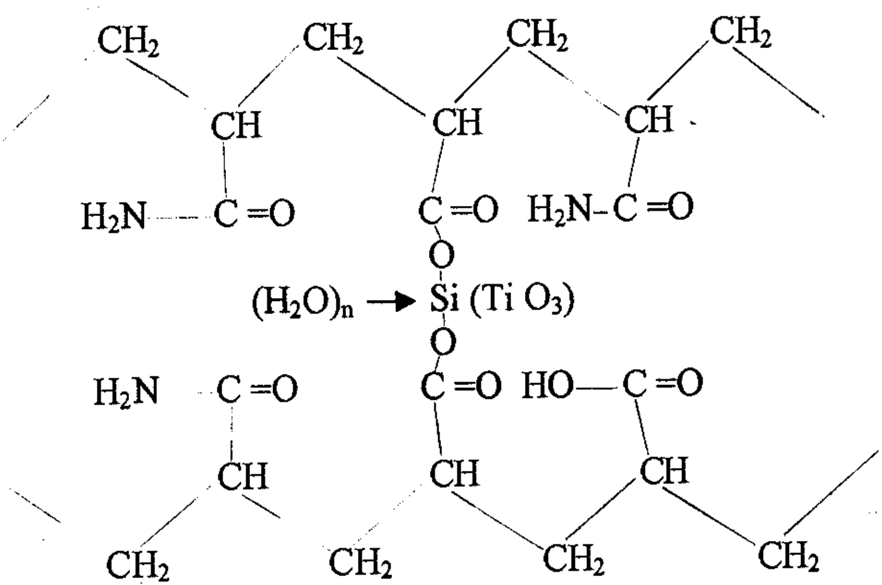


Structure(1)

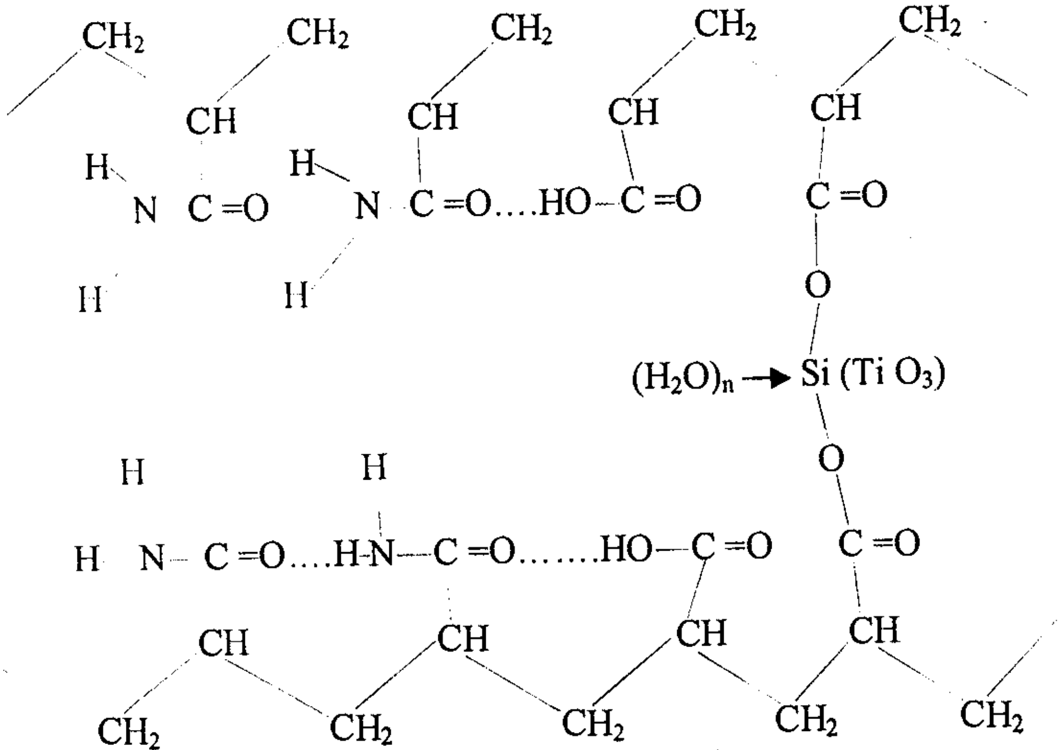


Structure(2)

Where the obtained polymeric structures 1 and 2 soaked in titanium tetrachloride, poly(acrylamide–acrylic acid)-silicon titanate {P(AM..AA)..SiTi} was formed as shown in structures 3 and 4.



Structure(3)



Structure(4)

The impregnation of silicon titanate with poly(acrylamide–acrylic acid) leads to the decreases of the swelling degree which may be due to the increases of the cross-linking between the chains [124,125] and the formation of ionic bonds between carboxylate groups and silicon ion.

3.2. Characterization of Poly(Acrylamide-Acrylic Acid)-Silicon Titanate {P(AM-AA)-SiTi}

3.2.1. Infrared spectroscopy (IR)

Infrared spectra of P(AM–AA) and P(AM–AA)-SiTi are shown in Figures(1 and 2), respectively. Figure (1) shows that the absorption bands at 3421 and 3209 cm^{-1} are related to free and bonded (>NH), respectively. The bands at 2938 and 1450 cm^{-1} are corresponding to stretching and bending repeated methylene groups along the chains. The absorption band related to interstitial water is appeared at 1650 cm^{-1}. Figure (2) shows the spectrum of P(AM–AA)–SiTi. The data showed that the broad bands at 3600 – 2800 cm^{-1} and 1686 cm^{-1} are assigned to stretching and bending modes of water molecules adsorbed in the resin [125]. The absorption bands of carboxylate group (COO$^-$ and COOH) and ester group ($>$C = O) are appeared at 1563, 1402 and 1216 cm^{-1} which may be due to the interaction of silicon atom with COOH or $>$C = O groups. The bands at 470 and 1080 cm^{-1} are related to Si-O bond (silicate group). Also, the band at 597 cm^{-1} may be due to Ti-O bond [126]. By comparing the data in figures (1 and 2) we concluded that the impregnation of SiTi in-situ P(AM–AA) leads to an increase in the cross-linking of the resin which may be due to the bonding of silicon and or titanium atoms with the function groups (COOH or $>$C = O) of the resin. This bonding leads to decreases of both the swelling degree and the capacity of P(AM–AA)–SiTi for the removal of heavy elements from waste water as we see later.

3.2.2. X-Ray diffraction patterns (XRD)

X-ray diffraction patterns of P(AM–AA) and P(AM–AA)-SiTi are shown in Figures(3 and 4). These Figure (3) show that poly(acrylamide-acrylic acid) resin has amorphous nature and there is no crystalinity in the synthesized. On the other hand, Figure (4) shows that poly(acrylamide-acrylic acid)-silicon titanate has a semicrystaline nature. This crystalinity may by assigned to the presence of inorganic species in P(AM-AA) [127].

3.2.3. X-Ray fluorescence spectroscopy (XRF)

X-ray fluorescence is a tool used in this work for the determination of the inorganic ion exchanger that impregnated with the solid resin. The rasin was grind in a mill to very fine polymer, then mixed with a pindyer (Polyvinyl methaylate) to facilate the pressing process. The pressed sample in sample holder was exposed to X-ray and the X-ray spectrometer data determined are represented in Table (4). Table (4) shows that the present of silicon and titanium impregnated in the resin are 4.19 and 30.07%, respectively.

3.2.4. Chemical stability

Chemical stability of poly(acrylamide–acrylic acid) and poly(acrylamide-acrylic acid)–silicon titanate resins were tested in water and different concentrations (0.1, 1, 2, 3 and 5 M) of nitric and hydrochloric acids media. The results are summarized in the Table (5). The data in the Table (5) show that both resins are very stable in water and sparingly soluble in nitric and hydrochloric acids up to 5 M. Also, the data in Table (5) indicated that the chemical stability of the resin was increased by impregnation of silicon titanate in-situ P(AM–AA) and the stability of the resin in HCl is higher than in HNO_3 medium.

3.2.5. Effect of pH on the dissociation of the resin

The effect of pH of the medium on the dissociation of silicon titanate ion exchanger from the resin was studied by analyzed the solid of the resin before and after contact with the solution of different pH using X-ray fluorescence spectrometer. The data are represented in Table (6) indicated that the dissociation percent of silicon and titanium from P(AM-AA)-SiTi resin are very low and below detection limit up to 3-4 pH values. That means P(AM-AA)-SiTi resin is stable in the low pH value and the dissociation of silicon and titanium appears in pH above 4.

3.3. Effect of NaOH Treatment

The treatment of poly(acrylamide–acrylic acid)– silicon titanate by different concentrations of NaOH was done by soaking of 100 mg of P(AM–AA)–SiTi in 5 ml NaOH in a shaker thermostat for 2 hrs. Figure (5) shows that the recovery of Zn^{2+} ion on the untreated P(AM-AAA)-SiTi is negligible and as the concentration of NaOH used in the treatment process increases, the % recovery of Zn^{2+} ion increased. This behavior can be explained as the following manner; the treatment of P(AM-AA)-SiTi resin with NaOH leads to break of the cross-linking of the resin and the active sides of the chain are opened and covert the resin to the Na- form. As the concentration of NaOH increased the percent of the cross-linking decreased and the percent recovery of Zn^{2+} ion increased as shown in Fig. (5). At higher concentration values of NaOH

(> 0.3 M) the swelling degree is very high and there is no solution remained in the bottle. According to the result obtained, P(AM-AA)-SiTi was firstly treated by 0.3 M NaOH before used in all further investigation.

3.4. Batch Investigations

3.4.1. Effect of contact time on sorption behavior of P(AM-AA)-SiTi

The effect of contact time on the removal percent (%) uptake of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi was studied at 25±1°C in a shaker thermostat with batch factor (V/m) = 100 $ml.g^{-1}$. The data obtained are represented in Fig. (6) and indicated that the maximum removal percent for all mentioned cations was attained within 3 hrs. In all experimental studies, the separation process was carried out within 4 hrs.

3.4.2. Effect of batch factor (V/m)

Effect of the batch factor {the ratio of volume of solution (V) to the amount of resin (m)} on the efficiency removal of Zn^{2+}, Cd^{2+}, Cu^{2+} and Ni^{2+} ions by P(AM–AA) and P(AM–AA)-SiTi resins was optimized by shaking 10 ml (50 ppm) of Zn^{2+}, Cd^{2+}, Cu^{2+} or Ni^{2+} ion solutions with the amount of the resins varied from 20 to 500 mg in a shaker thermostat at 25±1°C. The results of the effect of batch factor are represented in Figs. (7 and 8). Figures (7 and 8) show that as the batch factor increased the percent recovery of Zn^{2+}, Cd^{2+}, Cu^{2+} and Ni^{2+} ions are decreased. Also Figs. (7 and 8) depict that 50 mg of P(AM–AA) and 100 mg of

P(AM–AA)–SiTi are sufficient for the quantitative removal of Zn^{2+}, Cd^{2+}, Cu^{2+} and Ni^{2+} ions from their aqueous waste solutions. These amounts of P(AM–AA) and P(AM–AA)–SiTi were used for further investigations. Figure (6) shows also that at V/m ratio less than 200 the swelling degree of P(AM–AA) is very high and there is no residue solution sufficient for the determination of the metal ion concentration.

3.4.3. Effect of pH of the medium

The effect of pH of the medium on the absorption of Zn^{2+}, Cd^{2+}, Cu^{2+} and Ni^{2+} ions on P(AM–AA)–SiTi was studied in the pH range of 1.0 to 8.0. Where at pH > 8.0, the metal ions tend to precipitate. Figs. (9 and 10) show the effect of pH on the % uptake and the loading of Cu^{2+}, Zn^{+2}, Cd^{+2} and Ni^{2+} ions by P(AM–AA)–SiTi. Figs. (9 and 10) show that the % uptake and the loading (mg/g) are increase with increase in the pH range from 1.0 to 2.91, 4.64, 3.51 and 2.52 for all Ni^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} ions, respectively. Poly(acrylamide–acrylic acid)– silicon titanate contains acid groups through to be carboxylic and amide groups. These protons – donating groups are responsible for the cation exchange with a bond formation between the resin and metal ion [128-129]. The uptake of M^{2+} ion could be explanation in the following equilibrium:-

$$n^{*}\ \ COO^{-},\ Na^{+} + M^{2+} \longleftrightarrow {}^{*}(\text{—}COO)_{n}\, M^{(2-n)+} + n\ Na^{+}$$

$$n^{*}\ \ NH^{-},\ Na^{+} + M^{2+} \longleftrightarrow {}^{*}(\text{—}NH)_{n}\, M^{(2-n)+} + 2\ Na^{+}$$

Where n = 1 or 2 and water molecules are omitted.

At about pH 2.91, 4.64, 3.51 and 2.52 for all Ni^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} ions, respectively, the capacity is decreased with increasing the pH value. This decreasing in the capacity may be related to the hydrolysed of metal ions in solution which increases the swelling degree at higher pH values.

3.4.4. Sorption isotherm

To study the nature of the absorption processes of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi resin sorption isotherm were investigated by gradual increase of the sorbate concentration and measuring the amount sorbed at each equilibrium concentration. The amount absorbed at equilibrium (W) is plotted against equilibrium bulk concentration (C_{eq}) as shown in Figs. (11, 13, 15 and 17) for Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions, respectively. The linear relationship obtained by plotting of log W/m against log C_{eq} as shown in Figs.(12, 14, 16 and 18) for Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions, respectively indicated the applicability of Freundlish isotherm for the absorption of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi over the entire concentration range investigated.

$$\log W = K + \acute{K} \log C_{eq} \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_(7)}$$

Where; W: is amount sorbed

K and Ḱ : is the Freundlich constants measure the adsorption intensity and adsorption capacity of the sorbent, respectively and computed from the slope and intercept of the linear relationship.

C_{eq} : is the equilibrium concentration.

The data in Figs.(12, 14, 16 and 18) indicated that Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions are physically sorbet on P(AM-AA)-SiTi and the values of adsorption capacity (K) were found to 0.12, $1.66x10^{-2}$, $1.58x10^{-2}$ and $5.01x10^{-3}$ mmol/g for Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions, respectively and the adsorption intensity (Ḱ) were calculated and found 0.91, 0.8, 0.7 and 0.93, respectively. The numeric value of Ḱ (<1) suggests the nonapplicability of Henry's law and the surface of the resin is the heterogeneous type [130]. ***El-Naggar et. al.*** [68] studies the adsorption of some hazardous metals such as Cs^+, Na^+, Co^{2+} and Eu^{3+} ions on silicon titanate ion exchanger and found that all these elements physically adsorbed on the ion exchange. Also the retention behavior of Zn^{2+}, Cd^{2+}, Cu^{2+} and Ni^{2+} ions on cerium (IV) antimonate, titanium (IV) antimonate and poly(acrylamide-acrylic acid)-zirconium phosphate was investigated by ***El-Naggar et. al.*** [131] and find that inorganic ion exchanger selectivities to hazardous heavy metals as compared to with P(AM-AA)-ZrP where as the later has a higher capacity than inorganic ion exchangers. In a comparative study for the previous organic resin P(AM-AA)-SiTi with P(AM-AA)-ZrP we found that P(AM-AA)-SiTi has a higher capacity for heavy metals compared with P(AM-AA)-ZrP.

3.4.5. Effect of reaction temperature

The effect of reaction temperature on the retention behavior of P(AM-AA)-SiTi for Cu^{2+}, Cd^{2+}, Zn^{2+} and Ni^{2+} ions were studied in the temperature range 25 - 60°C. The data obtained were represented in Fig. (19) and indicated that, the percent of retention were decreased from 69.79 to 59.79 when the reaction temperature increased from 25 to 60°C, respectively for Cu^{2+} ion, from 68.67 to 56.88 for Cd^{2+} ion, from 84.85 to 74.59 for Zn^{2+} ion and from 67.84 to 58.71 for Ni^{2+} ion, respectively. In general there is decrease in the percent of retention with increase the temperature. This decreasing in the retention percent may be attributed to decrease in attraction adsorptive forces during increase of the reaction temperature.

3.4.6. Effect of some anionic species on the sorption behaviour of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi

The effect of some anions such as chloride, nitrate and sulphate all in sodium form on the retention behavior of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi resin were investigated and the data obtained are represented in Figs.(20-22) Generally, the presence of such anions leads to decreasing in retention percentage of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions and the retention decreased with increasing the concentration of such anions.

Figures (20-22) show the effect of different concentrations of $NaNO_3$, NaCl, Na_2SO_4, respectively, on the retention percentage of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi resin. The data indicated that the adsorption process for the metals are affect by the presence of these salts in the solution with different extent and the degree of affecting of these salts has the following sequence;

sulphate > nitrate > chloride

The data in figs. (20-22) show that the retention percent of Cu^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+} ions was decreased by 13, 63.85, 59.2 and 61.65 %, respectively, in the presence of 0.5 M Na_2SO_4 and 7.4, 21.52, 15.45 and 14.94 %, respectively, in the presence of 0.5 M $NaNO_3$ and 0.0, 22.92, 17.18 and 11.2 %, respectively, in the presence of 0.5 M NaCl.

