

## *Chapter 3*

# **RESULTS AND DISCUSSION**

### III.1 Composition of prepared chelating resins:

#### III.1.(a) Elemental analysis studies:

The elemental analysis of copolymer (XXXI) and its aminated chelating resins (XXXII), (XXXIII) and (XXXIV) are summarized with the theoretical compositions based on assumed structures in Table (1). Although the results of elemental analysis do not have much significance, but we can get some of information about the number of metal atoms attached to the polymeric chains. The deviation of the observed analysis data from the theoretical values may be attributed to the polymeric nature.

**Table 1:** Analytical data of copolymer and its aminated chelating resins.

Compounds	Elemental analysis					
	% C		% H		% N	
	Calc.	Found	Calc.	Found	Calc.	Found
<b>Copolymer XXXI</b> $C_{17}H_{20}O_3$	74.97	73.94	7.40	7.28	0.0	0.0
<b>Chelating resin XXXII</b> $C_{23}H_{28}O_3N_2$	72.60	71.99	7.42	7.33	7.36	7.18
<b>Chelating resin XXXIII</b> $C_{23}H_{27}O_4N$	72.41	72.06	7.13	6.88	3.67	3.52
<b>Chelating resin XXXIV</b> $C_{28}H_{33}O_4N_3$	70.71	70.49	6.99	6.15	8.83	8.61

#### III.1.(b) IR Spectral studies:

IR spectra of investigated compounds are shown in Figs. (5-8). The IR spectrum Fig (5a-b) of copolymer (XXXI) displays bands near 3440 (broad), 3054 (m), 2995-2945 (splitted), 1729 (s), 1601 (w) and 1258 (m)  $cm^{-1}$ . These bands are assigned to  $\nu OH$  of water,  $\nu CH-Ar$ ,  $\nu CH-Aliph.$ ,  $\nu C=O$ ,  $\nu C=C$  of phenyl and epoxide moiety, respectively. The

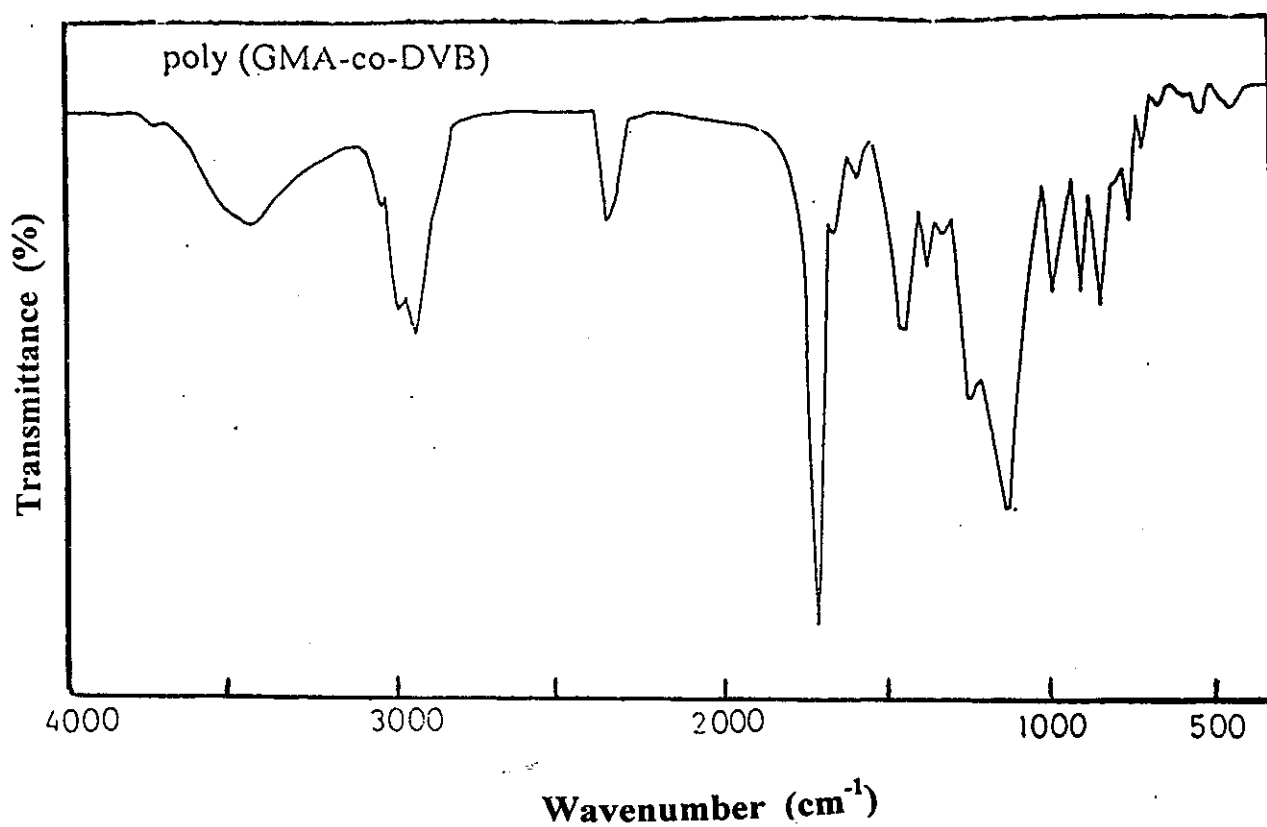
appearance of these bands confirming the formation of copolymer (XXXI).

The spectrum of chelating resin (XXXII) which obtained from the treatment of copolymer (XXXI) by *o*.phenylene diamine) Fig. (6) give the same bands except the appearance of two new bands near 3651 and 3439  $\text{cm}^{-1}$  which are assigned to  $\gamma\text{OH}$  and  $\gamma\text{NH}$ , respectively. The appearance of these bands confirming the formation of chelating resin (XXXII) from copolymer (XXXI) through the opening of epoxide ring by *o*.phenylene diamine.

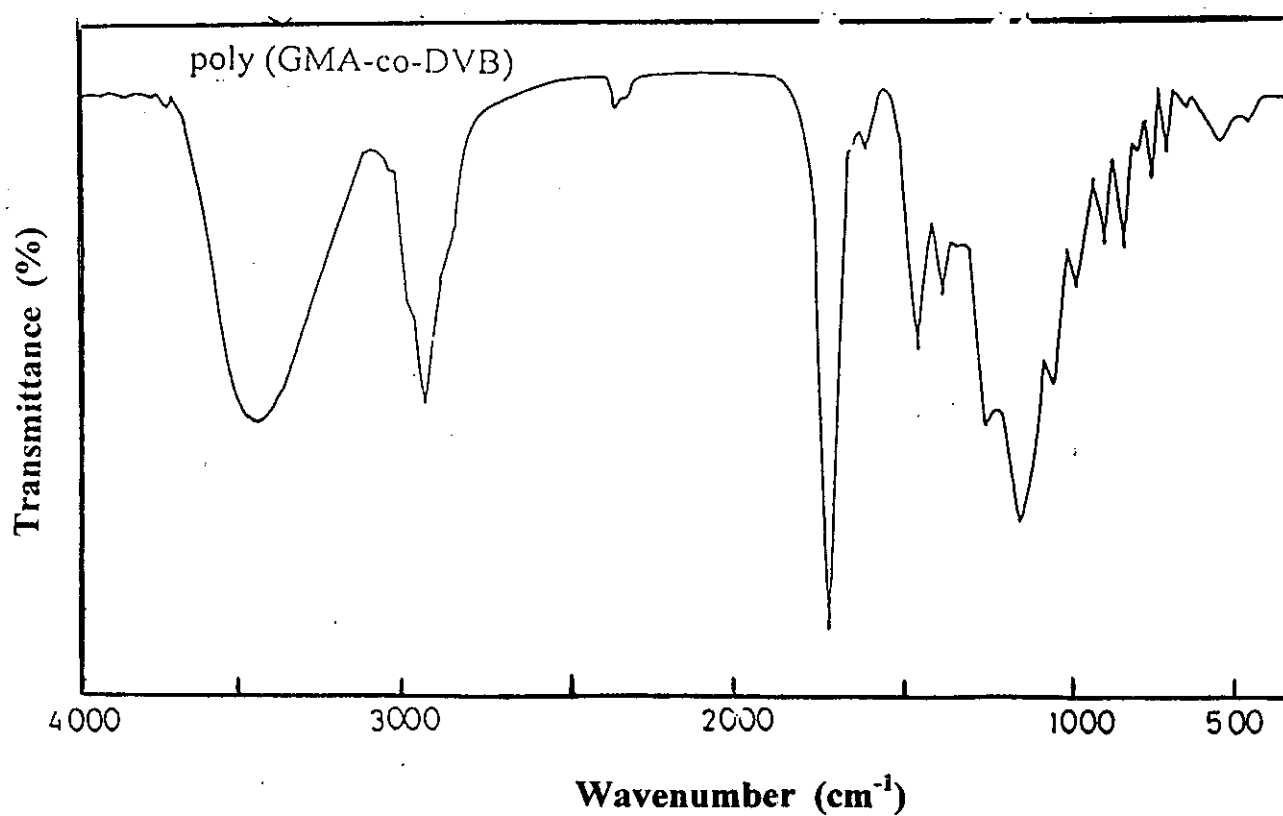
On the other hand, the appearance of epoxide band near 1265  $\text{cm}^{-1}$  indicates that the reaction of epoxy ring opening is not completed.

By the same way the spectrum of chelating resin (XXXIII) which obtained from the treatment of copolymer (XXXI) by *o*.amino phenol), Fig. (7), give the same bands appearing in Fig. (6) except the appearance of two new bands near 3567 and 3304-3375  $\text{cm}^{-1}$  which are assigned  $\nu\text{OH}$  and  $\nu\text{NH}$ , respectively. The appearance of these bands confirming the formation of chelating resin (XXXIII) from copolymer (XXXI) through the opening of epoxide ring by *o*.aminophenol.

Also, the spectrum of chelating resin (XXXIV) (which obtained from the treatment of copolymer (XXXI) by 4-amino antipyrine), Fig. (8), give the same bands appearing in Fig. (6) except the appearance of two new bands near 3651 and 3428  $\text{cm}^{-1}$  which are assigned  $\nu\text{OH}$  and  $\nu\text{NH}$ , respectively. The appearance of these bands confirming the formation of chelating resin (XXXIV) from copolymer (XXXI) through the opening of epoxide ring by 4-amino antipyrine.



**Fig. (5a):** IR spectrum of copolymer (XXXI).



**Fig. (5b):** IR spectrum of copolymer (XXXI).

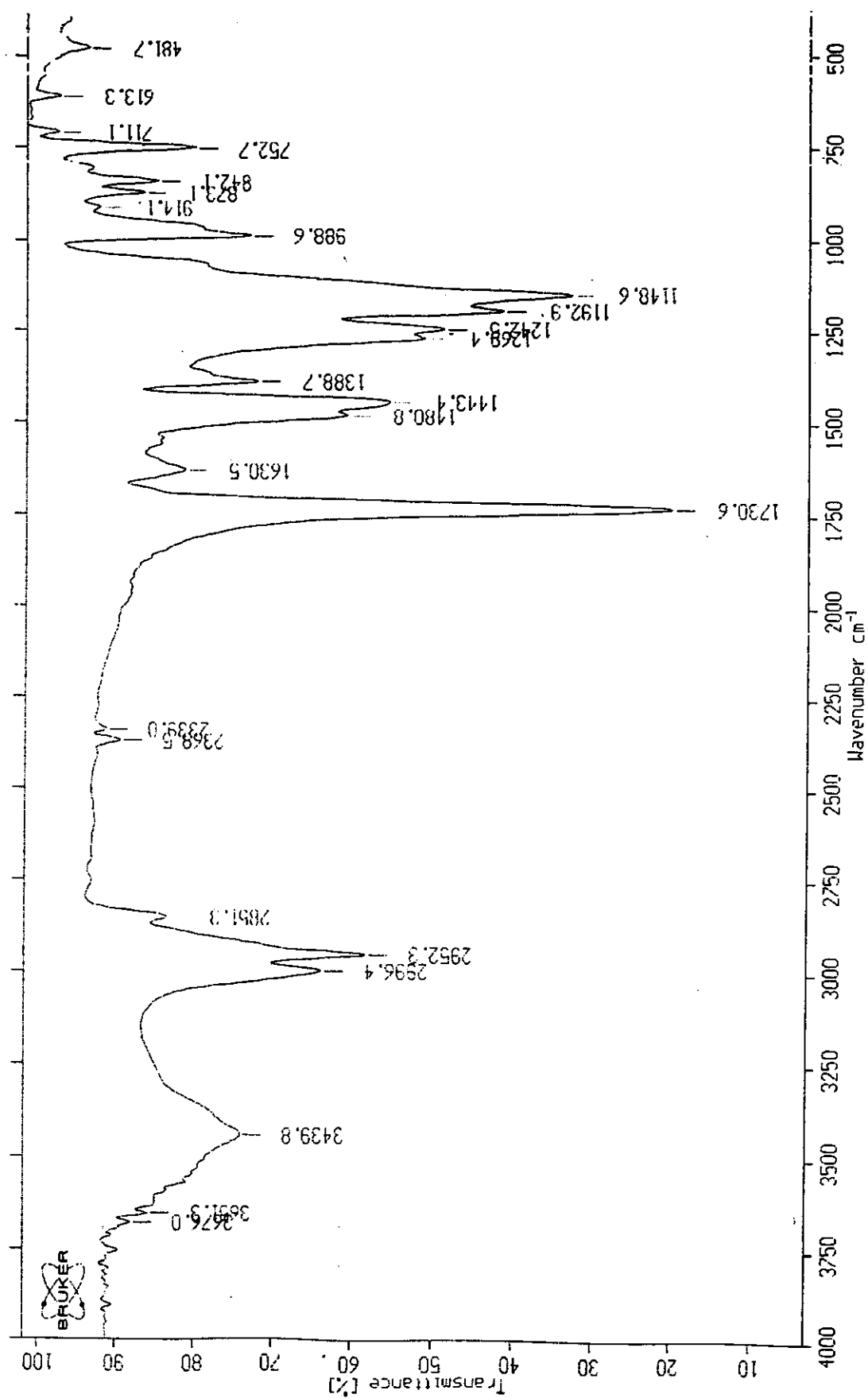


Fig. (6): IR spectrum of chelating resin (XXXII).