3.4.7. Effect of some complexing agents on the sorption behaviour of P(AM-AA)-SiTi

The effect of some complexing agents such as EDTA and tartrate all in sodium form on the retention behavior of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi resin were investigated and the data obtained are represented in Figs. (23,24). Generally, the presence of such complexing agents leads to decreasing in retention percentage of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions, on P(AM-AA)-SiTi resin. The results of the effect of EDTA and sodium hydrogen tartrate on the retention behavior of 50 ppm for each Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi are given in

Figs.(23 and 24), respectively. The data show the higher bad effect of EDTA and tartrate salts on the retention behavior compared to sulphate, nitrate and chloride anions Figs. (20-22). This bad effect may be attributed to the higher complexibility of both EDTA and tartrate with the heavy metals that forming a complex which make the adsorption process is difficult. Also the formation of complex leads to decrease of the concentration of the free metal ions in solution leading to low retention values. Figures (21 and 22) also show that EDTA has the highest bad effect compared to tartrate salt. Tables (7 and 8) are summarized the degree of affecting of the retention percentage of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi with different concentrations of some anions and complexing agents, respectively.

3.4.8. Apparent capacity measurements

The capacity of poly(acrylamide-acrylic acid)-silicon titanate for Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions was determined using chloride solutions of the metal ions containing 50 mg Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions per liter. Table (9) shows the capacity of P(AM-AA)-SiTi in mmol/g for Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions at natural pH. The data shows that the capacity of P(AM-AA)-SiTi for Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions has the selectivity sequence;

$$\mathbf{Cd^{2+} > Ni^{2+} > Cu^{2+} > Zn^{2+}}$$

This sequence is parallel to the order of the radius of this cations that means the absorption of these cations takes places in the hydrated state. This selectivity was the same as that of their increasing ionic radii, i.e. their decreasing hydrated ionic radii. This suggests that the energy required for the dehydration of the metal ions so that they can occupy a site in the exchanger plays an important role in the determination of the selectivity series for the heavy metal ions [132,133]. On the other hand, according to the principal of hard and soft acids and bases (the HSAB principal), hard acids prefer to bind of hard bases and soft acids to soft bases [134]. The hydrated resin can act as a lewis base and the heavy metal ions as lewis acids. The softness of the cations increases as the ionic radius of the heavy metal ions increases. The interaction of the heavy metal ions with the hydrated P(AM-AA)-SiTi, acting as a soft base can be expected to increase with an increase in the ionic radii. The high capacity of Cd^{2+} ions compared to the order cations may be due to the higher mobility of Cd^{2+} ion than other metals [135]. Similar results have been reported by ***Abou-Mesalam*** [136] in the adsorption of Zn^{2+} and Cd^{2+} ions on iron (III) titanate as inorganic ion exchanger.

3.5. Column Studies

In column investigation, the solution of industrial waste is percolated through a fixed bed of P(AM-AA)-SiTi. Ordinary, the column is operated drown flow by running the solution through glass column of the resin from top to bottom. The solution entered the column is called influent and the solution out from column is called effluent and the solid matrix packed the column is called stationary phase. The total capacity of the column is defined by the total number of exchanging groups in the column matrix. But in our study, another expression is for the filter capacity, namely the breakthrough capacity, which defined as the amount of ion taken up quantitatively by the column under the conditions of operation. Generally, the breakthrough capacity of the column is lower than the total capacity of the column and is department upon a number of different variables, such as particle size, flow rate and composition of the waste solution. The data of the column may be shown with curves of the raio C/C_o between the effluent and concentrations as a function of time or effluent volume. The curves are called breakthrough curves.

3.5.1. Removal of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions from simulated waste water on P(AM-AA)-SiTi columns

Glass column of 1.2 cm internal diameter and 5 cm bed height were filled with 1 g of P(AM-AA)-SiTi resin were used to study the sorption behavior of 50 ppm of Cu^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi. The simulated waste solutions with pH adjusted to 2.5 were allowed to percolate through the glass columns with flow rate 1 ml/min the breakthrough curves representing the uptake of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi are illustrated in Figs.(25-28). The data show the high selectivity of P(AM-AA)-SiTi for Cd^{2+} ion compared to Cu^{2+}, Ni^{2+} and Zn^{2+} ions and the order of selectivity;

$$\mathbf{Cd^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+}}$$

The breakthrough capacity (BCT) calculated from the breakthrough curves were found 11, 9.6, 5.5 and 3 mg/g for Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} ions, respectively. The tailing of cadmium breakthrough curve may be due to the slow dynamic equilibrium of Cd^{2+} ion on P(AM AA)-SiTi resin.

3.5.2. Applications on treatment and removal of some toxic heavy metals from waste water using P(AM-AA)-SiTi columns

Industrial wastes are varied in their quantity and strength of pollution according to the products, processes and as well as the manufactory plating from which they emerge. In this work me concerned on the treatment of industrial waste water produced from Kaha Company for Chemical Industries (KCCI) (Electroplating Plating Department) using column beds filled with P(AM-AA)-SiTi. The waste solutions were adjusted to pH = 2.5 and allowed to pass through the columns from top to bottom. The effluent were collected in equal time interval and analyzed before and after passing through the columns using an Inductively Coupled Plasma Spectrophotometer (ICPS). The data obtained were tabulated in Table (10). From the data represented in Table (10) it is clear that the use of poly(acrylamide-acrylic acid)-silicon titanate in the treatment of mentioned industrial waste water reduces the toxic heavy metals presented in it.

Table (4):- X-ray fluorescence data for Poly(Acrylamide-Acrylic Acid)-Silicon Titanate.

Elements	**%**
Na_2O	**6.642**
Al_2O_3	**0.153**
SiO_2	**4.197**
SO_3	**0.056**
Cl	**32.799**
TiO_2	**30.074**

Table(5):- Solubility of P(AM-AA) and P(AM-AA)-SiTi in different media (g/l)

Solvent	*Concentration, M*	*Solubility, g/l*	
		P(AM-AA)	*P(AM-AA)-SiTi*
H_2O		**nil**	**Nil**
HNO_3	**0.1**	**1.25**	**1.15**
	1.0	**1.45**	**1.35**
	2.0	**1.58**	**1.42**
	3.0	**1.74**	**1.61**
	5.0	**1.92**	**1.76**
HCl	**0.1**	**1.15**	**1.09**
	1.0	**1.32**	**1.15**
	2.0	**1.47**	**1.22**
	3.0	**1.66**	**1.39**
	5.0	**1.86**	**1.58**

Table (6): Dissociation percentage of silicon titanate from P(AM-AA)-SiTi at different pH values and 25±1°C.

pH	*Dissociation percent, %*	
	Titanium	*Silicon*
1.51	B.D.L	B.D.L
1.78	B.D.L	B.D.L
2.45	B.D.L	B.D.L
3.51	B.D.L	B.D.L
3.68	B.D.L	B.D.L
4.52	1.32	1.52
5.54	2.39	3.66
6.31	11.49	5.59
6.35	18.34	18.91

B.D.L :Below Detection Limit

Tables (7) The degree of affecting of the retention percentage of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi with different concentration of some anions.

Anion	*Concentration, M*	*Degree of Affecting, %*			
		Cu^{2+}	*Ni^{2+}*	*Cd^{2+}*	*Zn^{2+}*
Chloride	$5x10^{-3}$	0.0	2.52	9.9	7.58
	10^{-2}	0.0	11.84	10.99	8.04
	$5x10^{-2}$	0.0	14.82	12.99	9.95
	10^{-1}	0.0	15.3	14.58	10.17
	0.5	0.0	22.92	17.18	11.2
Nitrate	$5x10^{-3}$	4.42	13.2	13.38	7.38
	10^{-2}	6	14.28	13.87	10.99
	$5x10^{-2}$	6.32	17.54	15.29	12.21
	10^{-1}	6.85	19.88	15.39	12.67
	0.5	7.46	21.53	15.45	14.95
Sulphate	$5x10^{-3}$	2.41	33.31	24.74	1.97
	10^{-2}	2.56	33.27	29.07	24.9
	$5x10^{-2}$	2.22	65.54	46.17	47.38
	10^{-1}	3.88	72.78	56.79	54.51
	0.5	13.51	63.85	59.21	61.65

Tables (8) The degree of affecting of the retention percentage of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi with different concentration of complexing agents.

Complexing agent	*Concentration, M*	*Degree of Affecting, %*			
		Cu^{2+}	*Ni^{2+}*	*Cd^{2+}*	*Zn^{2+}*
EDTA	$5x10^{-4}$	18.44	56.65	5.16	71.32
	10^{-3}	20.63	58.36	62.87	92.04
	$5x10^{-3}$	20.77	75.45	61.84	93.94
	10^{-2}	20.74	76.98	62.11	90.9
	$5x10^{-2}$	20.72	80.19	66.65	87.62
Tartrate	10^{-3}	13.75	40.62	10.81	2.94
	$5x10^{-3}$	16.08	46.77	19.79	70.57
	10^{-2}	15.61	56.25	33.45	78.4
	$5x10^{-2}$	20.42	80.81	58.26	92.04
	10^{-1}	20.69	84.69	61.78	95.58

Table (9):- Capacity of P(AM-AA)-SiTi for [50ppm] Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions at natural pH and 25±1°C.

Metal	*Capacity x 10^2, mmol/g*
Cu^{2+}	3
Cd^{2+}	3.8
Ni^{2+}	3.6
Zn^{2+}	2.2

Table (10):- Concentrations of some toxic heavy metals collected from Kaha Company for Chemical Industries before and after treatment

Metal	***Conc. (ppm)***		***Permissible limits (ppm)***
	Before treatment	***After treatment***	
Zn	10.3	6.23	5.0
Cd	0.62	0.08	0.05
Cu	5.23	0.92	1.5
Ni	2.62	0.4	0.1
Cr	3.21	0.63	1.0
Fe	1.32	0.32	1.5

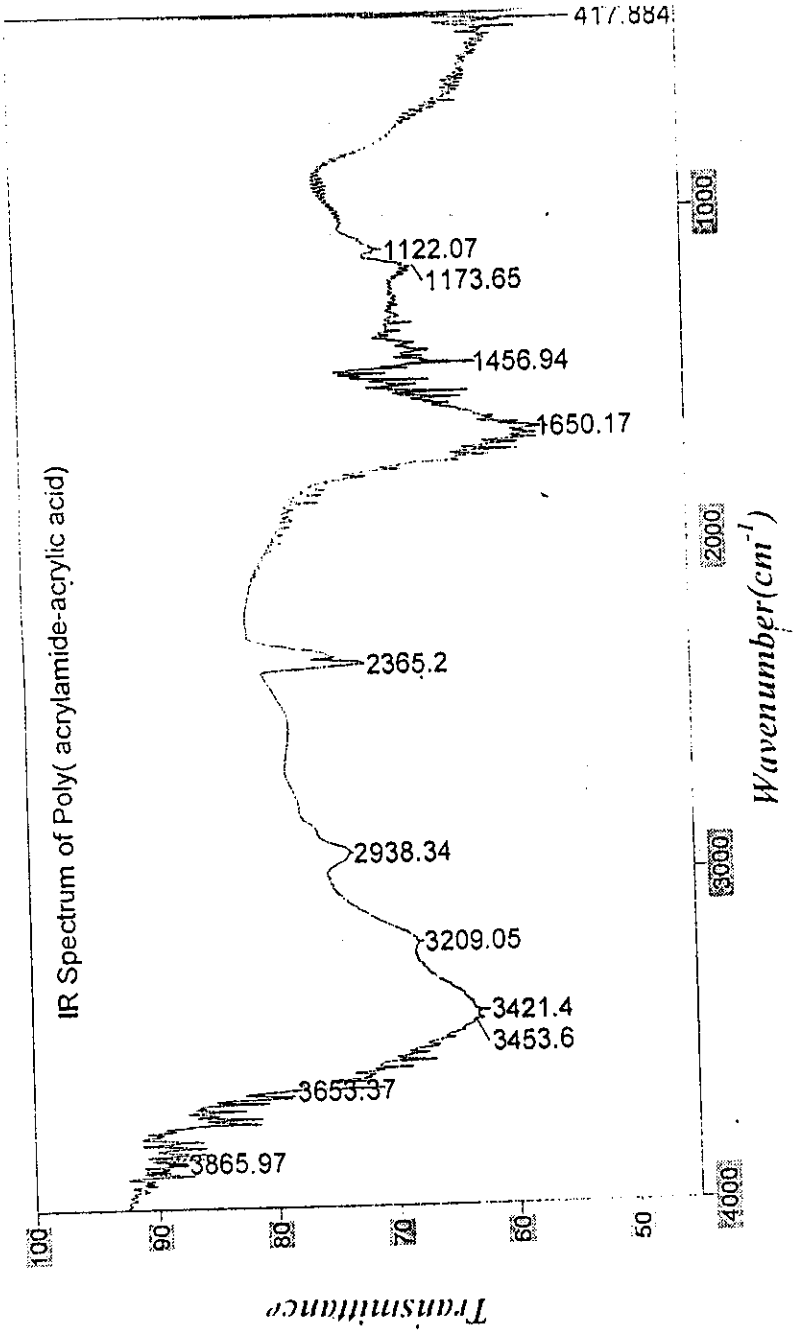


Fig. (1) IR Spectrum of Poly(acrylamide-acrylic acid) P(AM-AA) {P(AM-AA)} Resin

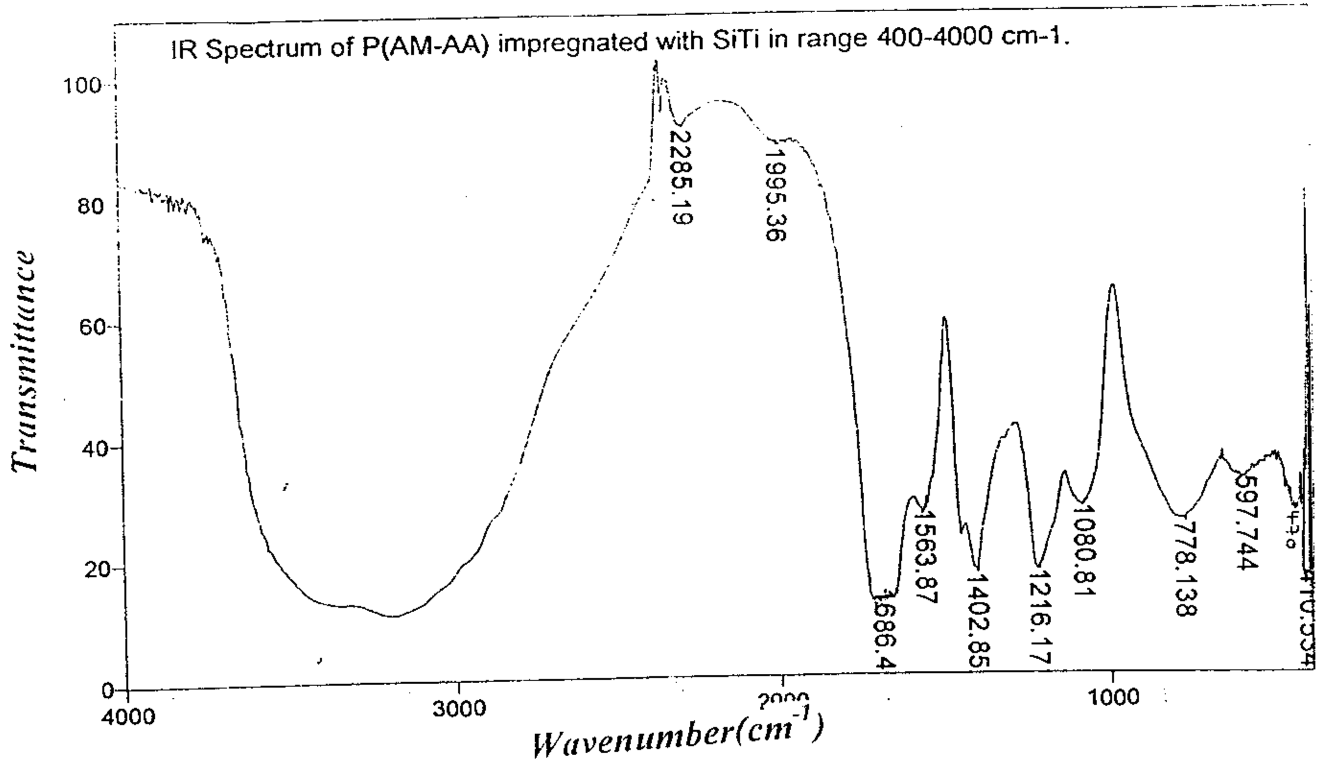


Fig. (2) IR Spectrum of Poly(acrylamide-acrylic acid)-silicon titanate {P(AM-AA)-SiTi} Resin

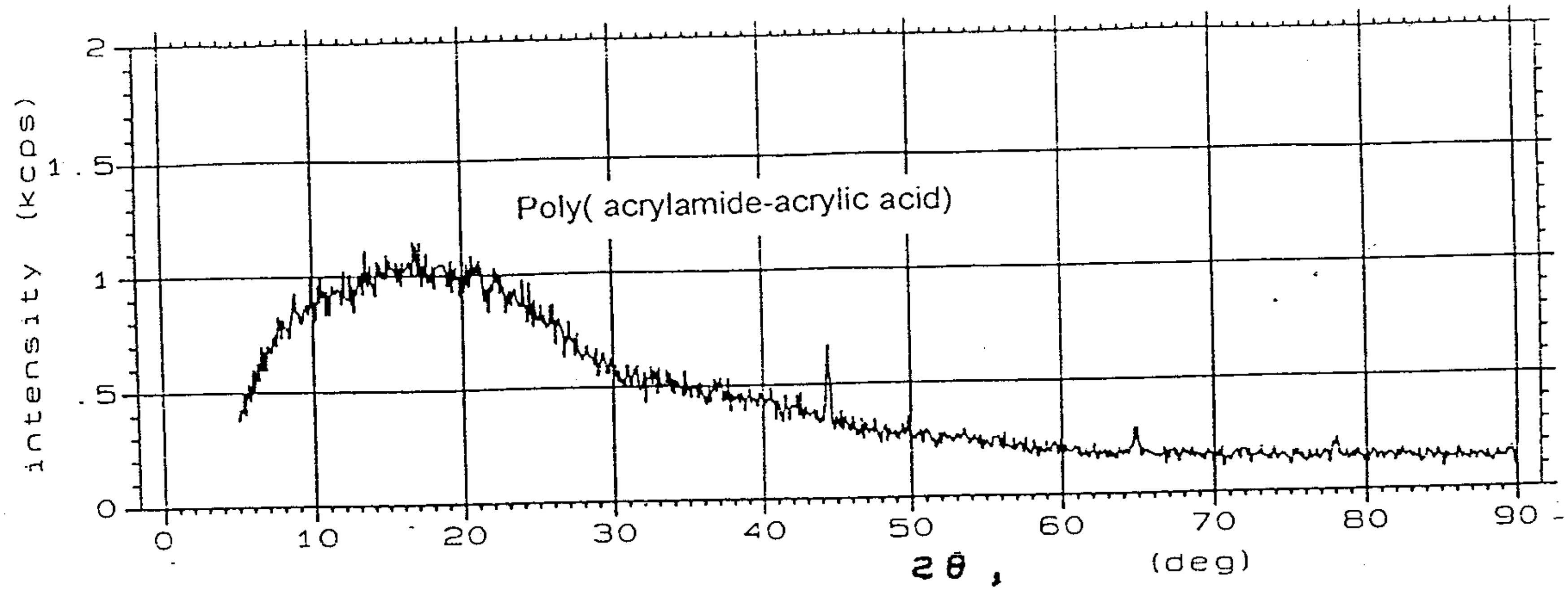


Fig. (3) X-ray diffraction pattern of poly(acrylamide-acrylic acid) P(AM–AA)

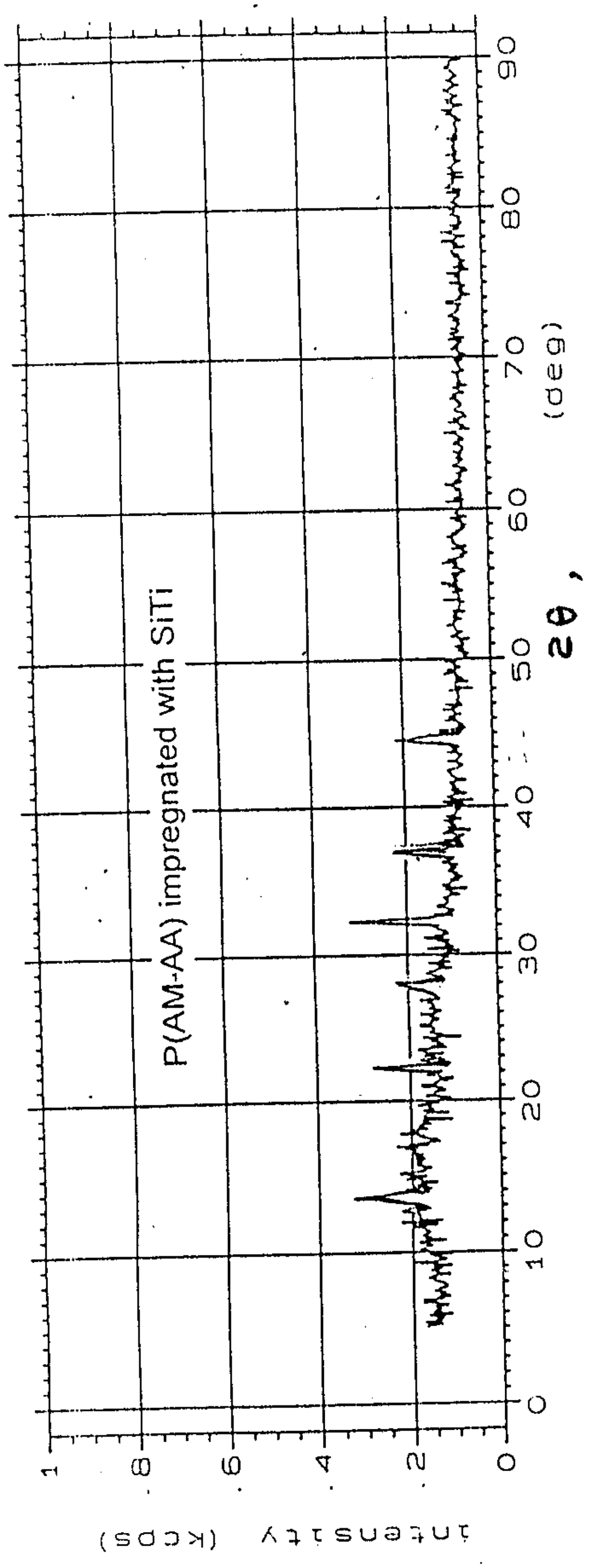


Fig. (4) X-ray diffraction pattern of poly(acrylamide-acrylic acid)-silicon titanate P(AM–AA)-SiTi

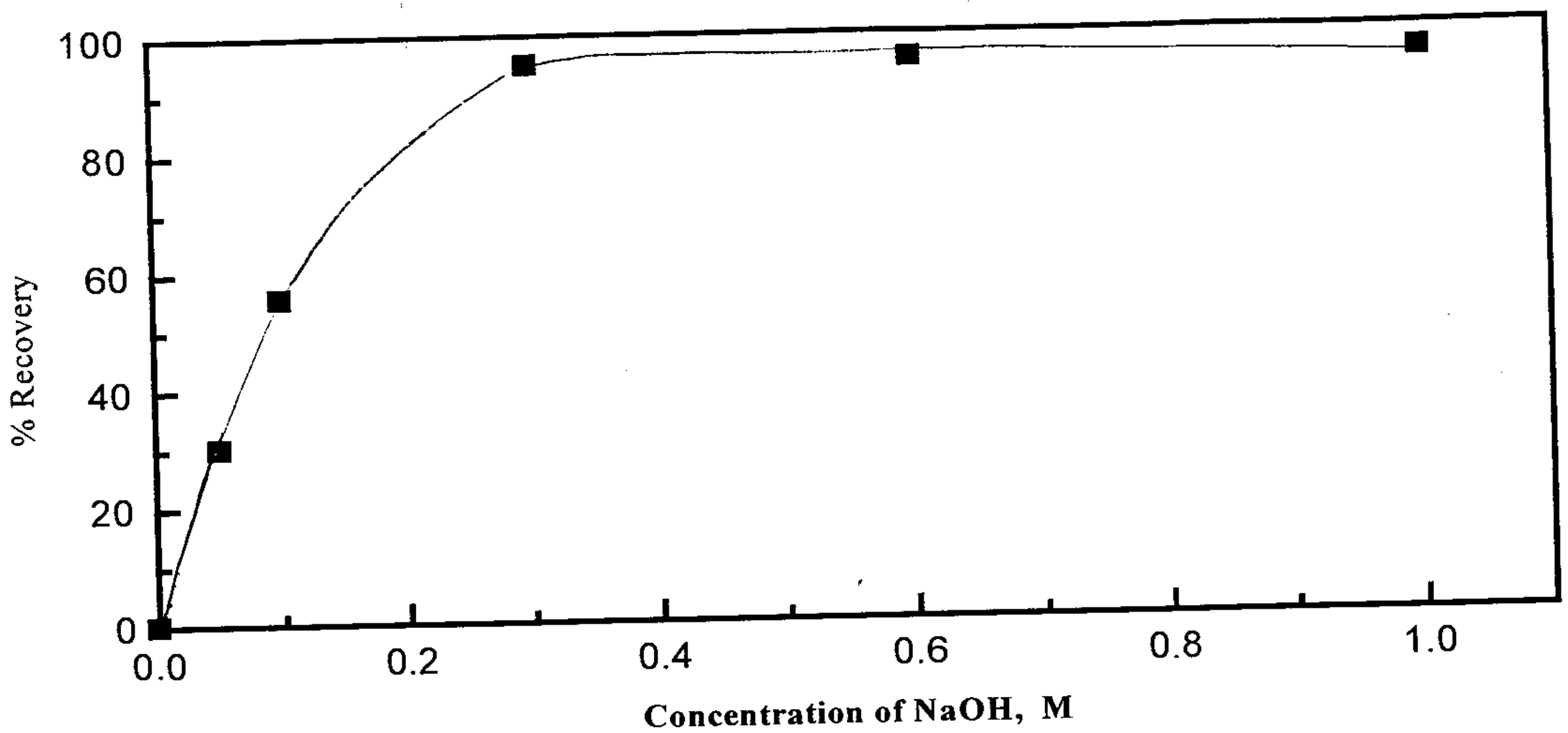


Fig.(5):- % Recovery of Zn^{2+} ion on P(AM-AA)-SiTi treated with different concentration of NaOH (V/m = 100 ml g^{-1}) and reaction temperature 25±1°C

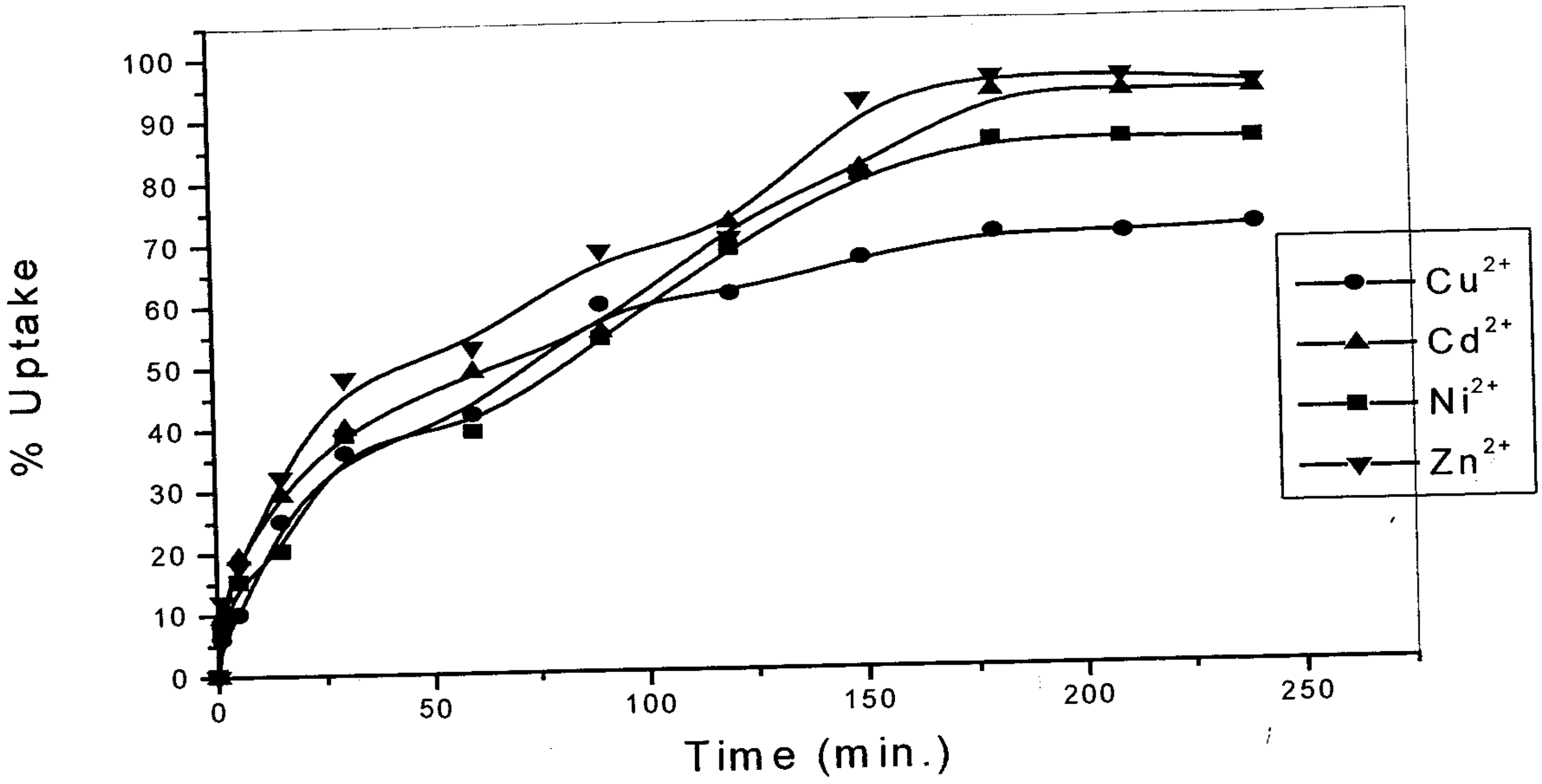


Fig. (6):- Effect of contact time on the removal percent (%) of Cu^{2+}, Cd^{2+}, Ni^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi at 25±1°C.

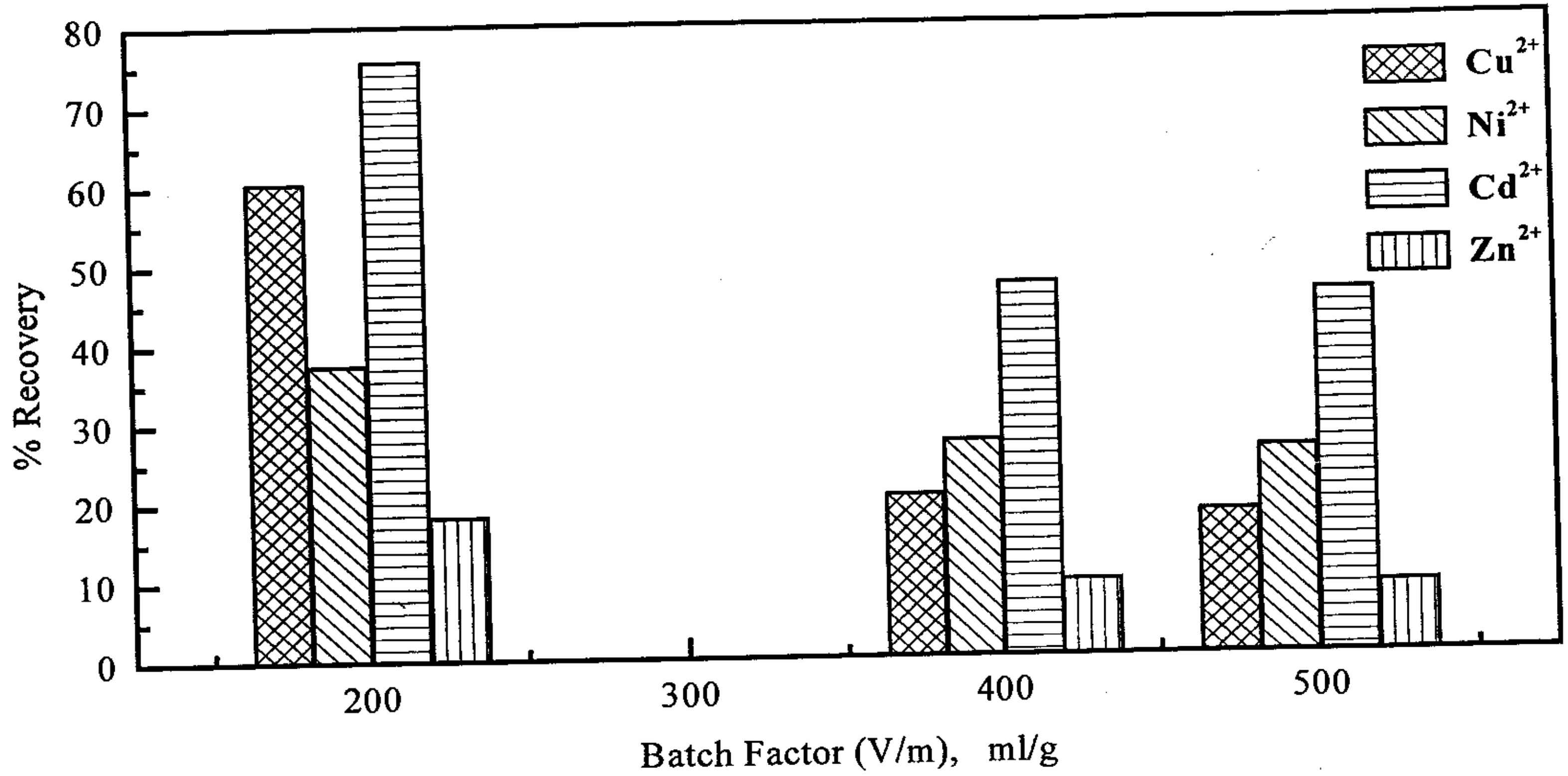


Fig.(7):- Effect of batch factor (V/m) on % recovery of Cu^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+} ions (50 ppm) on P(AM-AA) at 25±1°C.