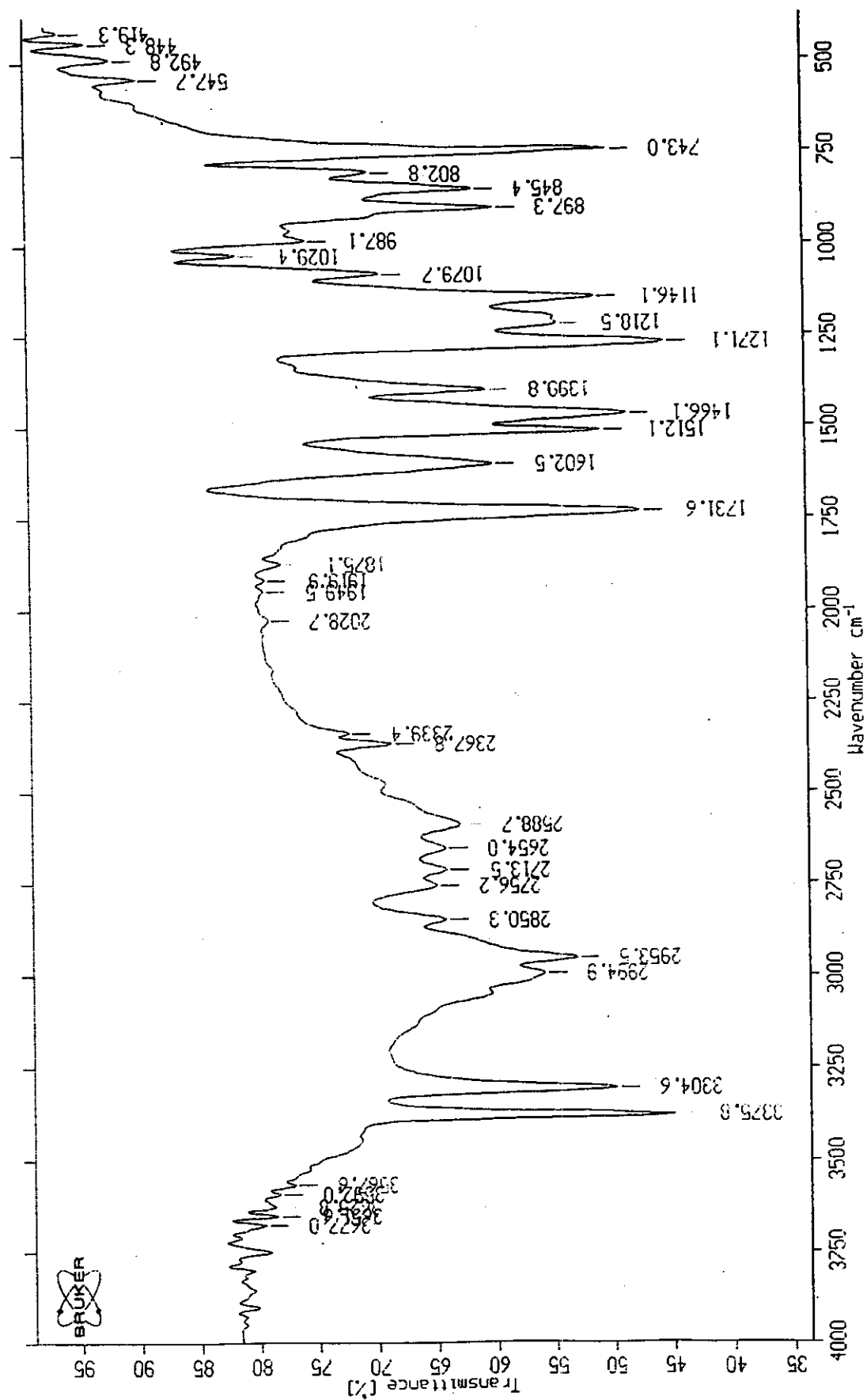


Fig. (7): IR spectrum of chelating resin (XXXIII).

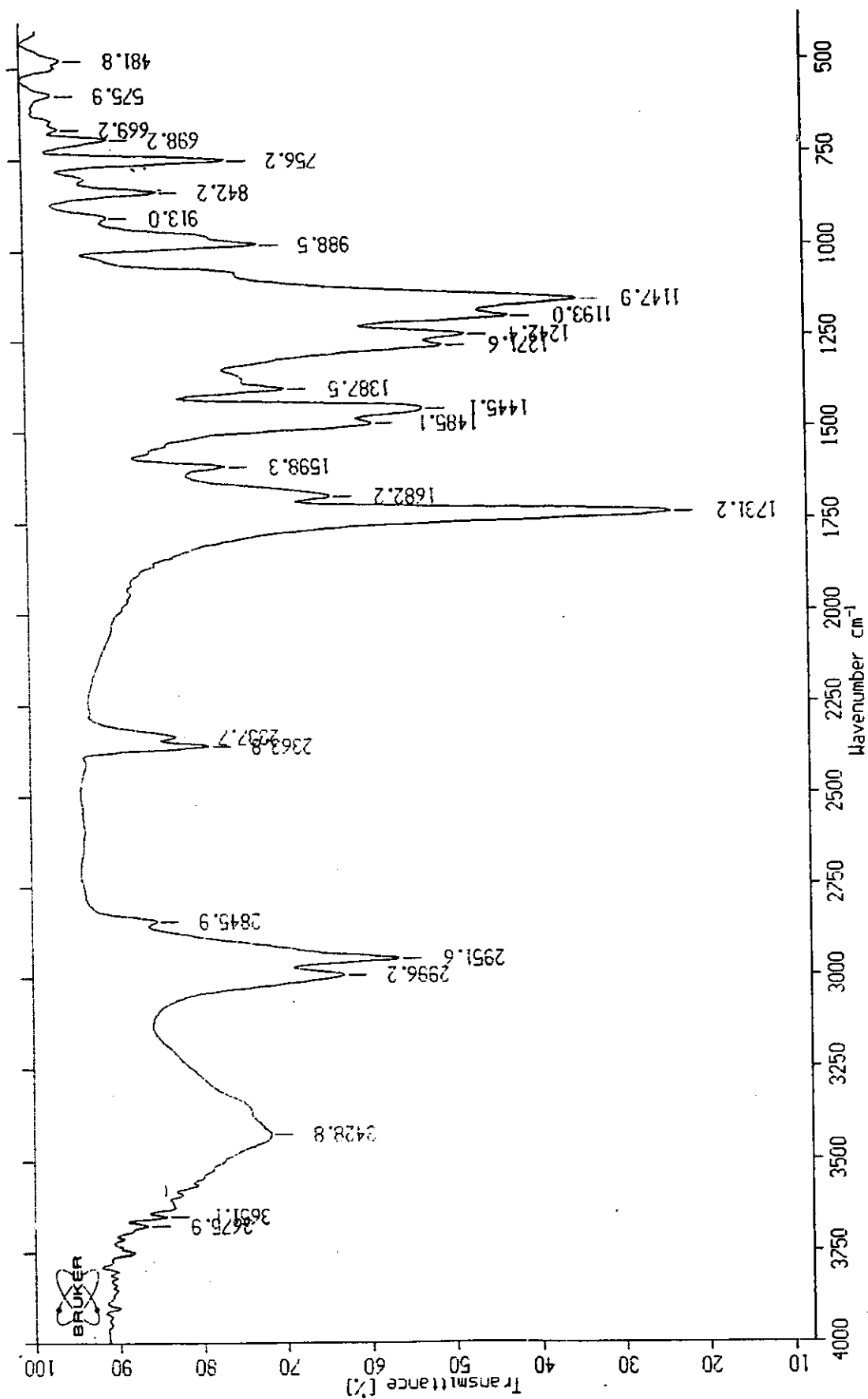


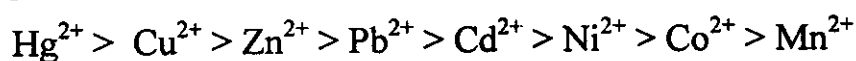
Fig. (8): IR spectrum of chelating resin (XXXIV).

## III.2 Selective uptake of metal ions using batch technique:

### III.2.1 Selective uptake of metal ions ( $\text{Hg}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Co}^{2+}$ and $\text{Ni}^{2+}$ ) by chelating resin containing o.phenylene diamine ligand (XXXII):

#### III.2.1.1 Optimum pH of metal ions uptake:

The complexation of heavy metal ions by a chelating resin is strongly dependent on the pH of the medium<sup>(132, 133)</sup>. In preliminary experiment, the uptake behavior of the investigated metal ions ( $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$ ) on (XXXII) chelating resin at different pH values has been examined by the batch technique, and the results are shown in Table (2), and Figs (9, 10). In general, the uptake of metal ions increases with increasing pH. High uptake at high pH value implies that metal ions interact preferably with unprotonated amine groups by chelating<sup>(134, 135)</sup>. The total uptake values of  $\text{Hg}^{2+}$  by the resin were higher than that of all other metal ions at lower pH. This can be explained by the higher affinity of  $\text{Hg}^{2+}$  towards (N) donor atom which enables its separation from other metal ions at this pH value<sup>(136)</sup>. Table (2) shows that the (XXXII) resin uptakes the metal ions according to the following order:

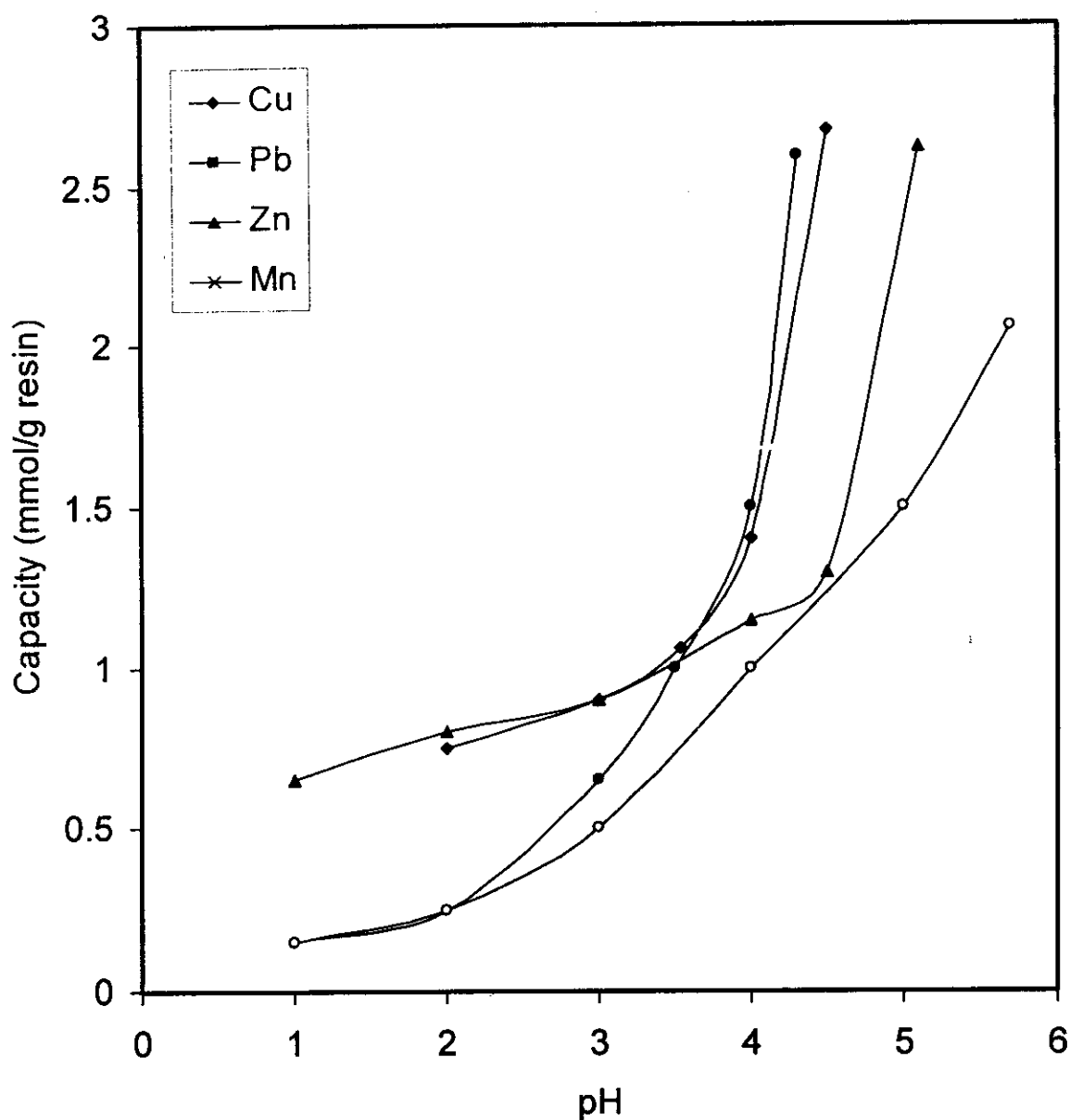




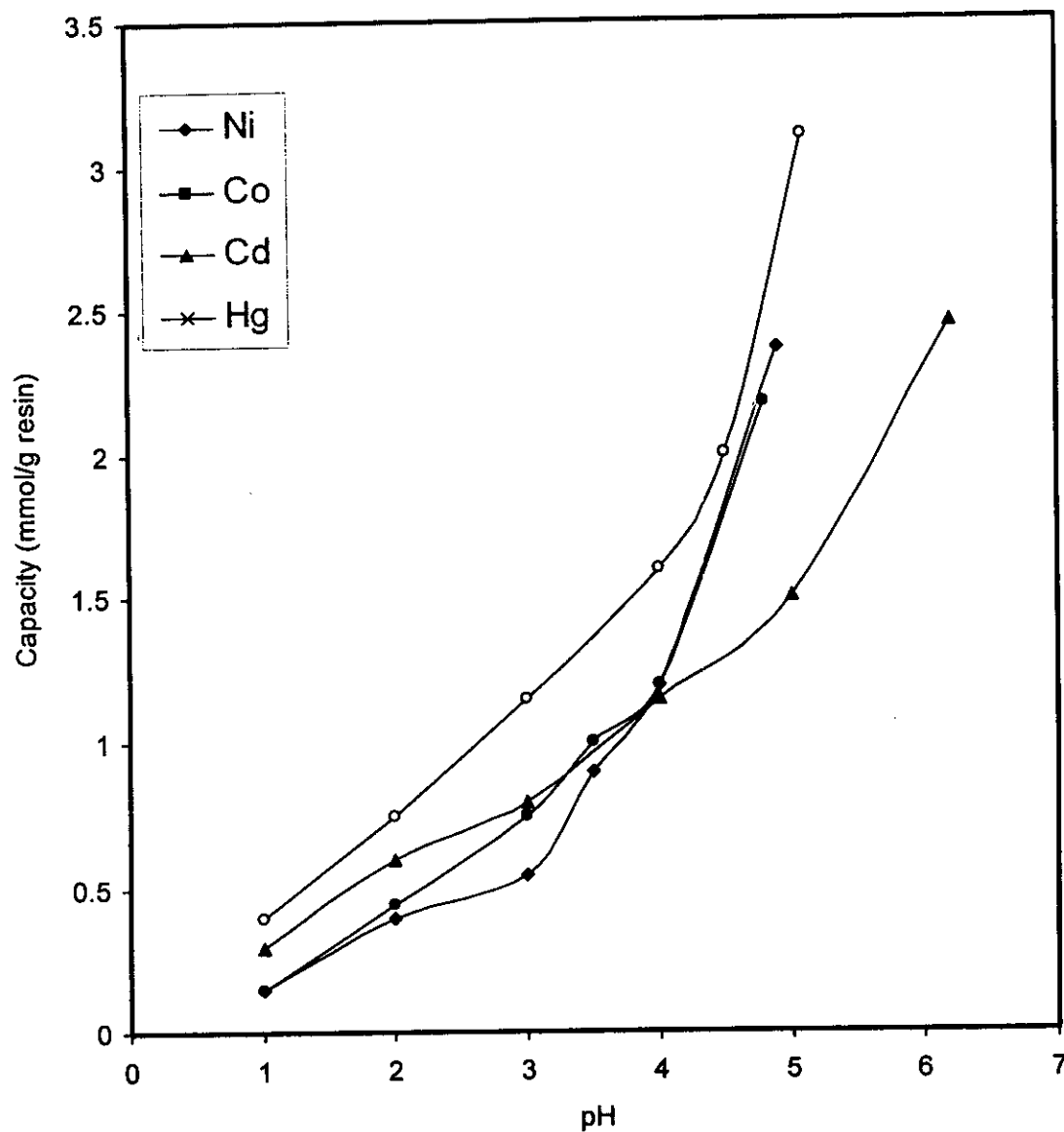
**Table 2.** Effect of pH on the uptake of metal ions for (XXXII) chelating resin\*.

Metal ion	Optimum pH	Capacity (mmol/g.resin)
$\text{Cu}^{2+}$	4.5	2.67
$\text{Pb}^{2+}$	4.3	2.59
$\text{Zn}^{2+}$	5.1	2.62
$\text{Mn}^{2+}$	5.7	2.06
$\text{Ni}^{2+}$	4.9	2.36
$\text{Co}^{2+}$	4.8	2.17
$\text{Cd}^{2+}$	6.2	2.45
$\text{Hg}^{2+}$	5.1	3.10

\* Resin, 0.1g, Metal ion, 0.005 M; volume of solution, 100ml; time of the reaction, 240 min.



**Fig. (9):** Effect of pH on the uptake of the metal ions ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ ) for (XXXII). Resin, 0.1g; metal ion, 0.005 M, volume of solution; 100 ml, shaking time, 240 min.



**Fig. (10):** Effect of pH on the uptake of the metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ) for (XXXII). Resin, 0.1g; metal ion, 0.005 M, volume of solution; 100 ml, shaking time, 240 min.

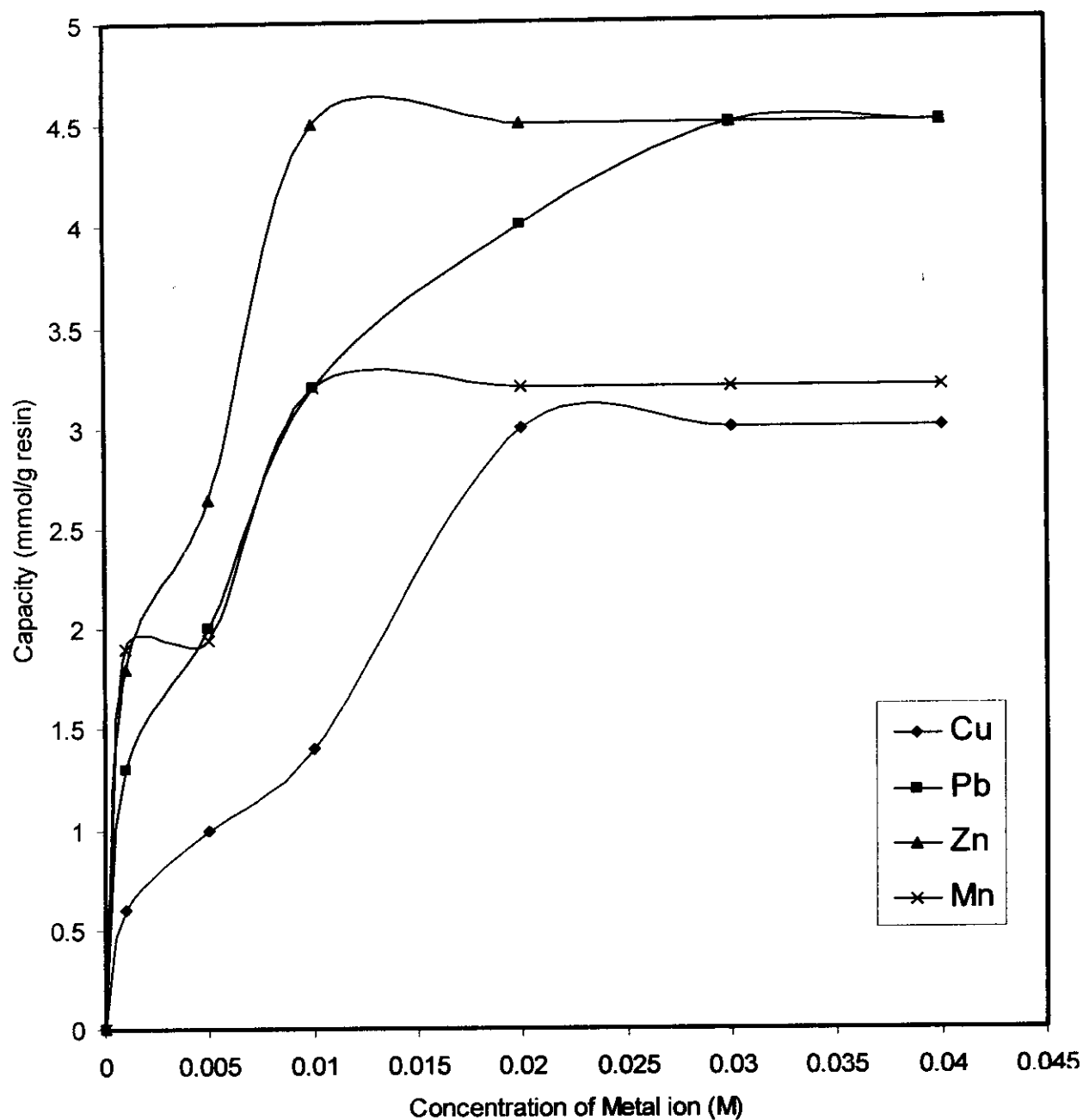
### III.2.1.2 Optimum concentration of metal ions uptake

Uptake isotherms are used to describe the relationship between the amount of uptake and equilibrium concentration of metal ions at constant temperature. The experimental data represented graphically in Figs. (11 & 12 ) shows the uptake isotherms of the studied metal ions at optimum pH and 28 °C. Inspection of Figs (11 & 12) reveals that the uptake increases with increasing equilibrium concentration until reaching the saturation value, after which the concentration no longer affects the uptake of the metal ion. The capacity of the resin is an important factor to determined how much resin is required to quantitatively remove a specific metal ion from the solution. The loading capacity was determined at optimum pH and the results expressed in (mmol /g resin) are presented in Table (3). The uptake of  $\text{Hg}^{2+}$  by the resin was higher than that of all metal ions at all concentration ranges.