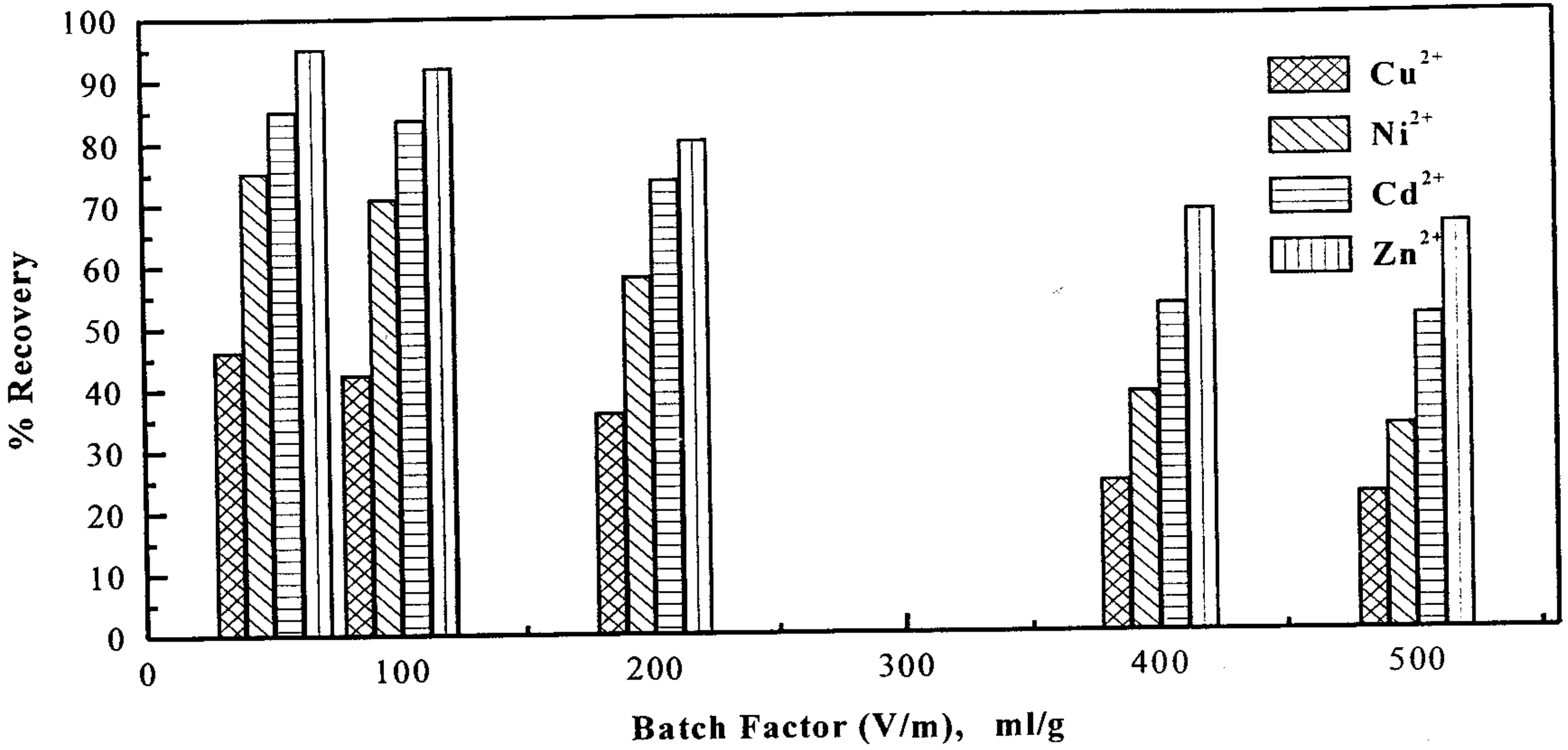


Fig.(8):- Effect of batch factor (V/m) on % recovery of Cu^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+} ions (50 ppm) on P(AM-AA)-SiTi at 25±1°C.

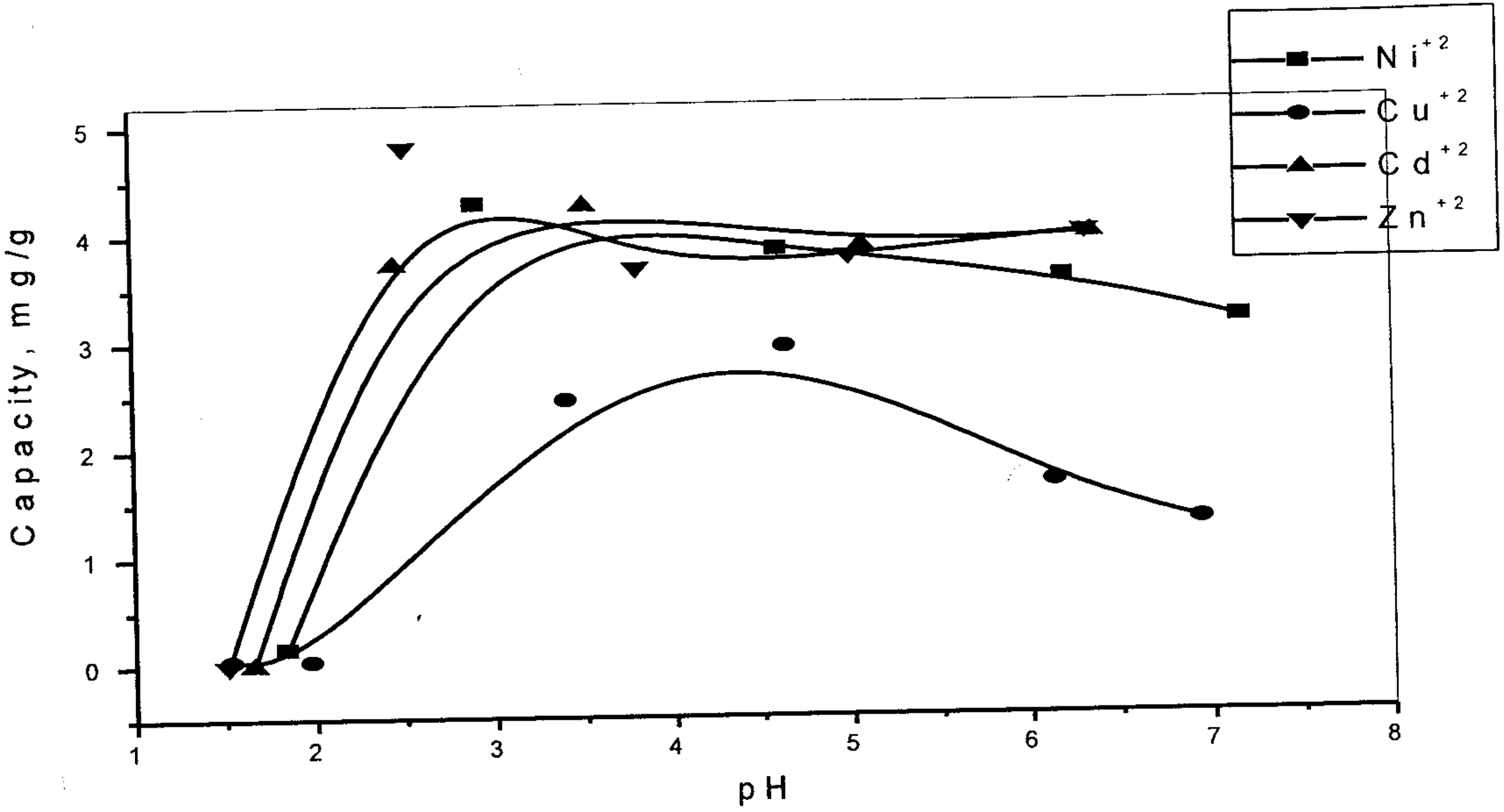


Fig.(9):- Effect of pH on the capacity of the treated P(AM-AA)-SiTi for Ni^{2+} ,Cd^{2+}, Zn^{2+} and Cu^{2+} ions at 25±1°C

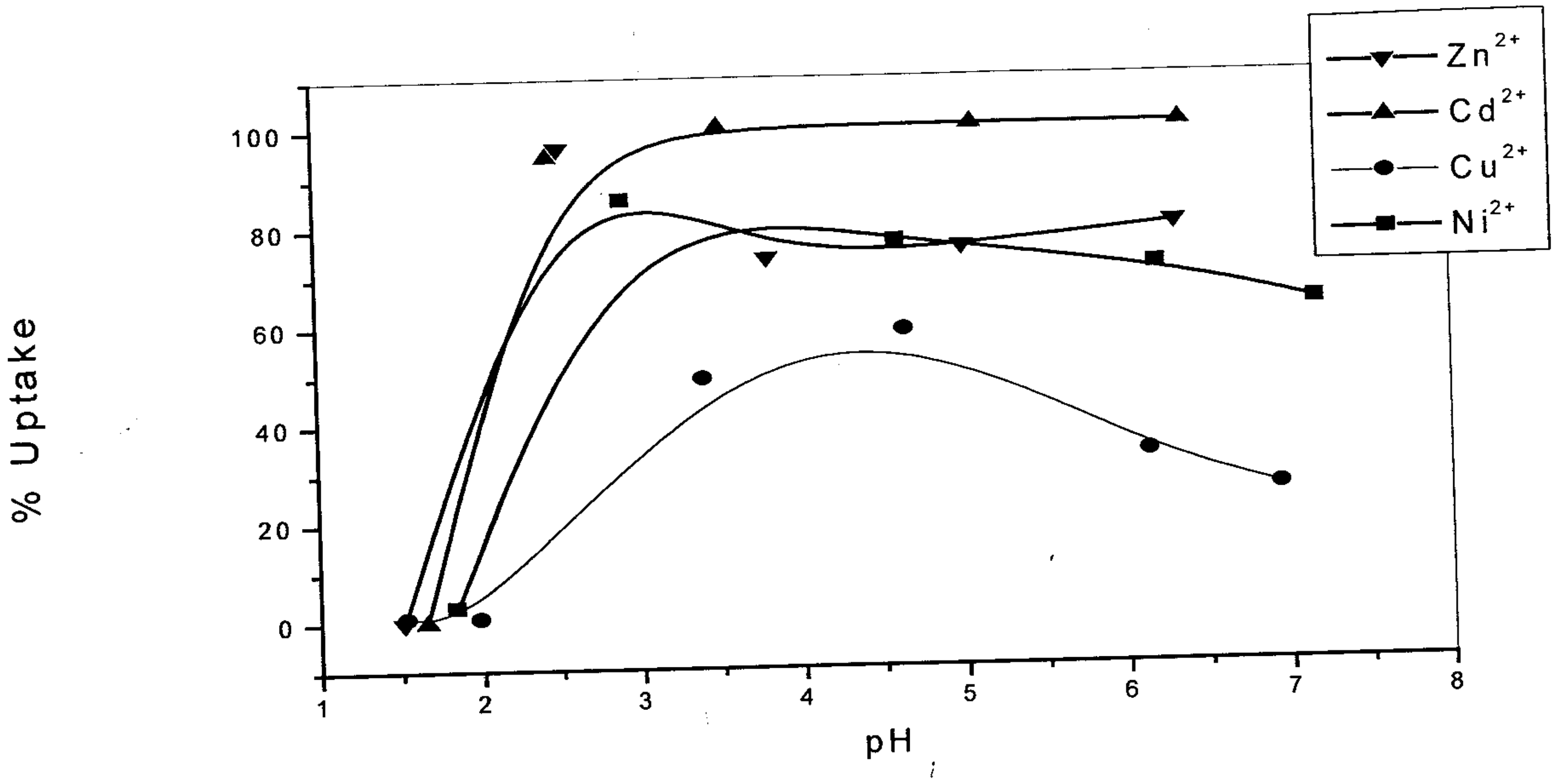


Fig. (10):- Effect of pH on the uptake of the treated P(AM-AA)-SiTi for Ni^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} ions at 25±1°C

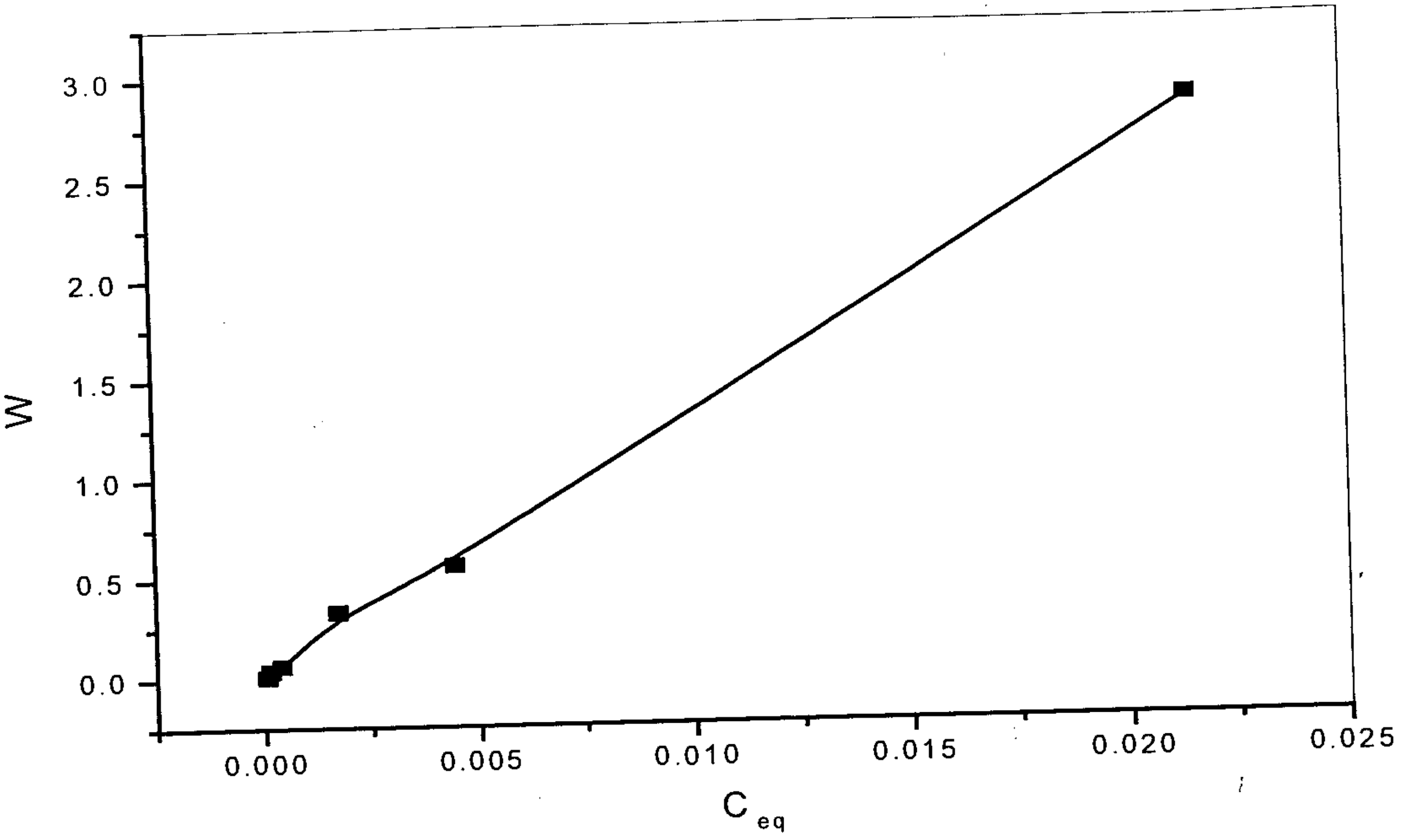


Fig.(11) Plots of amount uptake (W) against equilibrium concentration (C) for adsorption of Cu^{2+} on P(AM-AA)-SiTi at 25±1°C

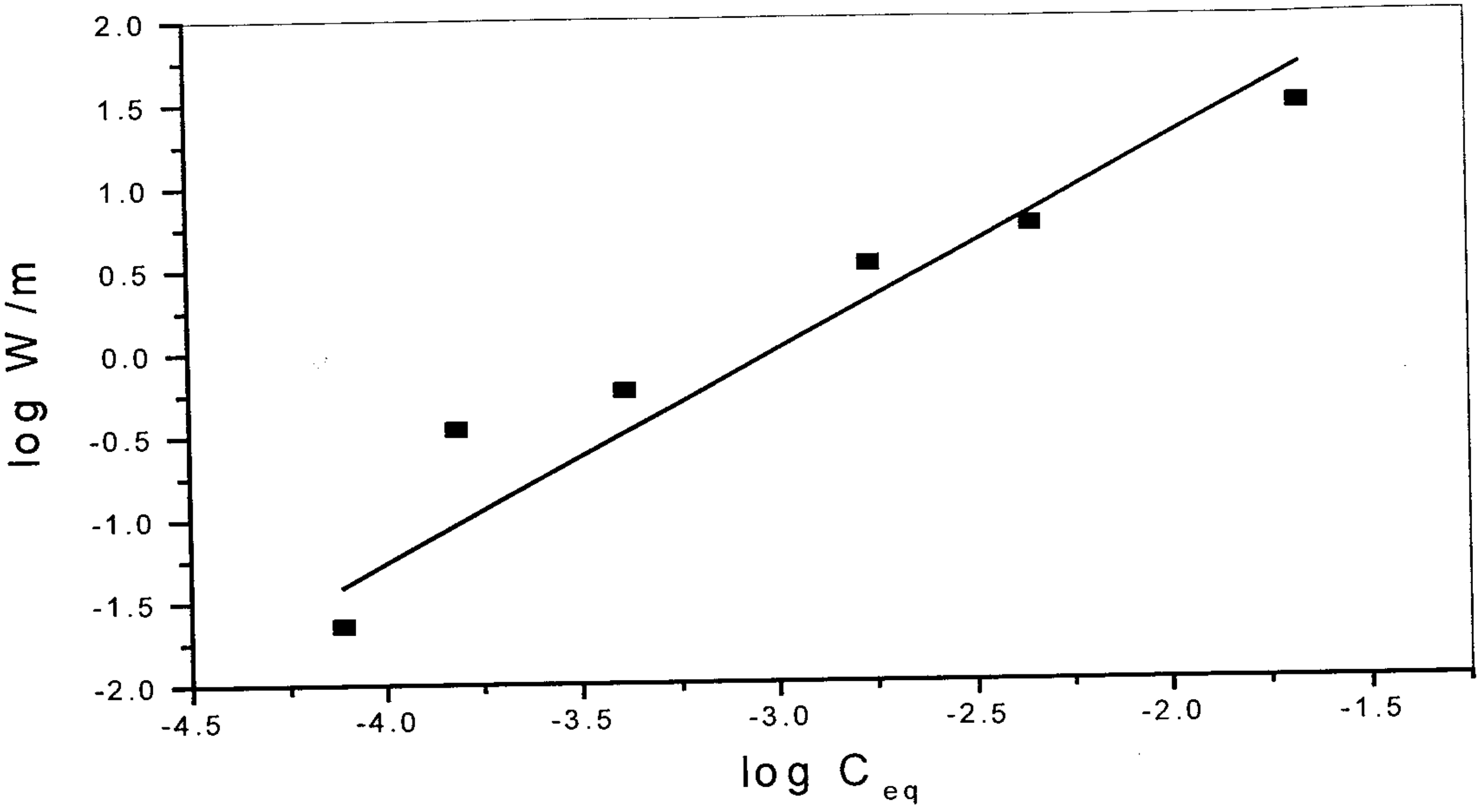


Fig.(12) ***Freundlich adsorption isotherm for the adsorption*** Cu^{2+} ***ion on P(AM-AA)-SiTi at 25±1°C***

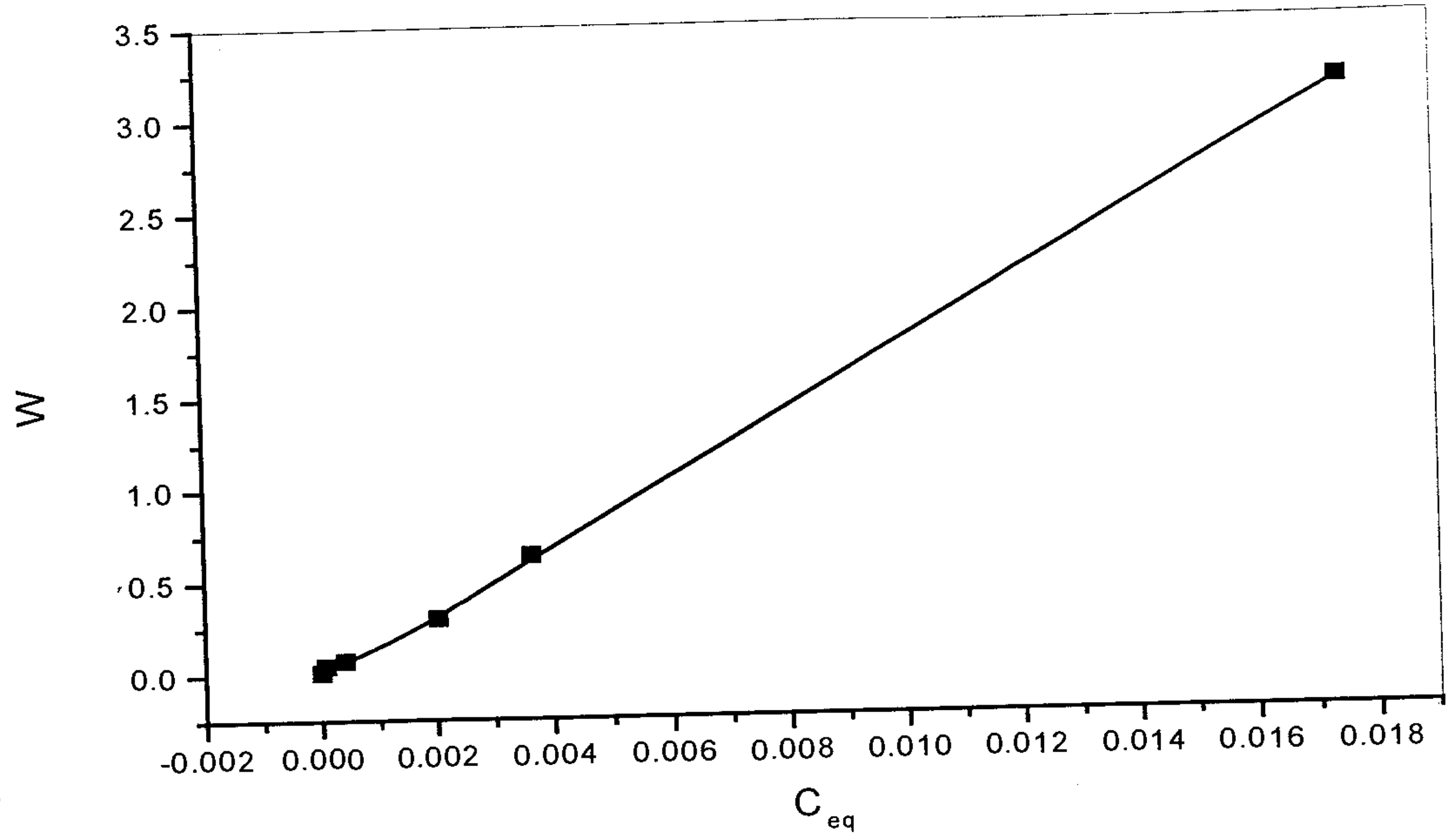


Fig.(13) Plots of amount uptake (W) against equilibrium concentration (C) for adsorption of Cd^{2+} on P(AM-AA)-SiTi at 25±1°C

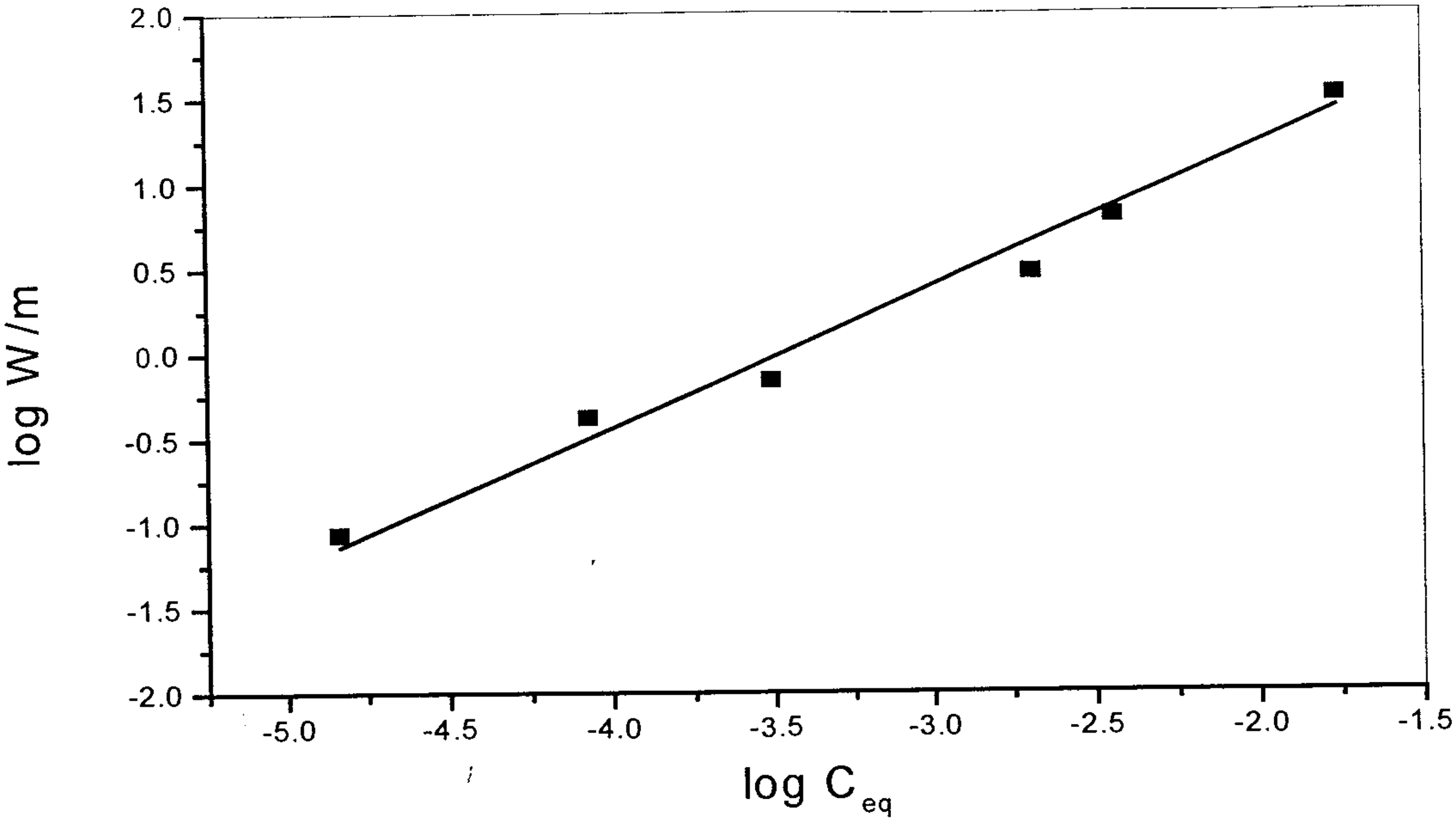


Fig.(14) Freundlich adsorption isotherm for the adsorption Cd^{2+} ion on P(AM-AA)-SiTi at 25±1°C

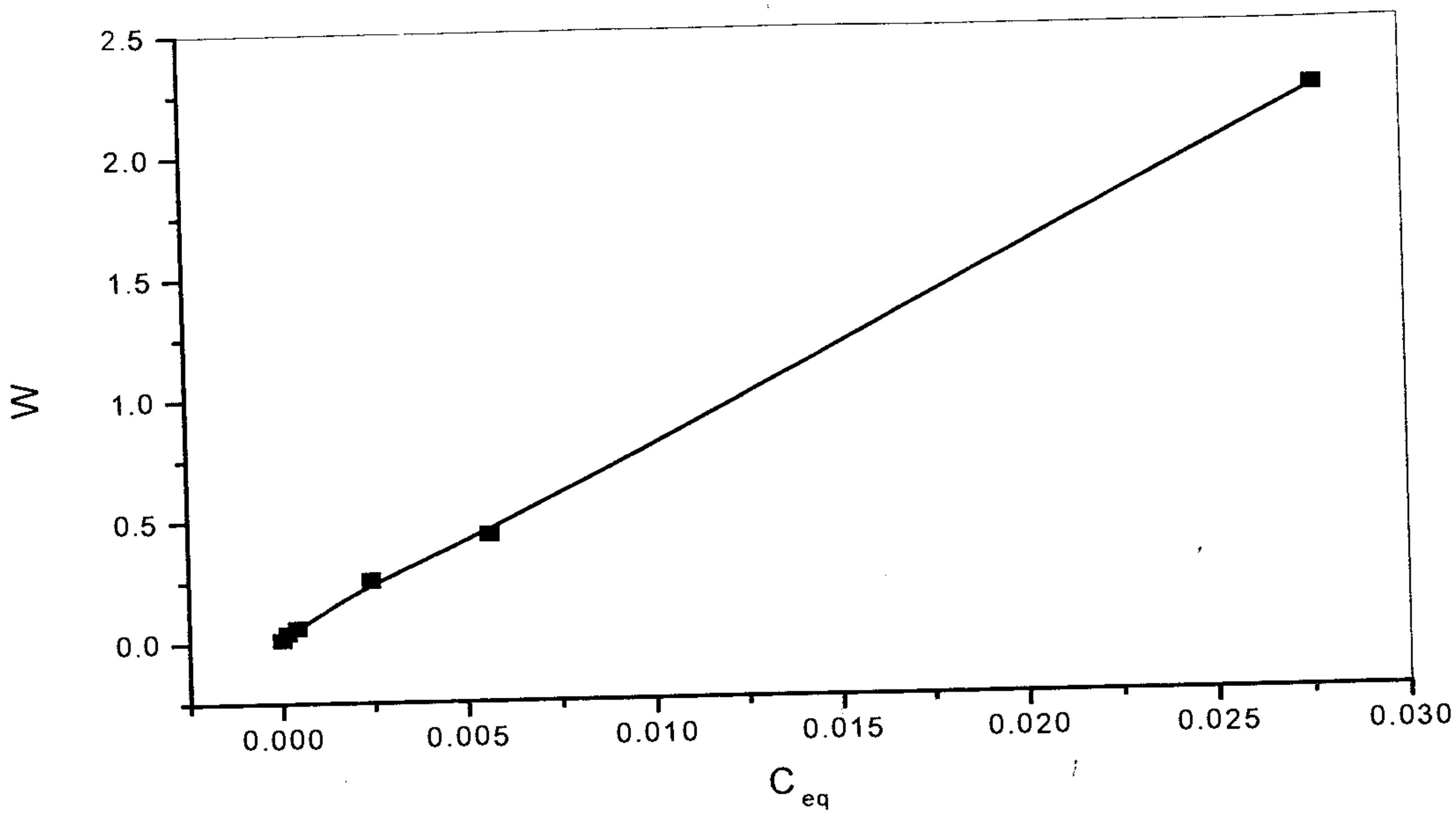


Fig.(15) Plots of amount uptake (W) against equilibrium concentration (C) for adsorption of Ni^{2+} on P(AM-AA)-SiTi at 25±1°C