**Table 3.** Effect of concentration on the uptake of metal ions for (XXXII) chelating resin\*.

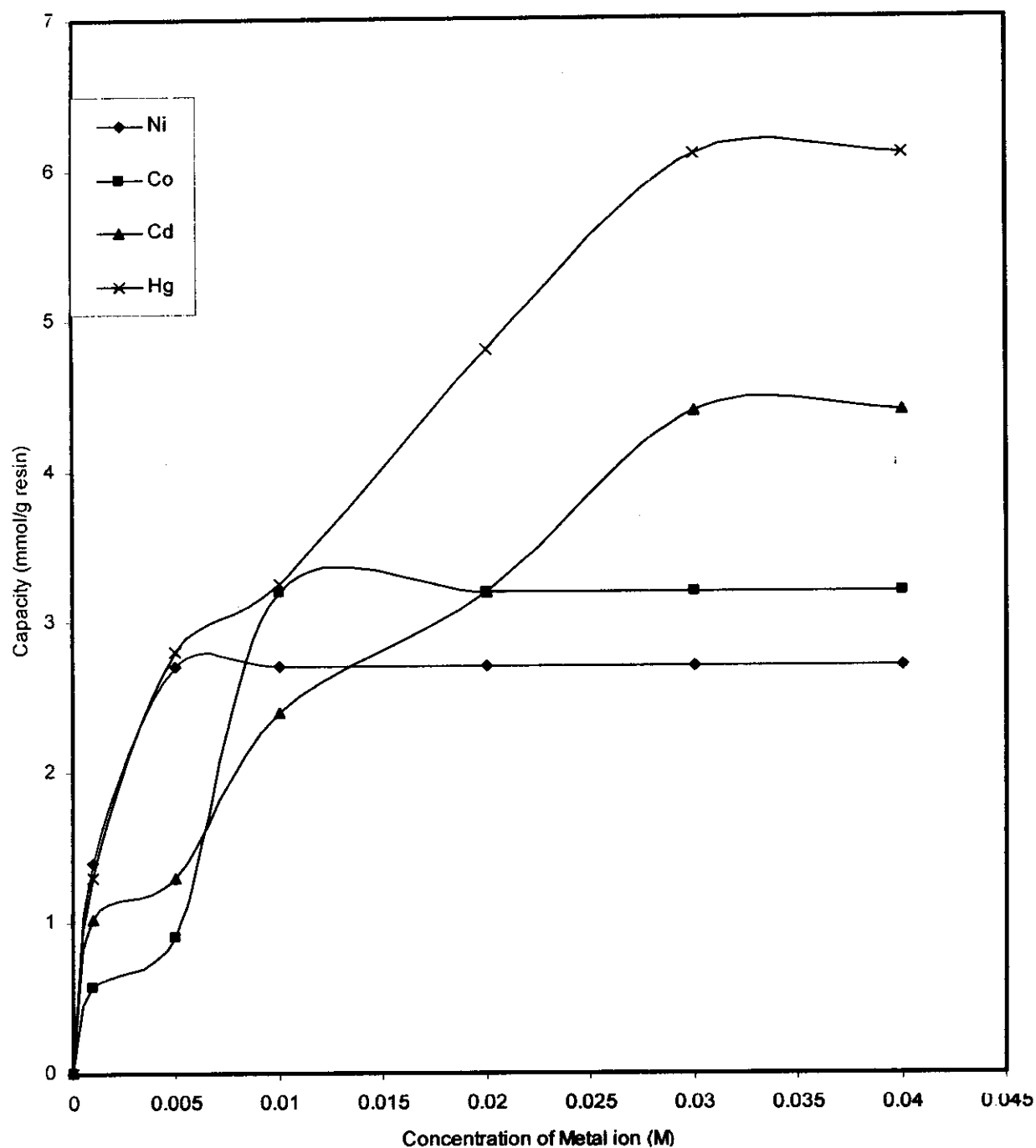
Metal ion	Optimum concentration	Capacity (mmol/g resin)
$\text{Cu}^{2+}$	0.02	3.0
$\text{Pb}^{2+}$	0.03	4.5
$\text{Zn}^{2+}$	0.01	4.5
$\text{Mn}^{2+}$	0.01	3.2
$\text{Ni}^{2+}$	0.005	2.7
$\text{Co}^{2+}$	0.01	3.2
$\text{Cd}^{2+}$	0.03	4.4
$\text{Hg}^{2+}$	0.03	6.1

\* Resin, 0.1g, volume of solution, 100ml; time of the reaction, 240 min.



**Fig. (11):** Effect of concentration on the uptake of the metal ions ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ ) for (XXXII). Resin, 0.1g; volume of solution; 100 ml, shaking time, 240 min.

\*  $\text{Cu}^{2+}$ , pH = 4.5;  $\text{Pb}^{2+}$ , pH = 4.3;  $\text{Zn}^{2+}$ , pH = 5.1;  $\text{Mn}^{2+}$ , pH = 5.7.



**Fig. (12):** Effect of concentration on the uptake of the metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ) for (XXXII). Resin, 0.1g; volume of solution; 100 ml, shaking time, 240 min.

\*  $\text{Ni}^{2+}$ , pH = 4.9;  $\text{Co}^{2+}$ , pH = 4.8;  $\text{Cd}^{2+}$ , pH = 6.6;  $\text{Hg}^{2+}$ , pH = 5.1.

### III.2.1.3 Effect of shaking time and rate constant studies on metal ions uptake

The kinetics of the resin-metal interaction are of considerable importance if the resin is to be used in dynamic system such as a packed column and a flowing stream. If the complexation is not sufficiently rapid for certain metals, then their concentration on a packed column is unlikely owing to the short contact time between the resin and the solution. In those cases a batch extraction with a large excess of resin should be conducted over an extended period. Kinetic experiments were performed at the optimum pH and optimum concentration of metal ions and the results are illustrated in Table (4), and represented graphically in Fig. (13 & 14). As shown in Table (4) and Figs. (13 & 14), equilibrium was attained within 20 min. for  $\text{Mn}^{2+}$ , 30 min. for  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  and 40 min. for  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$ . This suggests that the uptake occurs mainly on the polymer surface. The uptake capacity of chelating resin for different metal ions shows a maximum value of 6.1 mmol/g for  $\text{Hg}^{2+}$  and a minimum value of 3.0 mmol/g for  $\text{Cu}^{2+}$  and the other metal ions occur in between. This difference in uptake capacity may be attributed to the different stability constants of the formed complexes between the different metal ions and the ligand.

Predicting the rate at which uptake takes place for a given system is probably the most important factor. In order to investigate the mechanism of uptake, the rate constant of each metal ion was determined. The pseudo-first order mechanism was applied<sup>(129-131)</sup> according to the following equation:

$$\log \left( \frac{a}{a-x} \right) = \frac{k}{2.303} \times t \quad (2)$$

which is the integrated rate law for a Pseudo-first order reaction. Where  $x$  ( $\text{mg g}^{-1}$ ) is the amount of metal uptake at time  $t$ ,  $x$  ( $\text{mg g}^{-1}$ ) is the amount uptake at equilibrium and  $k$  is the equilibrium rate constant of Pseudo-first uptake, ( $\text{min}^{-1}$ ).

The plots of  $\ln(a-x)$  with versus time for selected metal ions " $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ " under investigation on resin (XXXII) are shown in Figs. (15 & 16). The straight line plots Figs. (15 & 16) of  $\ln(a-x)$  versus time for different metal ions indicate the validity of Eq. (3) and the process follow first order rate kinetics for all metals. The rate constant ( $k$ ) values were calculated from the slopes of these plots and are given in Table (5).

The results obtained show that the rate constant depends on the each of resin and metal types where for resins (XXXII), the rate decreases according to:  $\text{Pb} > \text{Cu} > \text{Mn} > \text{Co} > \text{Ni} > \text{Zn} > \text{Cd} > \text{Hg}$ .

While for resins (XXXIII), the rate follows the order:  $\text{Pb} > \text{Zn} \cong \text{Cu} > \text{Co} > \text{Ni} \cong \text{Cd} > \text{Hg} > \text{Mn}$  and for resin (XXXIV) follows the order:  $\text{Cd} > \text{Cu} > \text{Pb} > \text{Zn} > \text{Mn} > \text{Co} > \text{Ni} \cong \text{Hg}$ .

By investigating the effect of ionic radius on the uptake rate constant of metal ions it was observed that the ionic radius does not play a high significant role in determining the rate of the reaction.

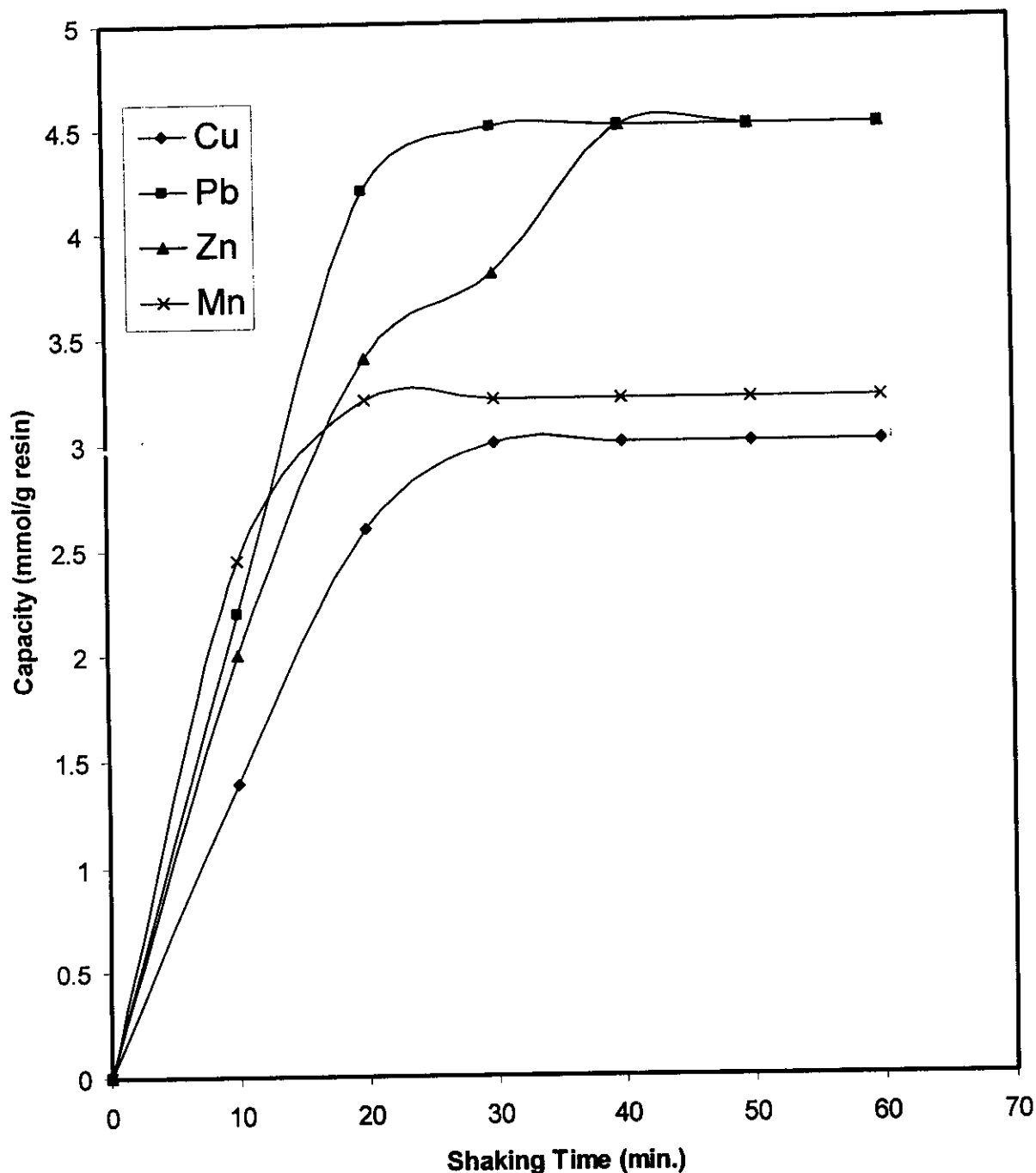
For example, for the resins (XXXII and XXXIII) the highest uptake rate constant was observed for  $\text{Pb}^{2+}$ , which possess the largest ionic radius ( $1.20 \text{ \AA}$ ) in investigated metal ions. This refers to the effect of resins composition upon the selectivity towards the metal ion present in solution.



**Table 4.** Effect of shaking time on the uptake of metal ions for (XXXII) chelating resin\*.

Time (min.)	Capacity (mmol Metal ion/g resin)							
	$\text{Cu}^{2+}$	$\text{Pb}^{2+}$	$\text{Zn}^{2+}$	$\text{Mn}^{2+}$	$\text{Ni}^{2+}$	$\text{Co}^{2+}$	$\text{Cd}^{2+}$	$\text{Hg}^{2+}$
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	1.4	2.2	2.0	2.45	2.6	1.2	0.6	2.53
20	2.6	4.2	3.4	3.2	3.0	2.6	2.8	3.1
30	3.0	4.5	3.8	3.2	3.53	3.2	3.2	4.3
40	3.0	4.5	4.5	3.2	3.53	3.2	4.4	6.1
50	3.0	4.5	4.5	3.2	3.53	3.2	4.4	6.1
60	3.0	4.5	4.5	3.2	3.53	3.2	4.4	6.1

\* Resin, 0.1g; volume of solution, 100 ml.



**Fig. (13):** Effect of shaking time on the uptake of the metal ions ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ ) for (XXXII). Resin, 0.1g; volume of solution; 100 ml.

\*  $\text{Cu}^{2+}$ , pH = 4.5, M = 0.02;  $\text{Pb}^{2+}$ , pH = 4.3, M = 0.03;  $\text{Zn}^{2+}$ , pH = 5.1, M = 0.01;  $\text{Mn}^{2+}$ , pH = 5.7, M = 0.01.

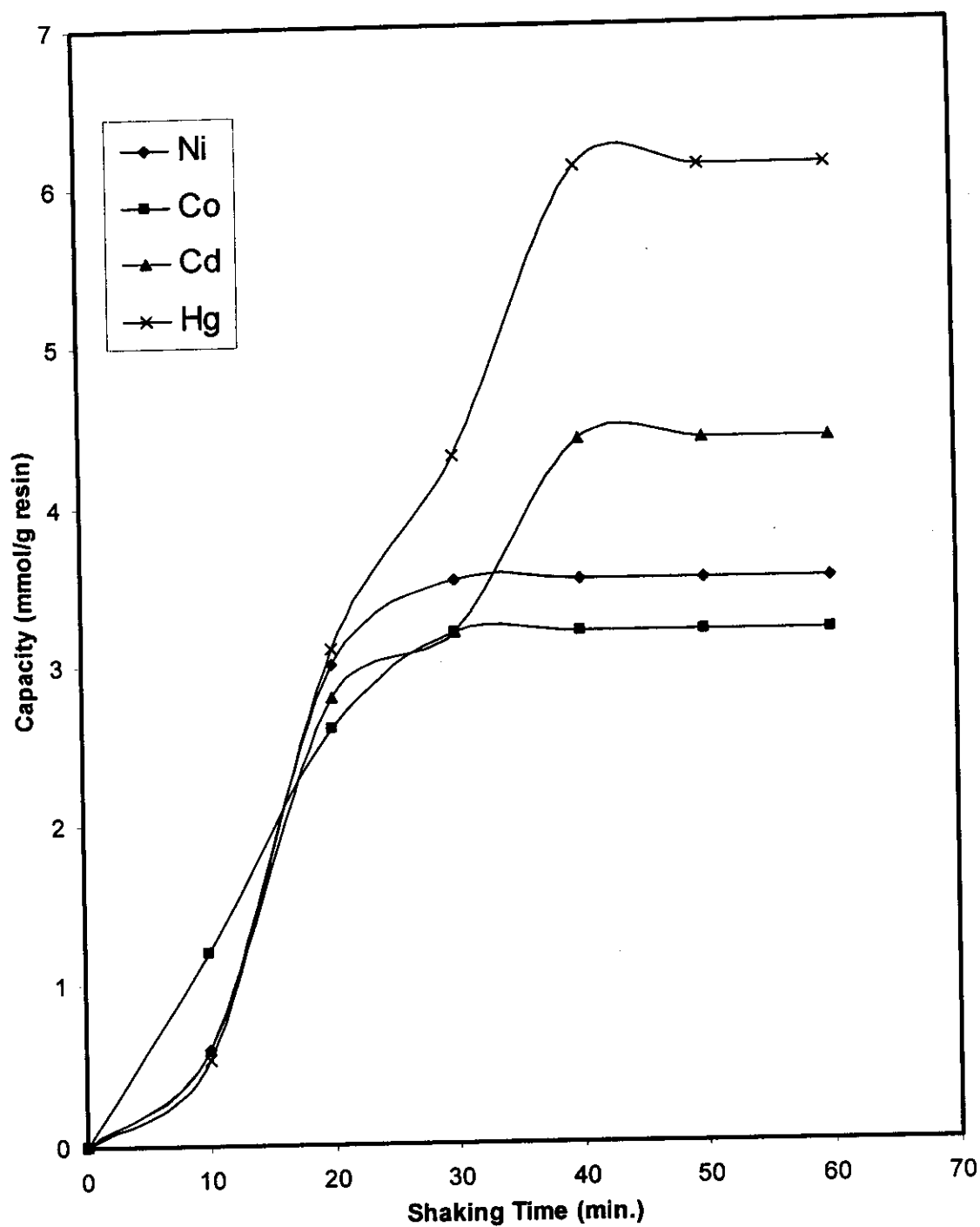


Fig. (14): Effect of shaking time on the uptake of the metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ) for (XXXII). Resin, 0.1g; volume of solution; 100 ml.

\*  $\text{Ni}^{2+}$ , pH = 4.9, M = 0.05;  $\text{Co}^{2+}$ , pH = 4.8, M = 0.01;  $\text{Cd}^{2+}$ , pH = 6.2, M = 0.03;  $\text{Hg}^{2+}$ , pH = 5.1, M = 0.03.

**Table 5.** Relation between rate constant and capacity of resins.

Metal ions	(XXXII)		(XXXIII)		(XXXIV)	
	$k \times 10^2$ ( $\text{min}^{-1}$ )	Capacity ( $\text{mmol/g resin}$ )	$k \times 10^2$ ( $\text{min}^{-1}$ )	Capacity ( $\text{mmol/g resin}$ )	$k \times 10^2$ ( $\text{min}^{-1}$ )	Capacity ( $\text{mmol/g resin}$ )
$\text{Cu}^{2+}$	14.34	3.00	7.37	4.40	12.85	4.600
$\text{Pb}^{2+}$	22.64	4.50	21.06	4.50	11.42	5.600
$\text{Zn}^{2+}$	4.82	4.50	7.81	4.70	9.64	5.500
$\text{Mn}^{2+}$	13.15	3.20	2.45	2.97	7.73	3.050
$\text{Ni}^{2+}$	9.01	3.53	5.33	3.00	3.53	2.700
$\text{Co}^{2+}$	11.58	3.20	6.09	3.00	5.07	3.800
$\text{Cd}^{2+}$	3.86	4.40	5.33	3.70	13.23	3.615
$\text{Hg}^{2+}$	2.51	6.10	3.47	6.00	3.53	6.300

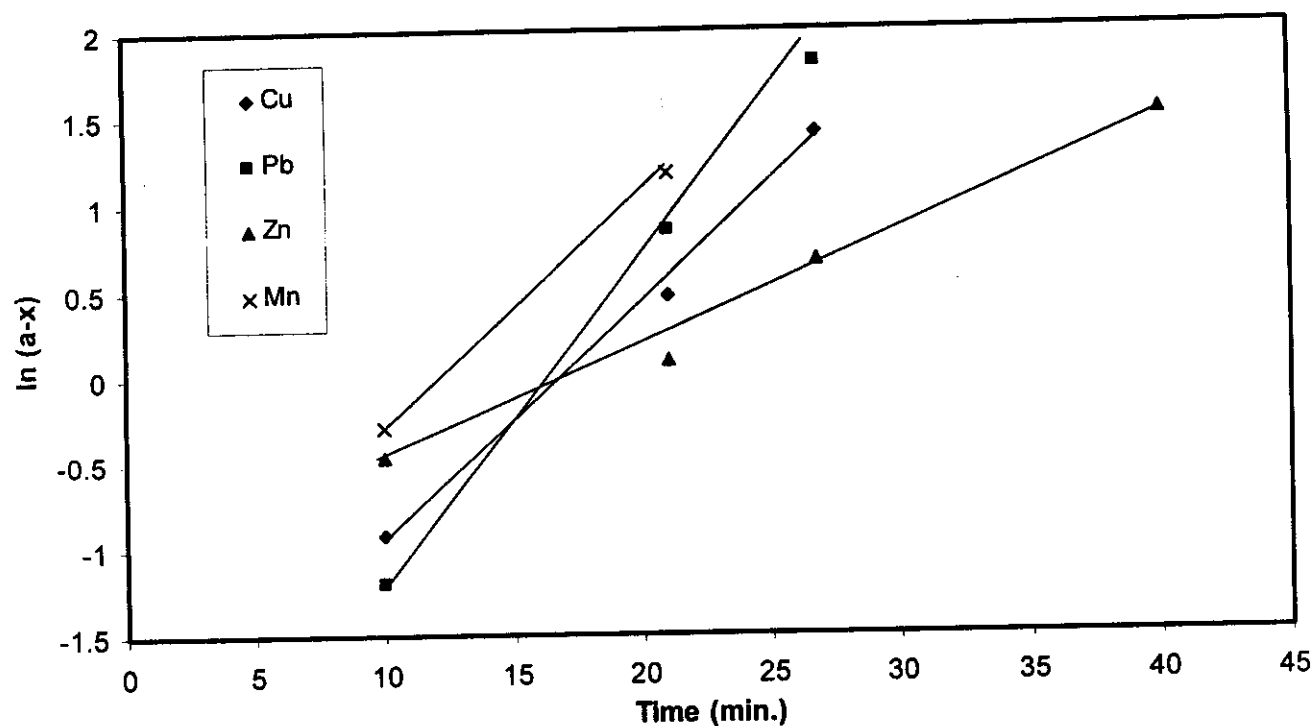


Fig. (15): Effect of rate constant on the uptake of the metal ions ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ ) for (XXXII) resin.

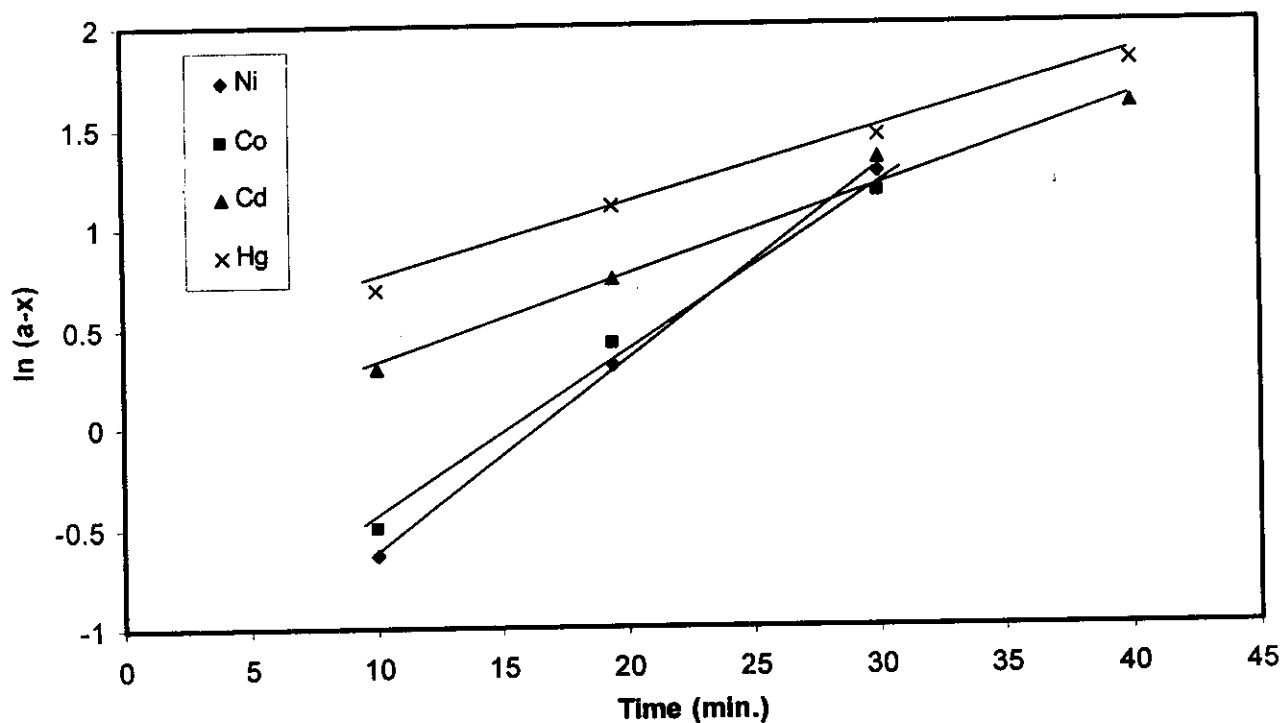
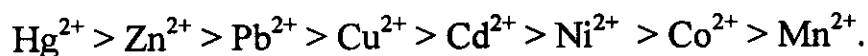


Fig. (16): Effect of rate constant on the uptake of the metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ) for (XXXII) resin.