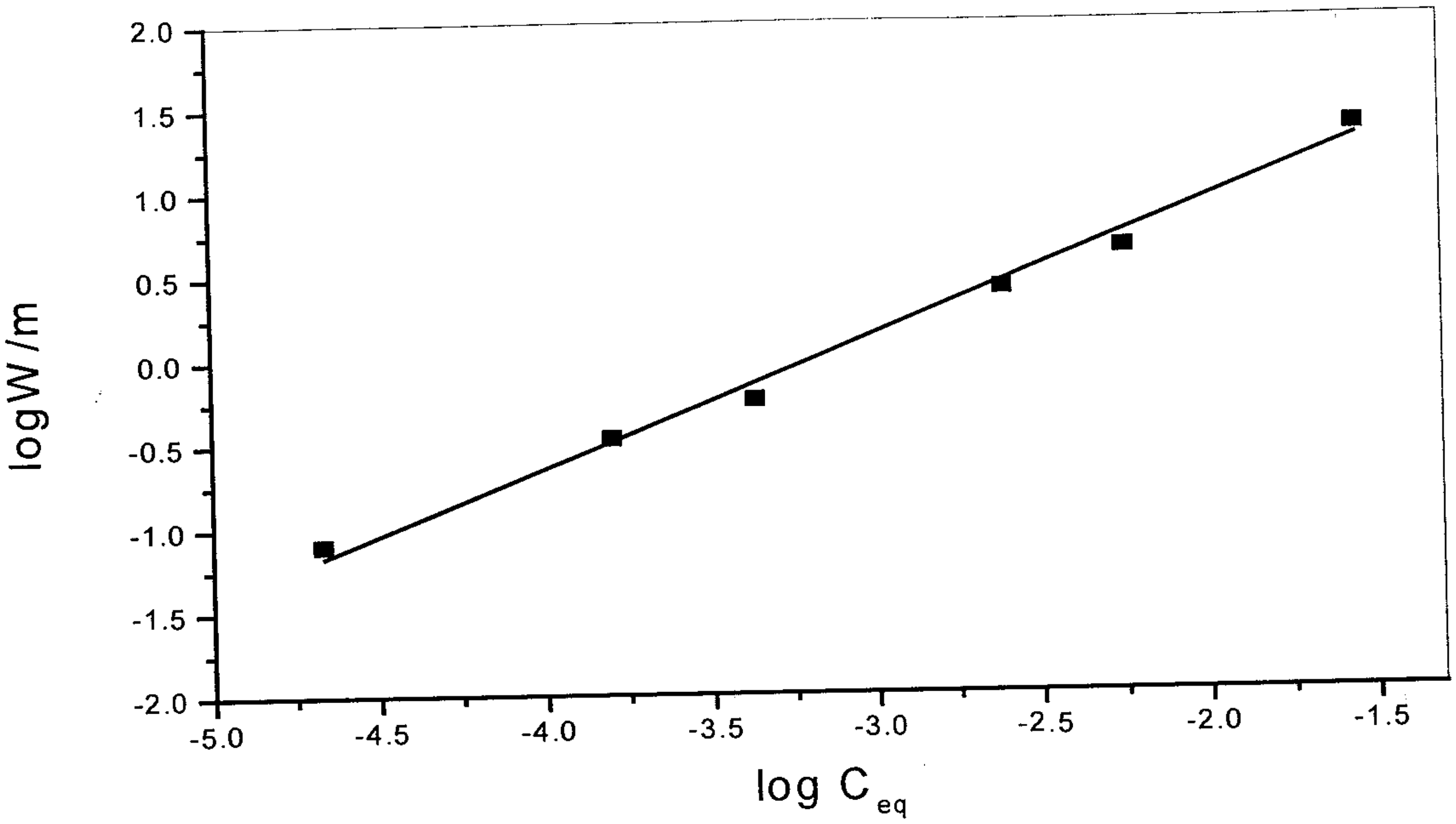


Fig.(16) Freundlich adsorption isotherm for the adsorption Ni^{2+} ion on P(AM-AA)-SiTi at 25±1°C

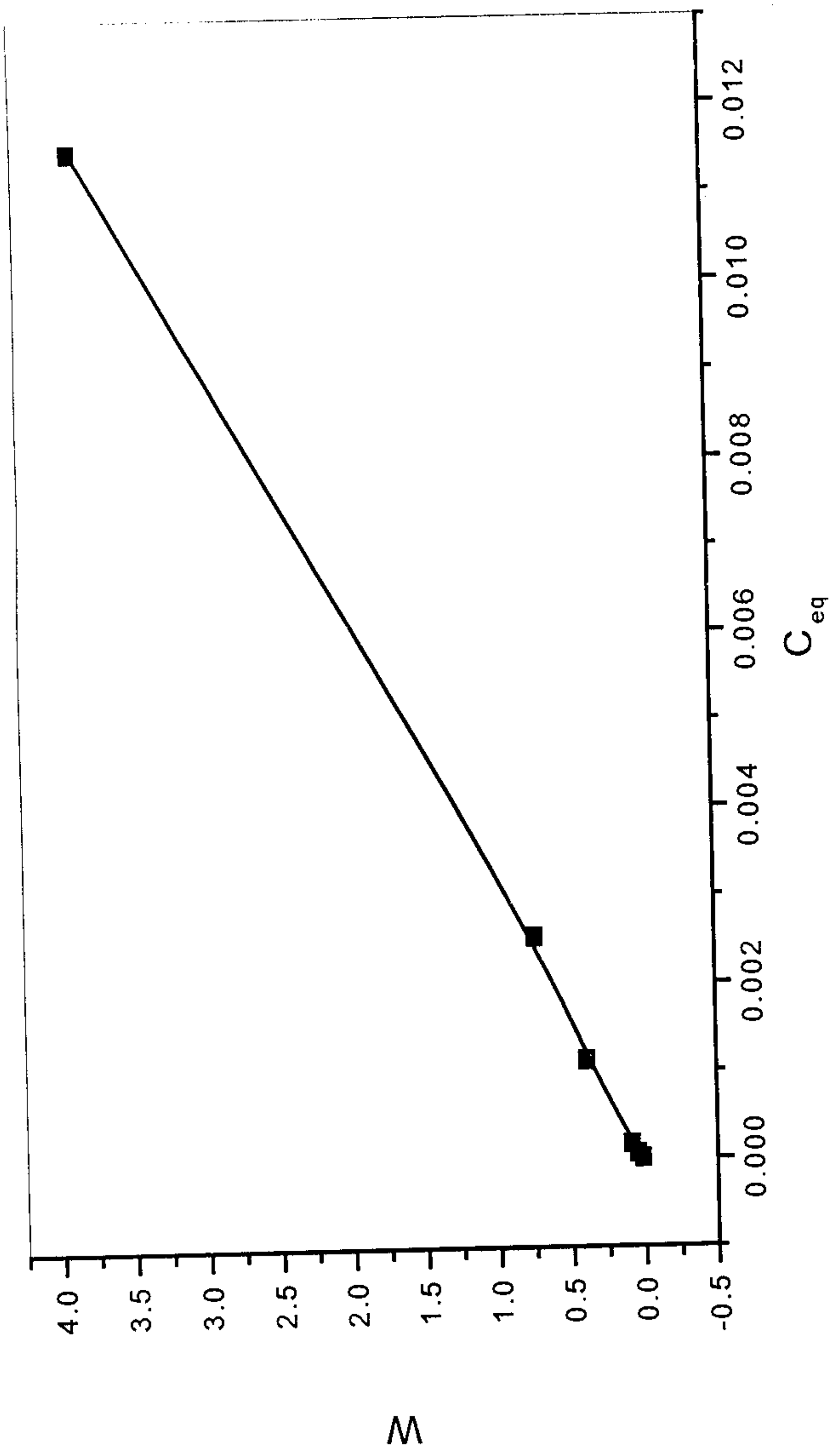


Fig.(17) Plots of amount uptake (W) against equilibrium concentration (C) for adsorption of Zn^{2+} on P(AM-AA)-SiTi at 25±1°C

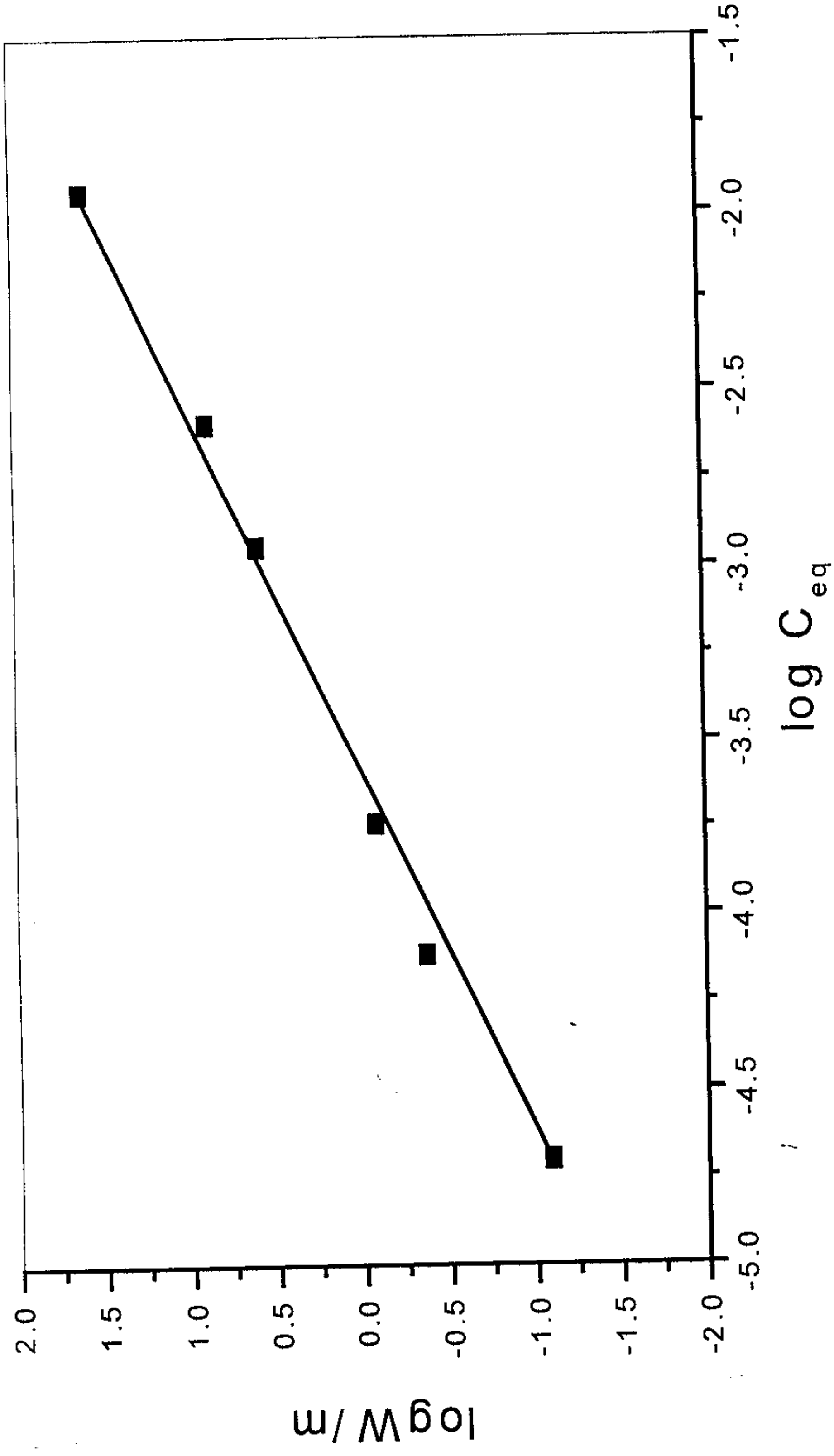


Fig.(18) Freundlich adsorption isotherm for the adsorption Zn^{2+} ion on P(AM-AA)-SiTi at 25 ± 1^oC

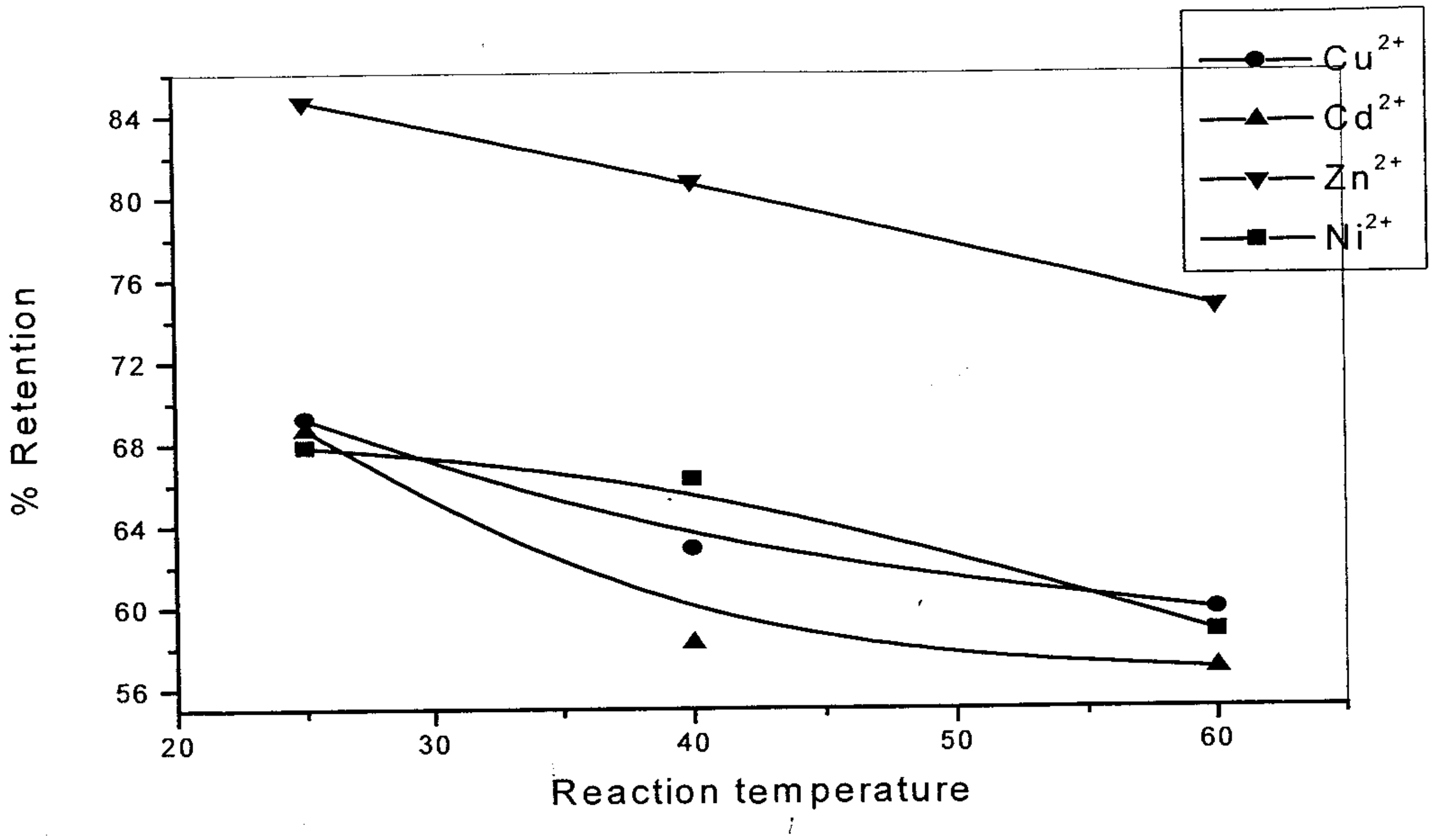


Fig.(19) Effect of reaction temperature on the adsorption of Cu^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi

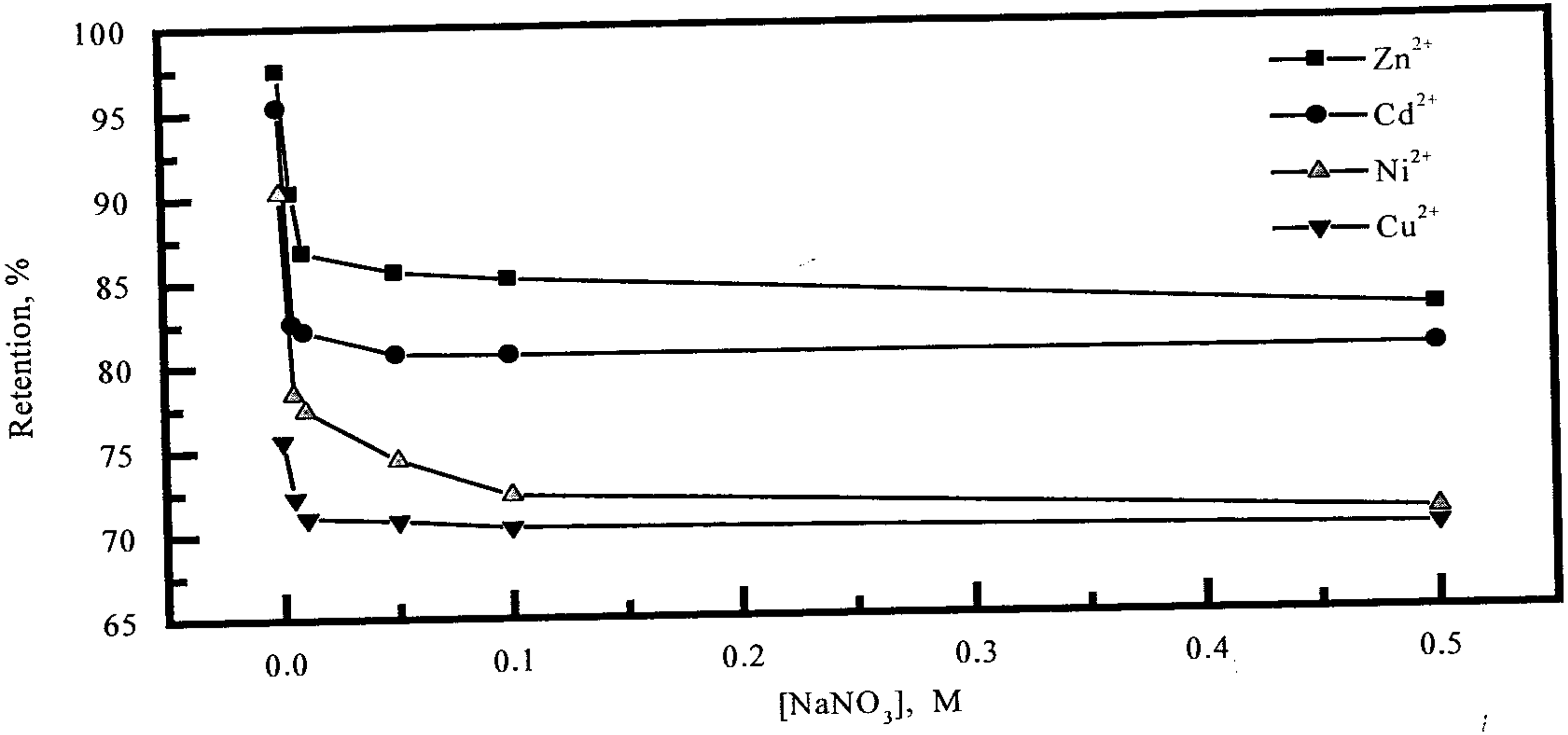


Fig.(20) *Effect of different concentrations of NaNO$_3$ on the retention behavior of Cu^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi at 25±1°C*

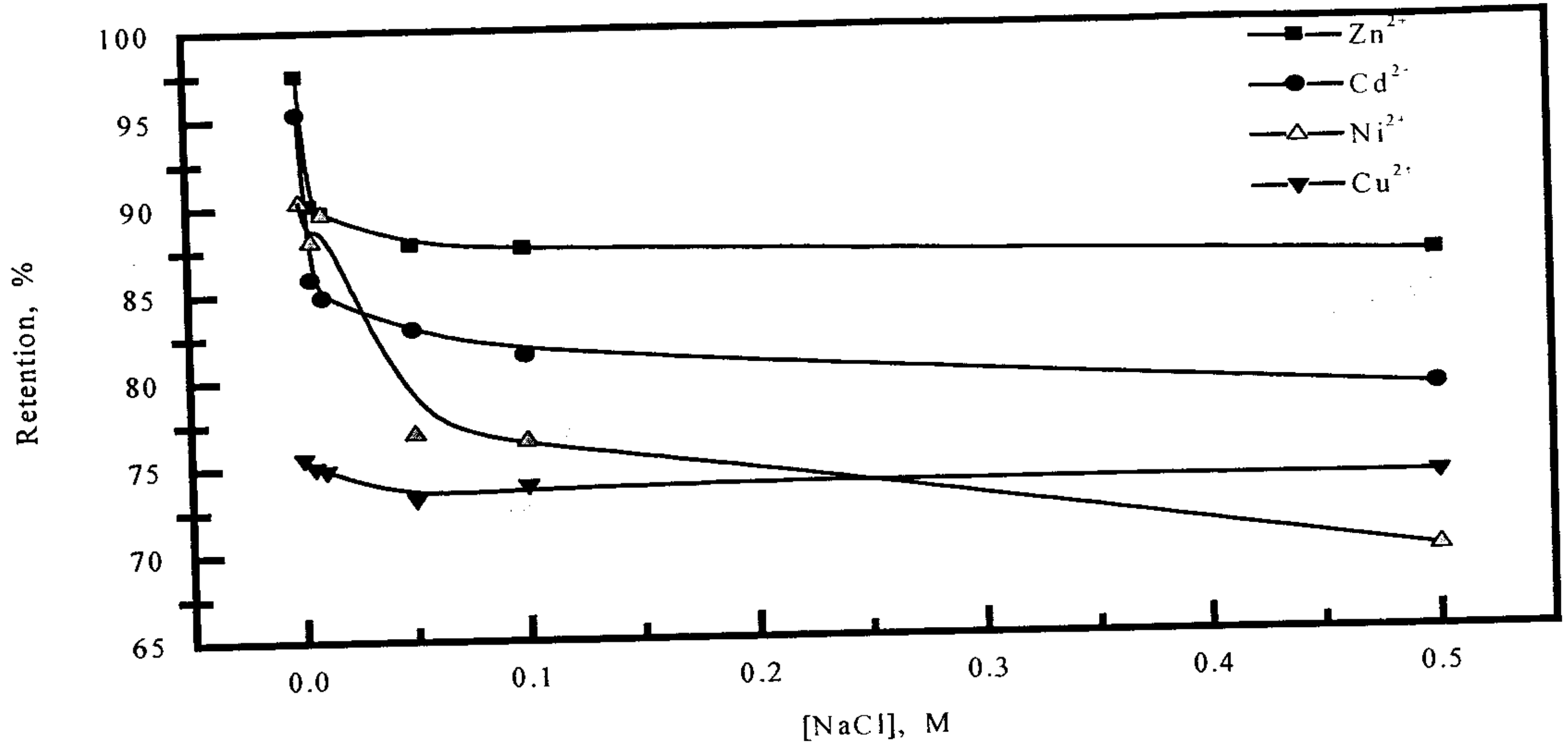


Fig.(21) Effect of different concentrations of NaCl on the retention behavior of Cu^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi at 25±1°C

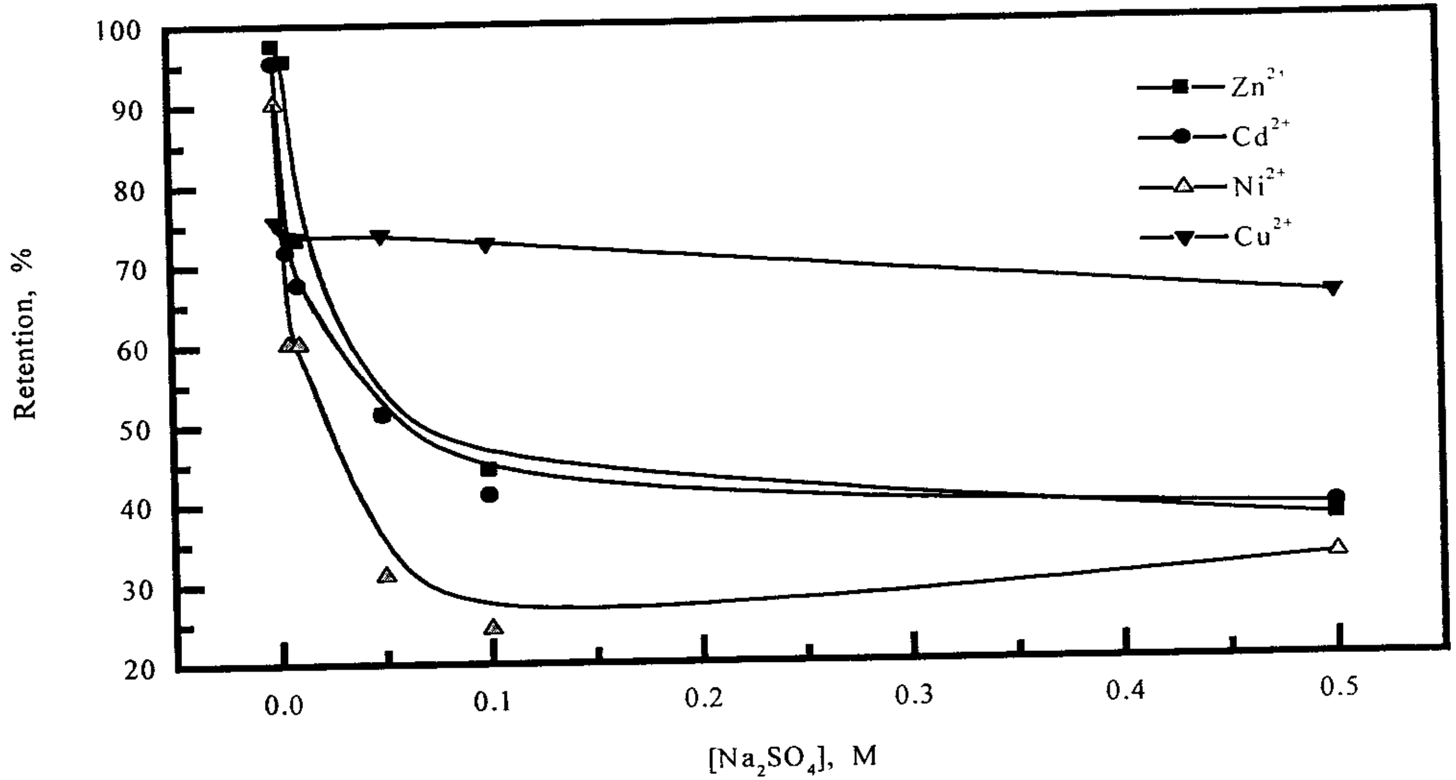


Fig.(22) Effect of different concentrations of Na$_2$SO$_4$ on the retention behavior of Cu^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi at 25±1°C

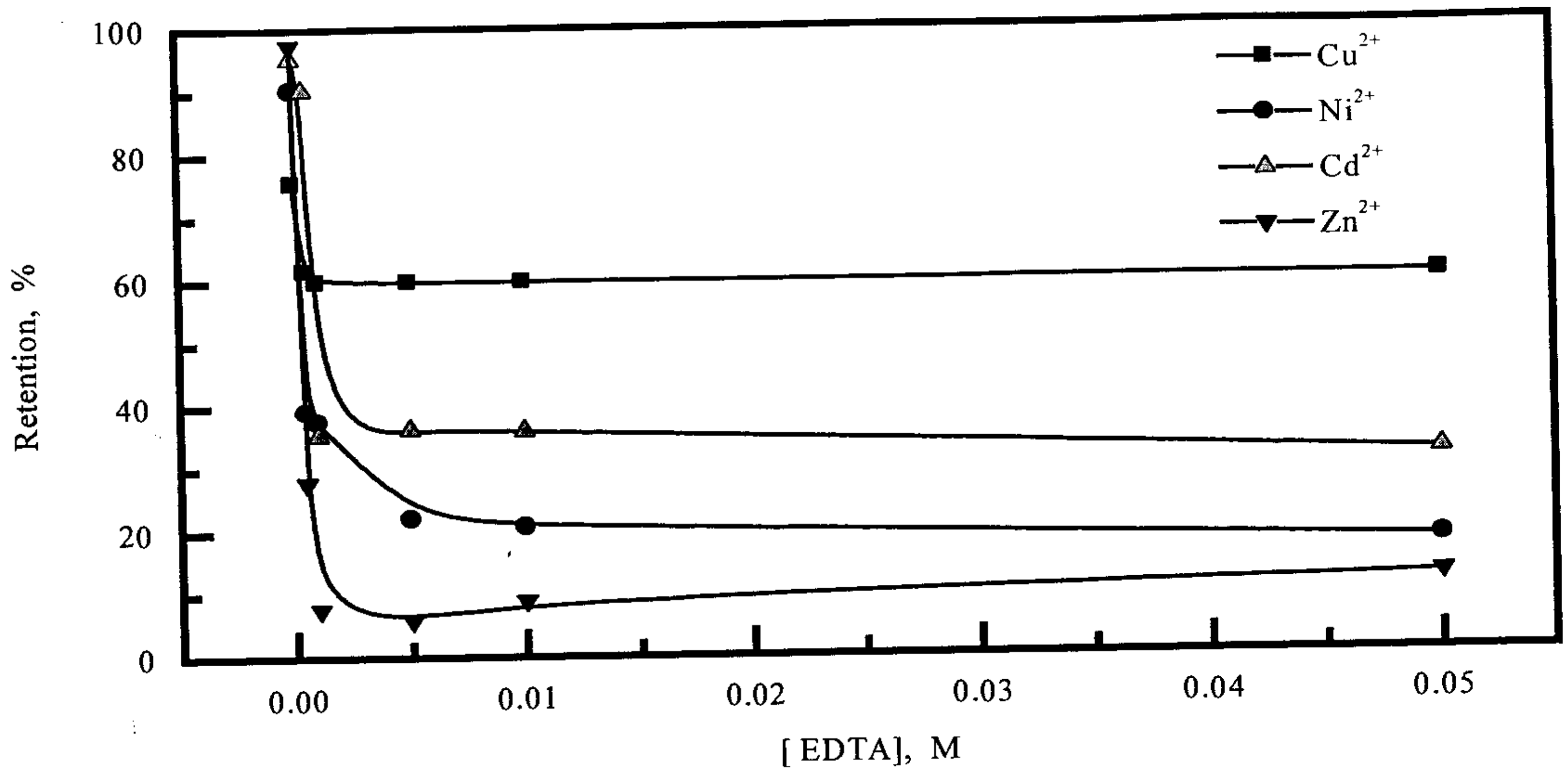


Fig.(23) Effect of different concentrations of EDTA on the retention behavior of Cu^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi at 25±1°C

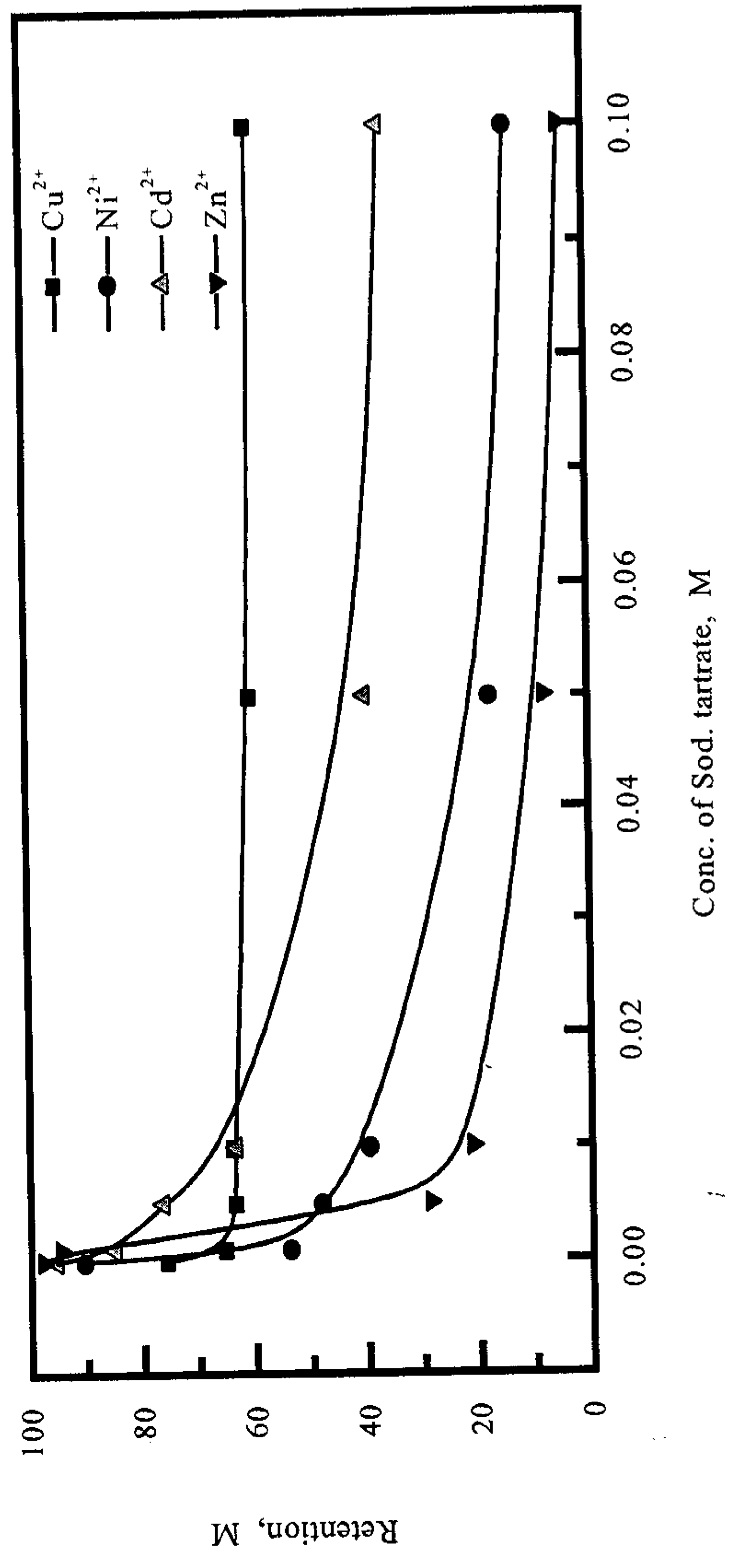


Fig.(24) Effect of different concentrations of sodium tartrate on the retention behavior of Cu^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+} ions on P(AM-AA)-SiTi at 25±1°C