### **III.2.2 Selective uptake of metal ions ( $\text{Hg}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Co}^{2+}$ and $\text{Ni}^{2+}$ ) by chelating resin containing o.amino phenol ligand (XXXIII):**

#### **III.2.2.1 Optimum pH of metal ions uptake:**

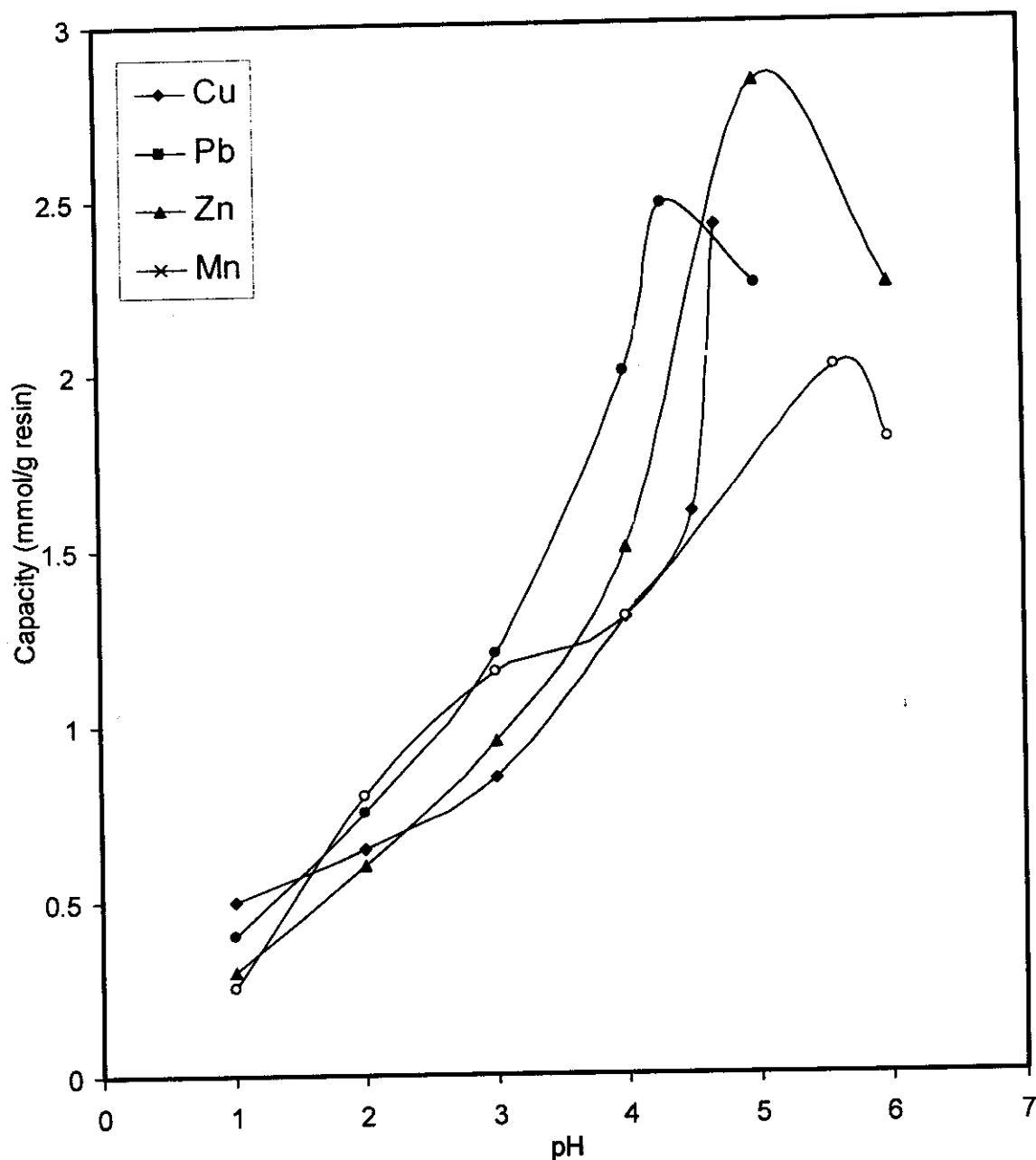
The complexation of heavy metal ions by a chelating resin is strongly dependent on the pH of the medium<sup>(132, 133)</sup>. In preliminary experiment, the uptake behavior of the investigated metal ions ( $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$ ) on (XXXIII) chelating resin at different pH values has been examined by the batch technique, and the results are shown in Table (6), and Figs (17 & 18). In general, the uptake of metal ions increases with increasing pH. High uptake at high pH value implies that metal ions interact preferably with unprotonated amine groups by chelating<sup>(134, 135)</sup>. The total uptake values of  $\text{Hg}^{2+}$  by the resin were higher than that of all other metal ions at lower pH. This can be explained by the higher affinity of  $\text{Hg}^{2+}$  towards (N) donor atom which enables its separation from other metal ions at this pH value<sup>(136)</sup>. Table (6) shows that the (XXXIII) resin uptakes the metal ions according to the following order:



**Table 6.** Effect of pH on the uptake of metal ions for (XXXIII) chelating resin\*.

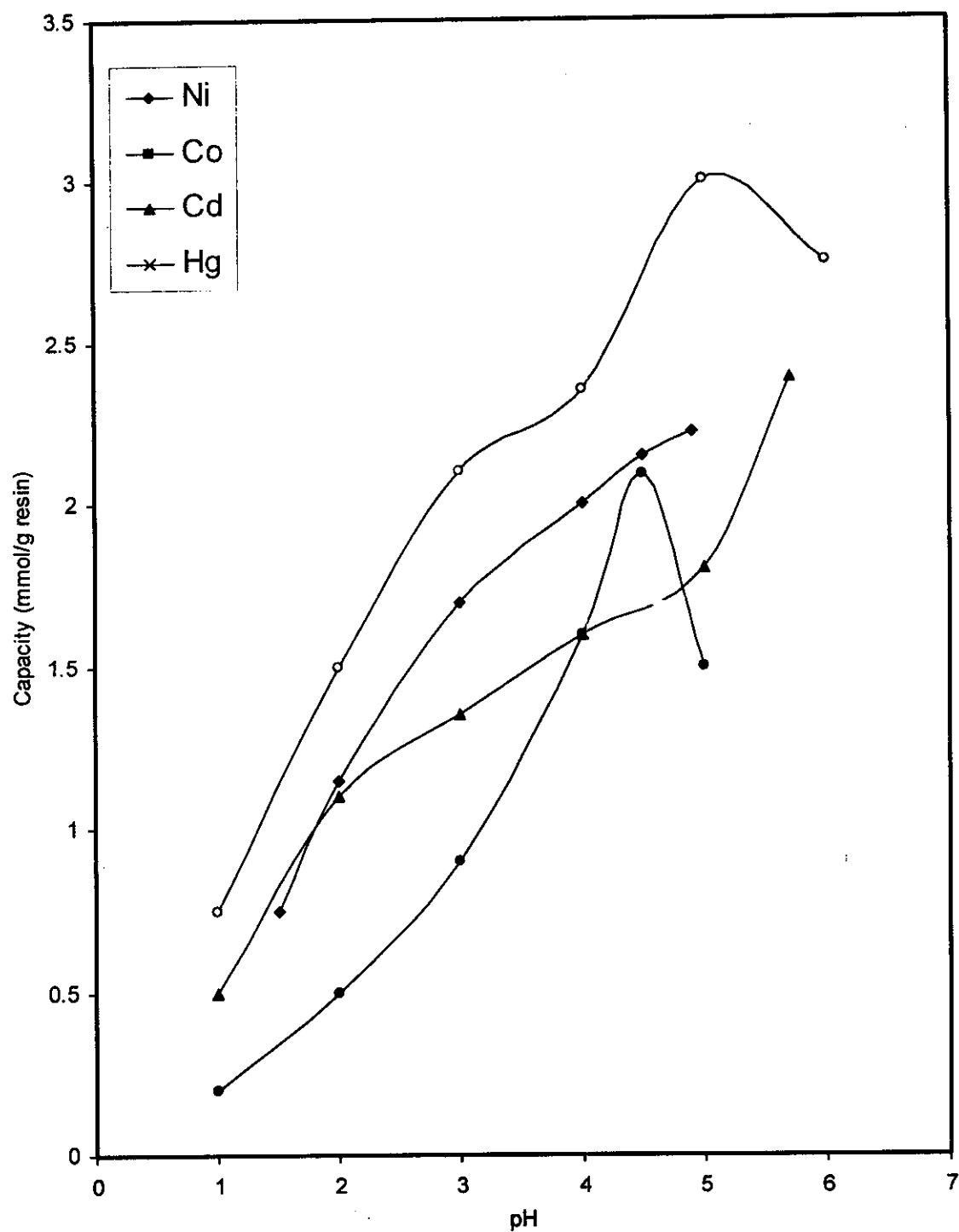
Metal ion	Optimum pH	Capacity (mmol/g.resin)
$\text{Cu}^{2+}$	4.7	2.42
$\text{Pb}^{2+}$	4.3	2.48
$\text{Zn}^{2+}$	5.0	2.83
$\text{Mn}^{2+}$	5.6	2.01
$\text{Ni}^{2+}$	4.9	2.22
$\text{Co}^{2+}$	4.5	2.09
$\text{Cd}^{2+}$	5.7	2.39
$\text{Hg}^{2+}$	5.0	3.00

\* Resin, 0.1g, Metal ion, 0.005 M; volume of solution, 100ml; time of the reaction, 240 min.



**Fig. (17):** Effect of pH on the uptake of the metal ions ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ ) for (XXXIII). Resin, 0.1g; metal ion, 0.005 M, volume of solution; 100 ml, shaking time, 240 min.





**Fig. (18):** Effect of pH on the uptake of the metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ) for (XXXIII). Resin, 0.1g; metal ion, 0.005 M, volume of solution; 100 ml, shaking time, 240 min.

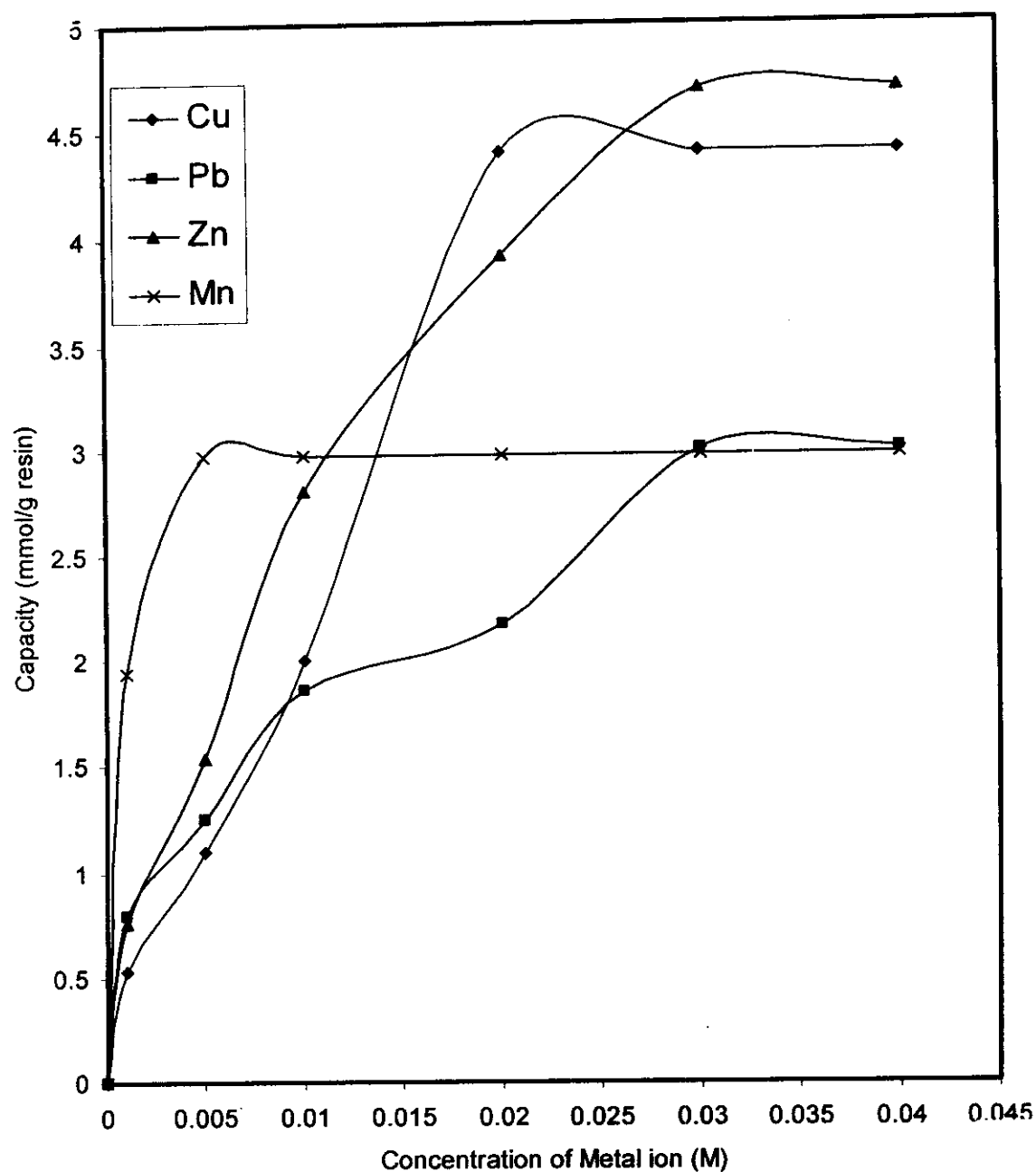
### III.2.2.2 Optimum concentration of metal ions uptake

Uptake isotherms are used to describe the relationship between the amount of uptake and equilibrium concentration of metal ions at constant temperature. The experimental data represented graphically in Figs. (19 & 20) shows the uptake isotherms of the studied metal ions at optimum pH and 28 °C. Inspection of Figs (19 & 20) reveals that the uptake increases with increasing equilibrium concentration until reaching the saturation value, after which the concentration no longer affects the uptake of the metal ion. The capacity of the resin is an important factor to determine how much resin is required to quantitatively remove a specific metal ion from the solution. The loading capacity was determined at optimum pH and the results expressed in (mmol /g resin) are presented in Table (7). The uptake of  $\text{Hg}^{2+}$  by the resin was higher than that of all metal ions at all concentration ranges.

**Table 7.** Effect of concentration on the uptake of metal ions for (XXXIII) chelating resin\*.

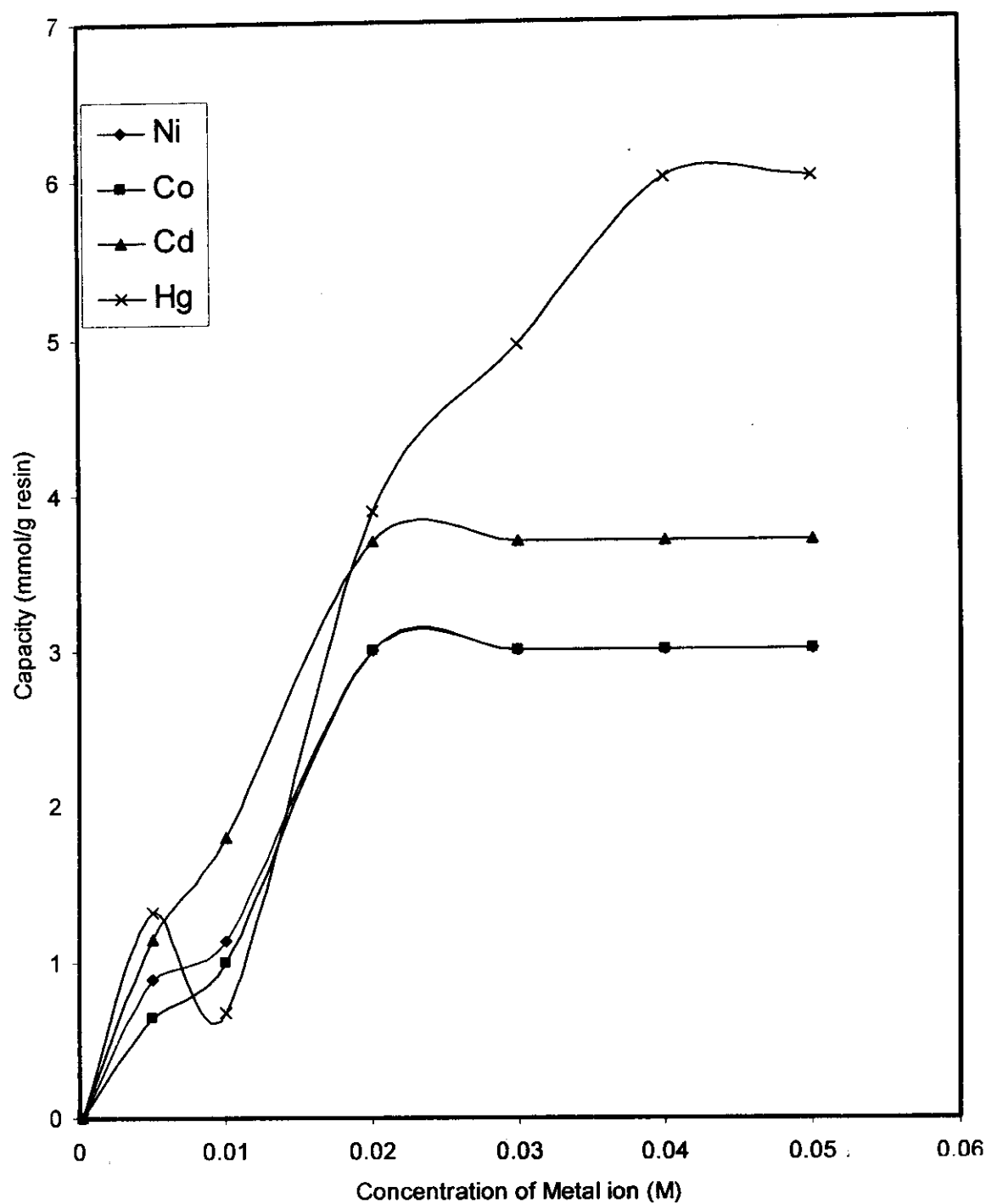
Metal ion	Optimum concentration (M)	Capacity (mmol/g resin)
$\text{Cu}^{2+}$	0.02	4.4
$\text{Pb}^{2+}$	0.03	3.0
$\text{Zn}^{2+}$	0.03	4.7
$\text{Mn}^{2+}$	0.005	2.97
$\text{Ni}^{2+}$	0.01	3.0
$\text{Co}^{2+}$	0.01	3.0
$\text{Cd}^{2+}$	0.01	3.7
$\text{Hg}^{2+}$	0.03	6.0

\* Resin, 0.1g, volume of solution, 100ml; time of the reaction, 240 min.



**Fig. (19):** Effect of concentration on the uptake of the metal ions ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ ) for (XXXIII). Resin, 0.1g; volume of solution; 100 ml, shaking time, 240 min.

\*  $\text{Cu}^{2+}$ , pH = 4.7;  $\text{Pb}^{2+}$ , pH = 4.3;  $\text{Zn}^{2+}$ , pH = 5.0;  $\text{Mn}^{2+}$ , pH = 5.6.



**Fig. (20):** Effect of concentration on the uptake of the metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ) for (XXXIII). Resin, 0.1g; volume of solution; 100 ml, shaking time, 240 min.

\*  $\text{Ni}^{2+}$ , pH = 4.9;  $\text{Co}^{2+}$ , pH = 4.5;  $\text{Cd}^{2+}$ , pH = 5.7;  $\text{Hg}^{2+}$ , pH = 5.0.

### III.2.2.3 Effect of shaking time and rate constant studies on metal ions uptake

The kinetics of the resin-metal interaction are of considerable importance if the resin is to be used in dynamic system such as a packed column and a flowing stream. If the complexation is not sufficiently rapid for certain metals, then their concentration on a packed column is unlikely owing to the short contact time between the resin and the solution. In those cases a batch extraction with a large excess of resin should be conducted over an extended period. Kinetic experiments were performed at the optimum pH and optimum concentration of metal ions and the results are illustrated in Table (8), and represented graphically in Fig. (21 & 22). As shown in Table (8) and Figs. (21 & 22), equilibrium was attained within 30 min. for  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$ , 40 min. for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ . This suggests that the uptake occurs mainly on the polymer surface. The uptake capacity of chelating resin for different metal ions shows a maximum value of 6.0 mmol/g for  $\text{Hg}^{2+}$  and a minimum value of 2.97 mmol/g for  $\text{Mn}^{2+}$  and the other metal ions occur in between. This difference in uptake capacity may be attributed to the different stability constants of the formed complexes between the different metal ions and the ligand.

Predicting the rate at which uptake takes place for a given system is probably the most important factor. In order to investigate the mechanism of uptake, the rate constant of each metal ion was determined. The pseudo-first order mechanism was applied<sup>(129-131)</sup> as mentioned before.

The plots of  $\ln(a-x)$  with versus time for selected metal ions " $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ " under investigation on resin (XXXIII) are shown in Figs. (23 & 24). The straight line plots

Figs. (23 & 24) of  $\ln(a-x)$  versus time for different metal ions indicate the validity of Eq. (3) and the process follow first order rate kinetics for all metals. The rate constant (k) values were calculated from the slopes of these plots and are given in Table (5).

**Table 8.** Effect of shaking time on the uptake of metal ions for (XXXIII) chelating resin\*.

Time (min.)	Capacity (mmol Metal ion/g resin)							
	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Mn <sup>2+</sup>	Ni <sup>2+</sup>	Co <sup>2+</sup>	Cd <sup>2+</sup>	Hg <sup>2+</sup>
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	2.0	2.2	1.2	0.4	1.1	1.8	1.0	1.8
20	2.9	4.2	2.65	1.2	2.0	2.2	1.4	2.6
30	4.0	4.5	3.8	2.97	2.6	3.0	3.0	4.0
40	4.4	4.5	4.7	2.97	3.0	3.0	3.7	6.0
50	4.4	4.5	4.7	2.97	3.0	3.0	3.7	6.0
60	4.4	4.5	4.7	2.97	3.0	3.0	3.7	6.0

\* Resin, 0.1g; volume of solution, 100 ml.