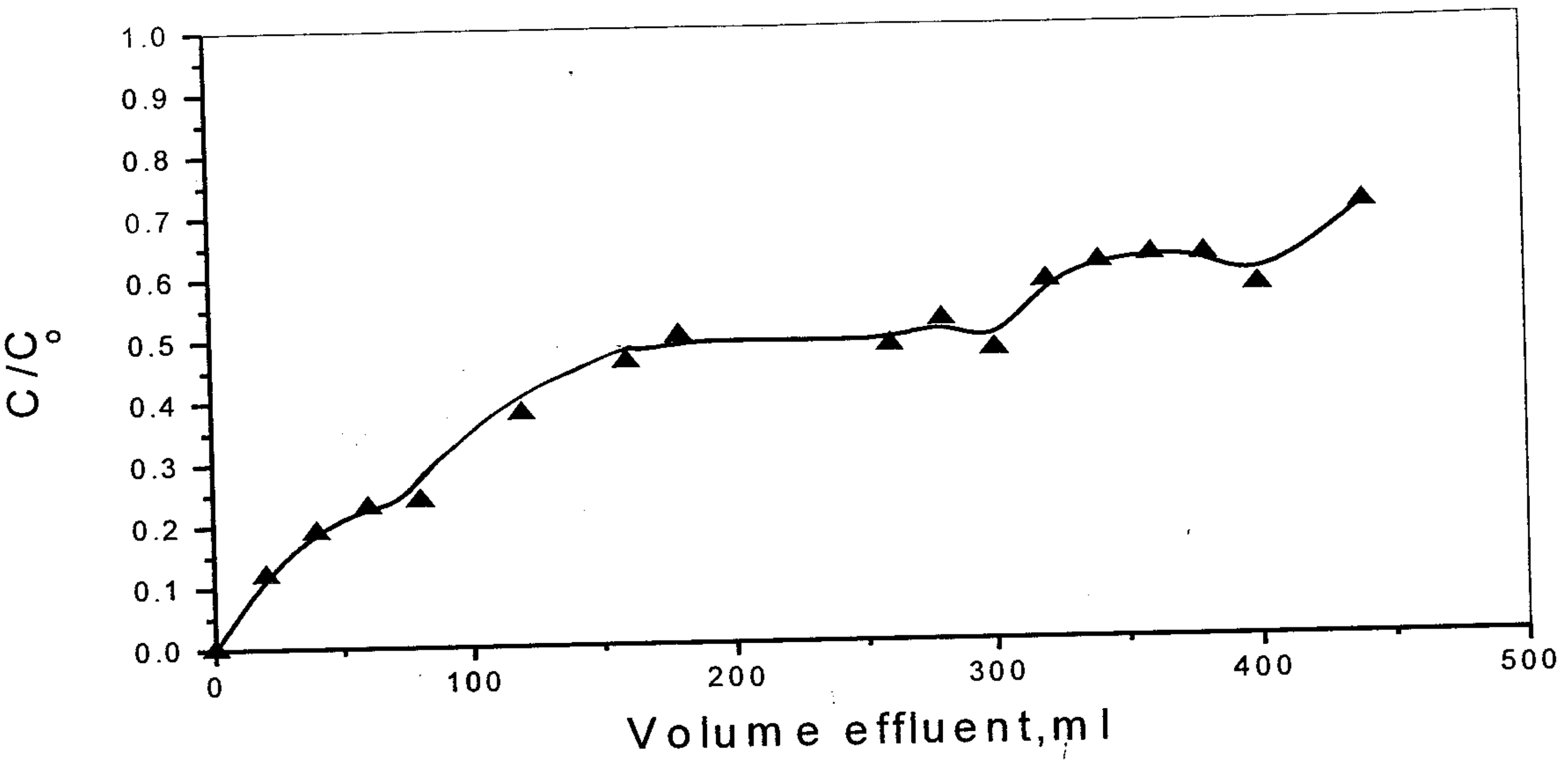


Fig.(25): C/C$_o$ against effluent volume for the loading of Ni^{2+} ion from simulated Waste water on P(AM-AA)-SiTi columns at 25±1°C.

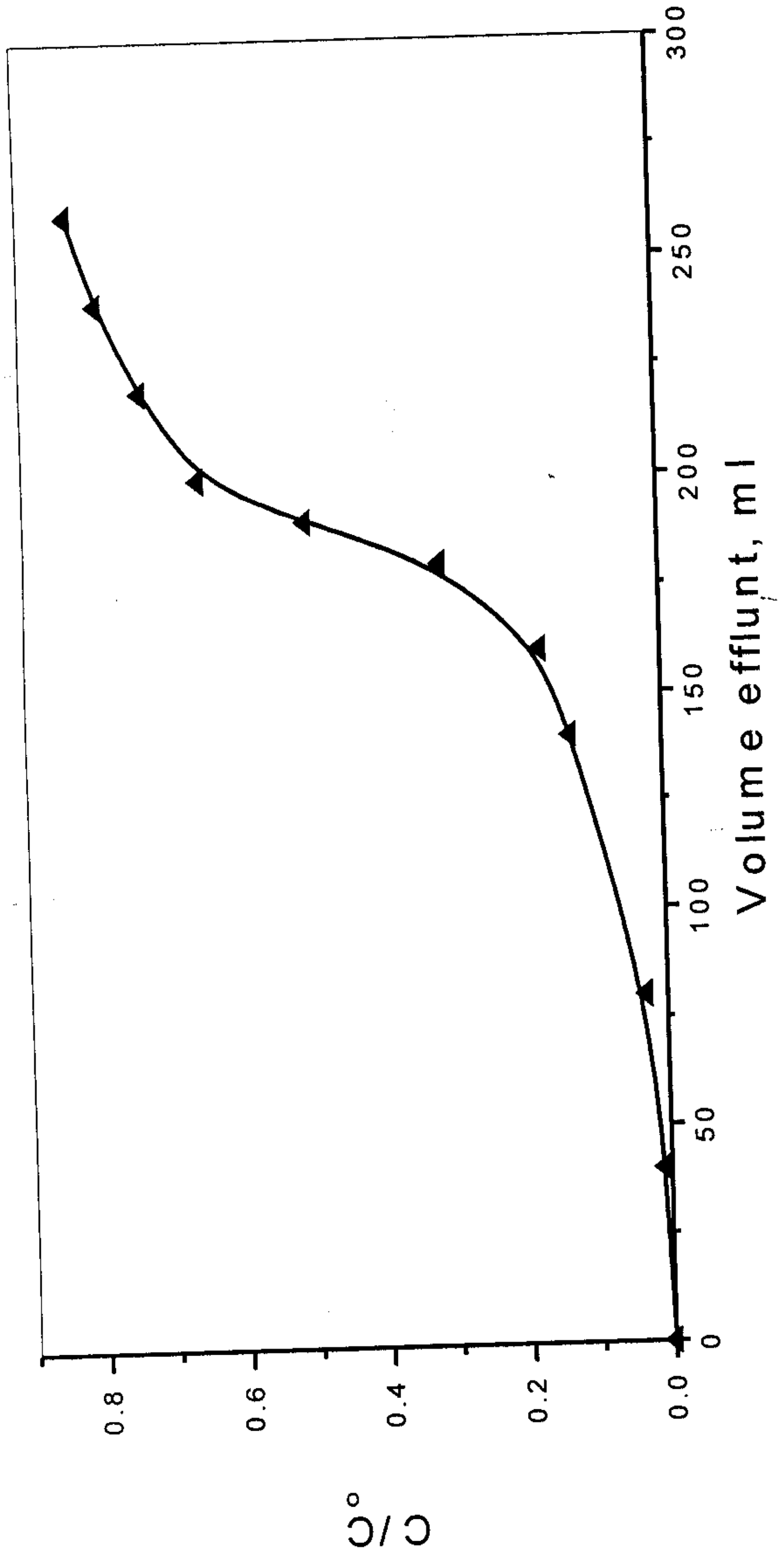


Fig.(26):- C/C$_o$ against effluent volume for the loading of Cu^{2+} ion from simulated Waste water on P(AM-AA)-SiTi columns at 25±1°C.

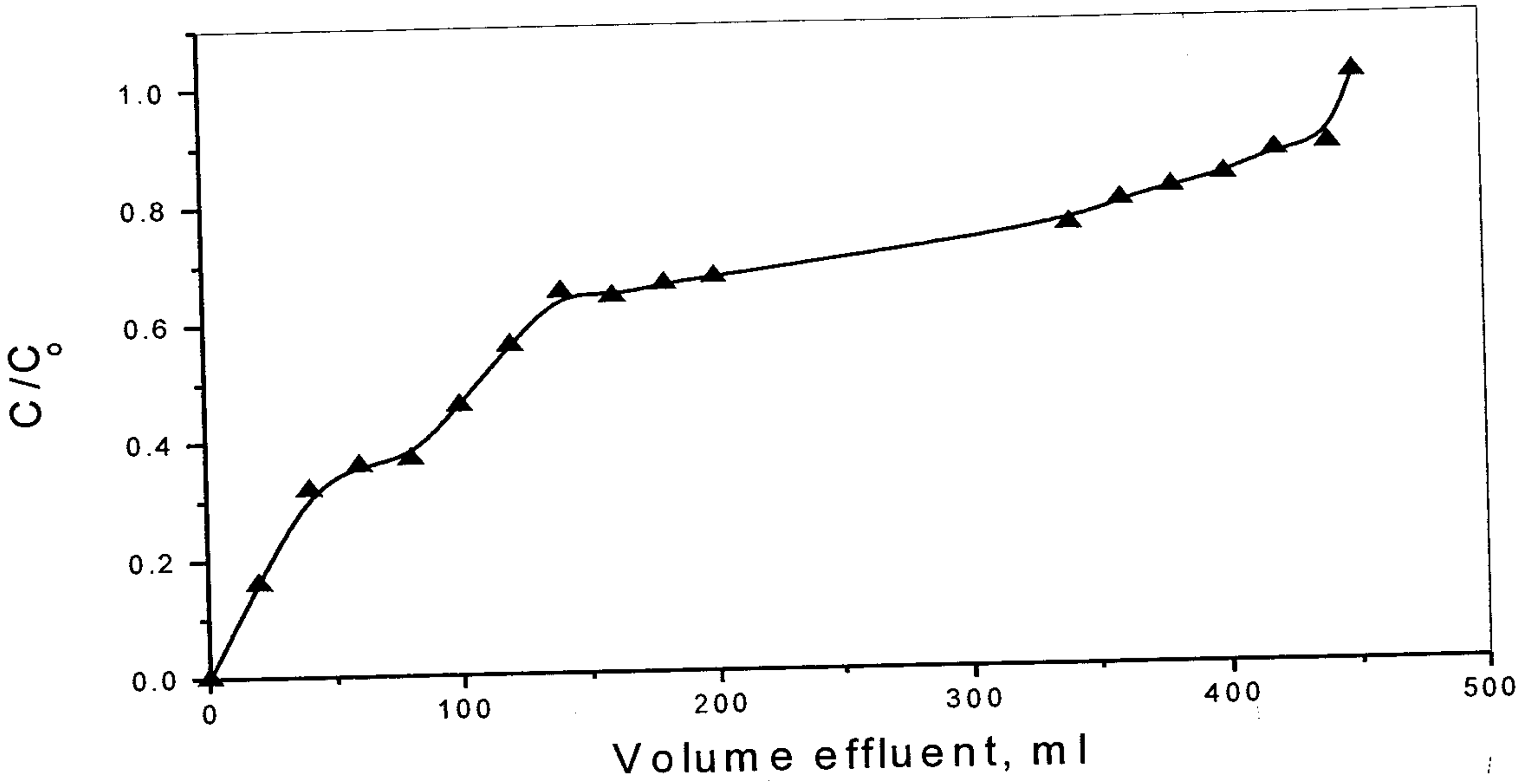


Fig.(27):- C/C_o against effluent volume for the loading of Ni^{2+} ion from simulated Waste water on P(AM-AA)-SiTi columns at 25±1°C.

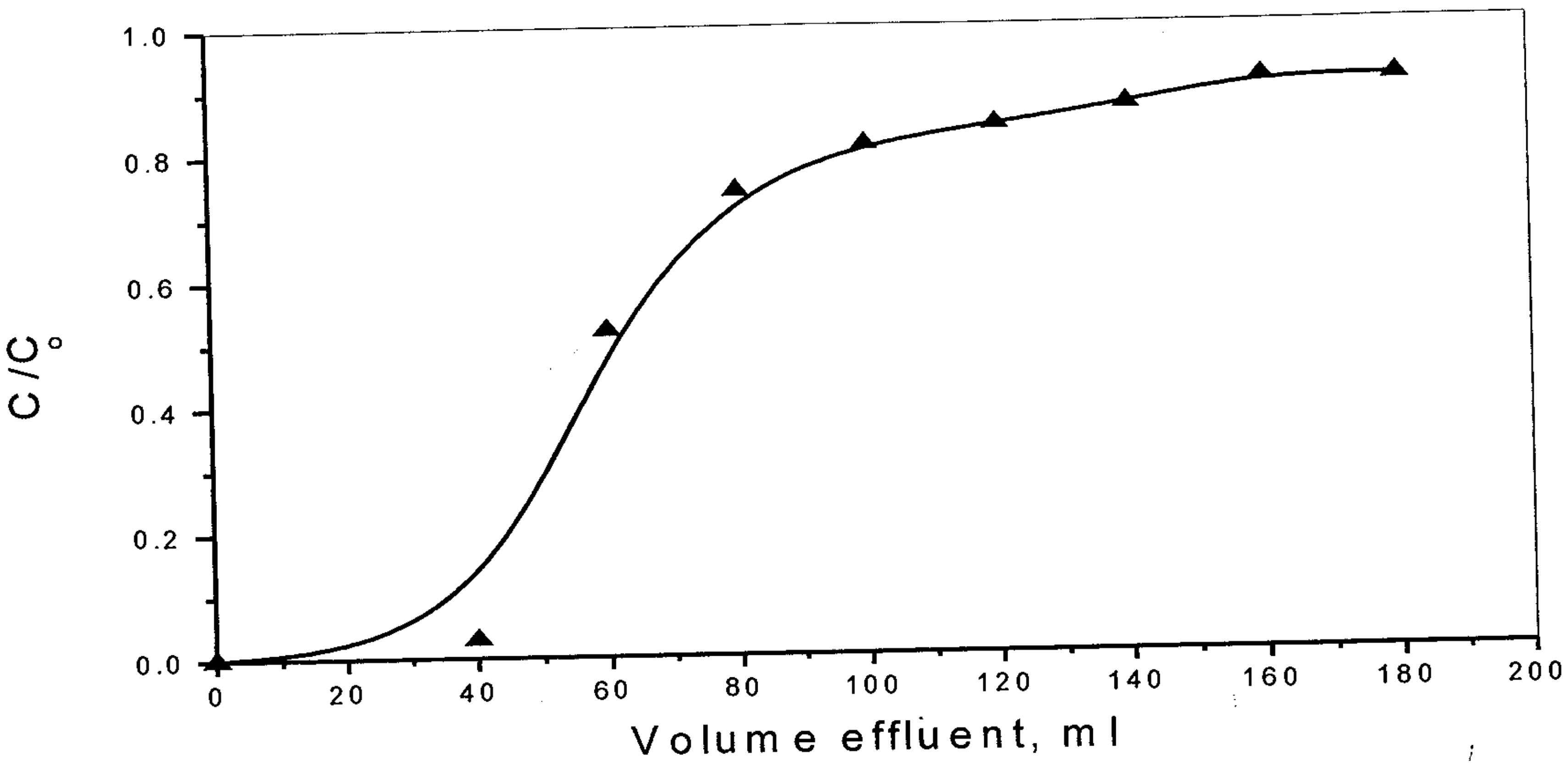


Fig.(28):- C/C_o against effluent volume for the loading of Zn^{2+} ion from simulated Waste water on P(AM-AA)-SiTi columns at 25±1°C.