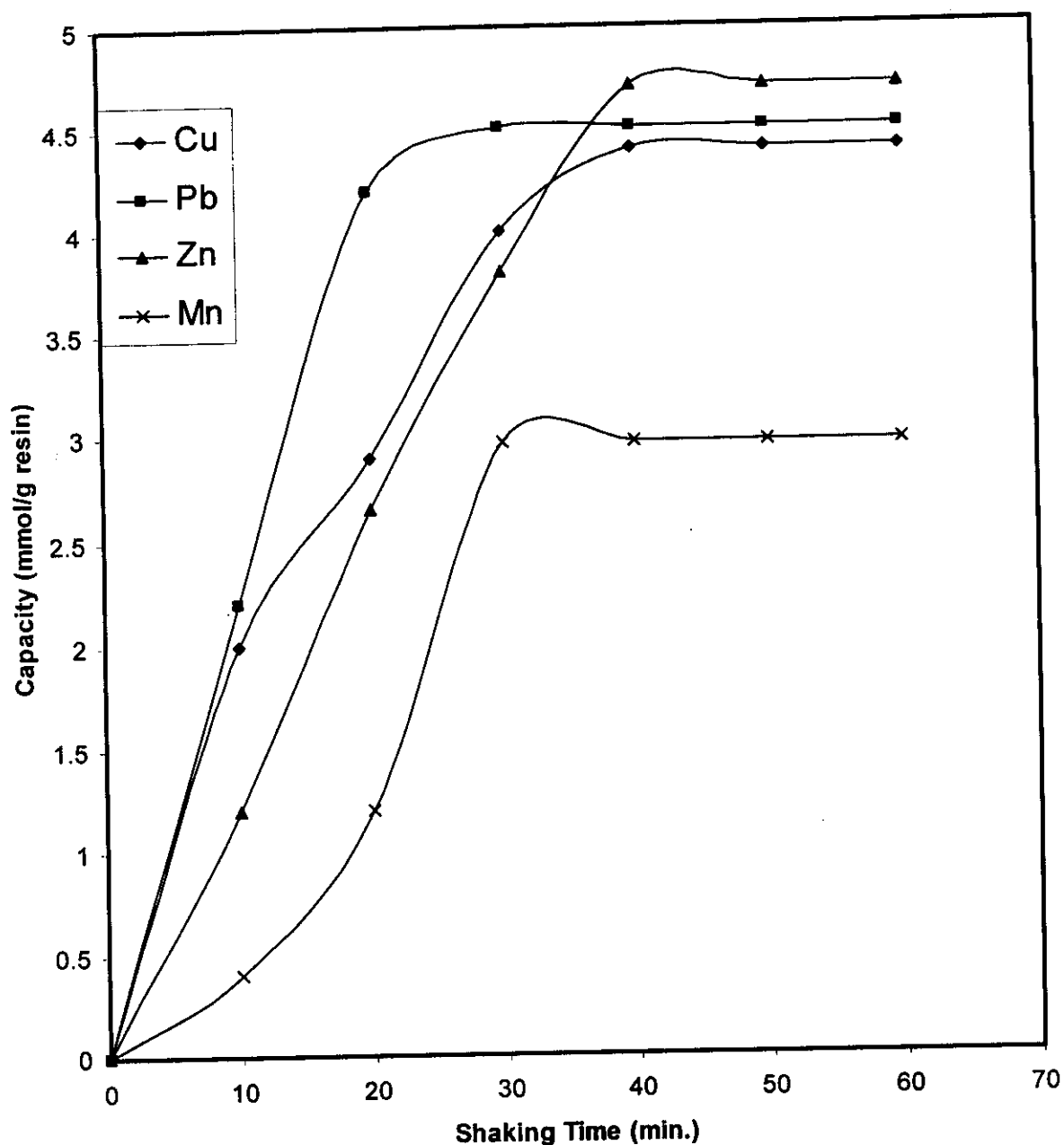
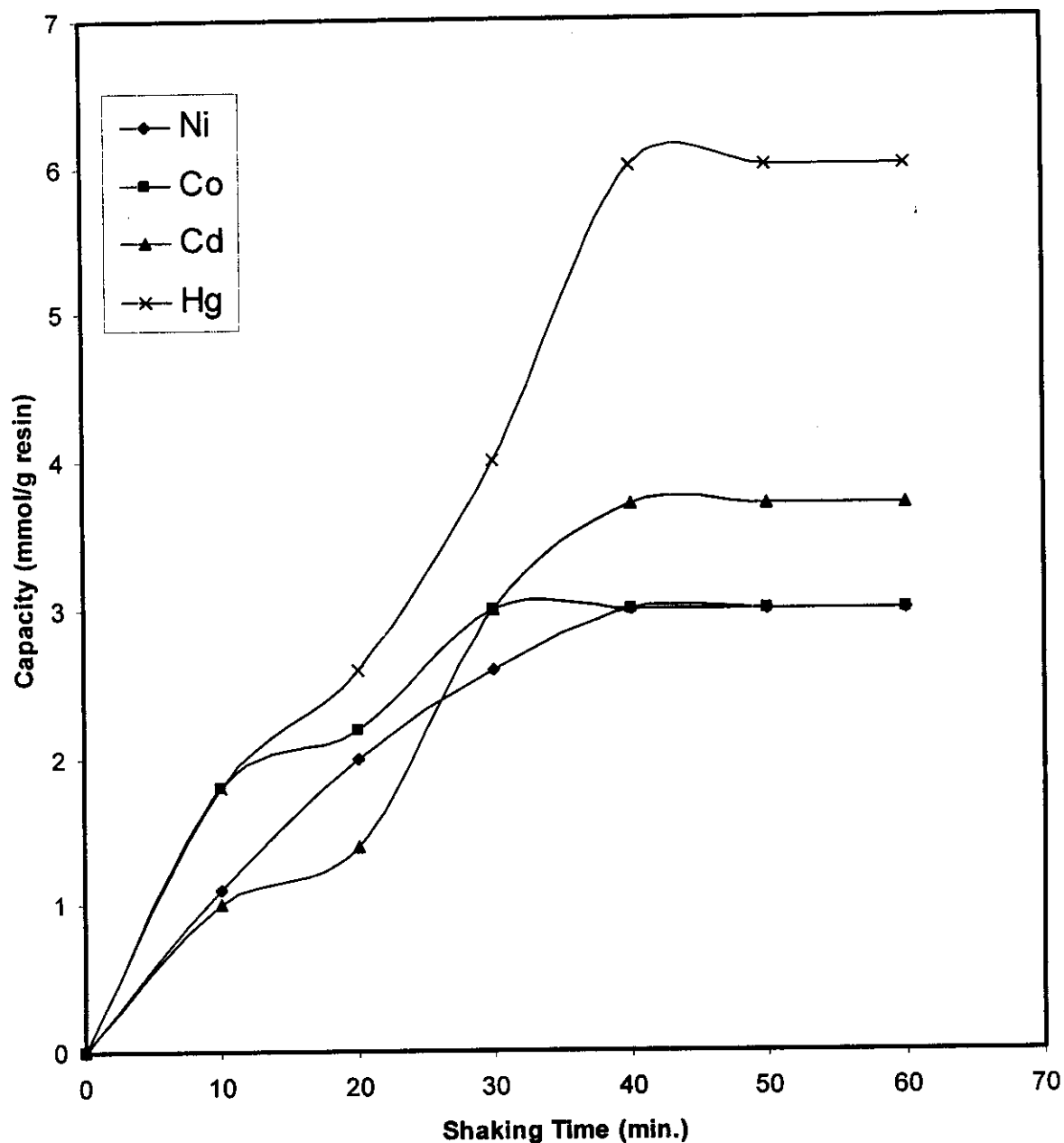


Fig. (21): Effect of shaking time on the uptake of the metal ions ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ ) for (XXXIII). Resin, 0.1g; volume of solution; 100 ml.

\*  $\text{Cu}^{2+}$ , pH = 4.7, M = 0.02;  $\text{Pb}^{2+}$ , pH = 4.3, M = 0.03;  $\text{Zn}^{2+}$ , pH = 4.0, M = 0.03;  
 $\text{Mn}^{2+}$ , pH = 5.6, M = 0.005.





**Fig. (22):** Effect of shaking time on the uptake of the metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ) for (XXXIII). Resin, 0.1g; volume of solution; 100 ml.

\*  $\text{Ni}^{2+}$ , pH = 4.9, M = 0.01;  $\text{Co}^{2+}$ , pH = 4.53, M = 0.01;  $\text{Cd}^{2+}$ , pH = 5.7, M = 0.01;  $\text{Hg}^{2+}$ , pH = 5.0, M = 0.03.

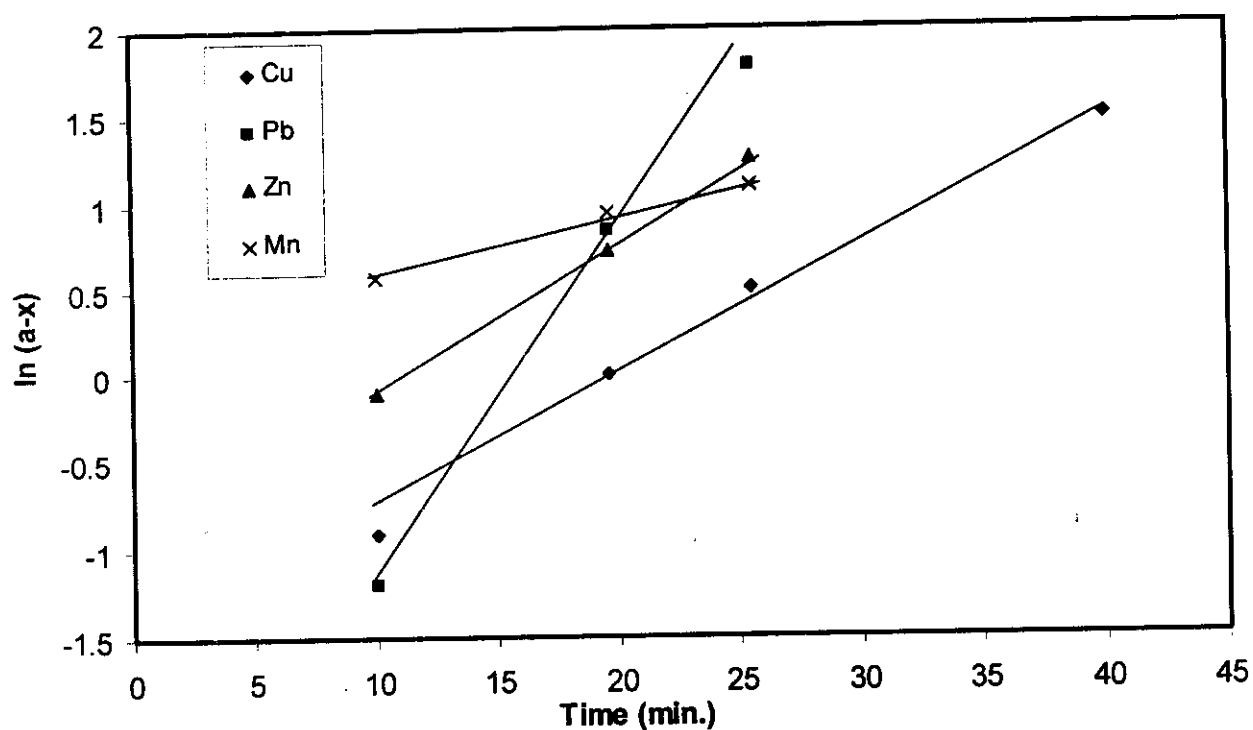


Fig. (23): Effect of rate constant on the uptake of the metal ions ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ ) for (XXXIII) resin.

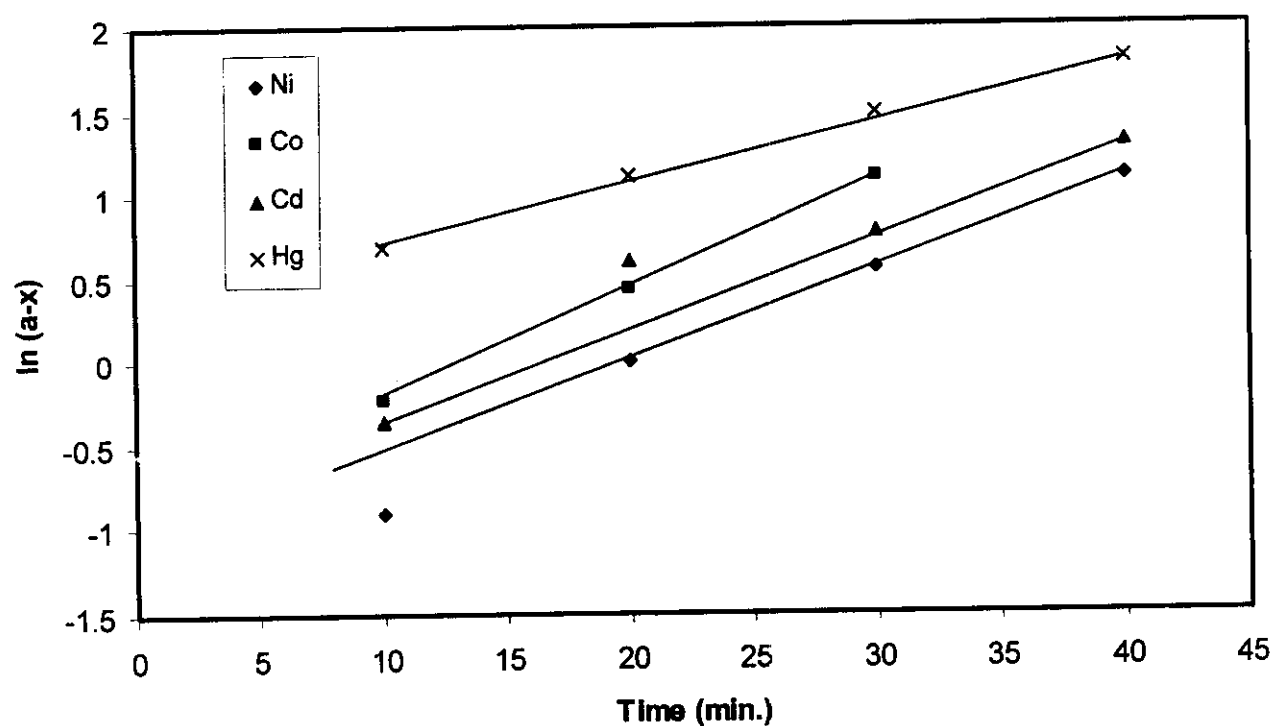
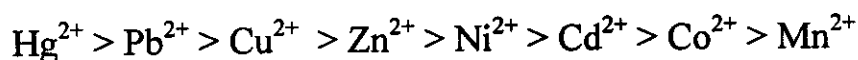


Fig. (24): Effect of rate constant on the uptake of the metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ) for (XXXIII) resin.

### **III.2.3 Selective uptake of metal ions ( $\text{Hg}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Co}^{2+}$ and $\text{Ni}^{2+}$ ) by chelating resin containing 4-amino antipyrine ligand (XXXIV):**

#### **III.2.3.1 Optimum pH of metal ions uptake:**

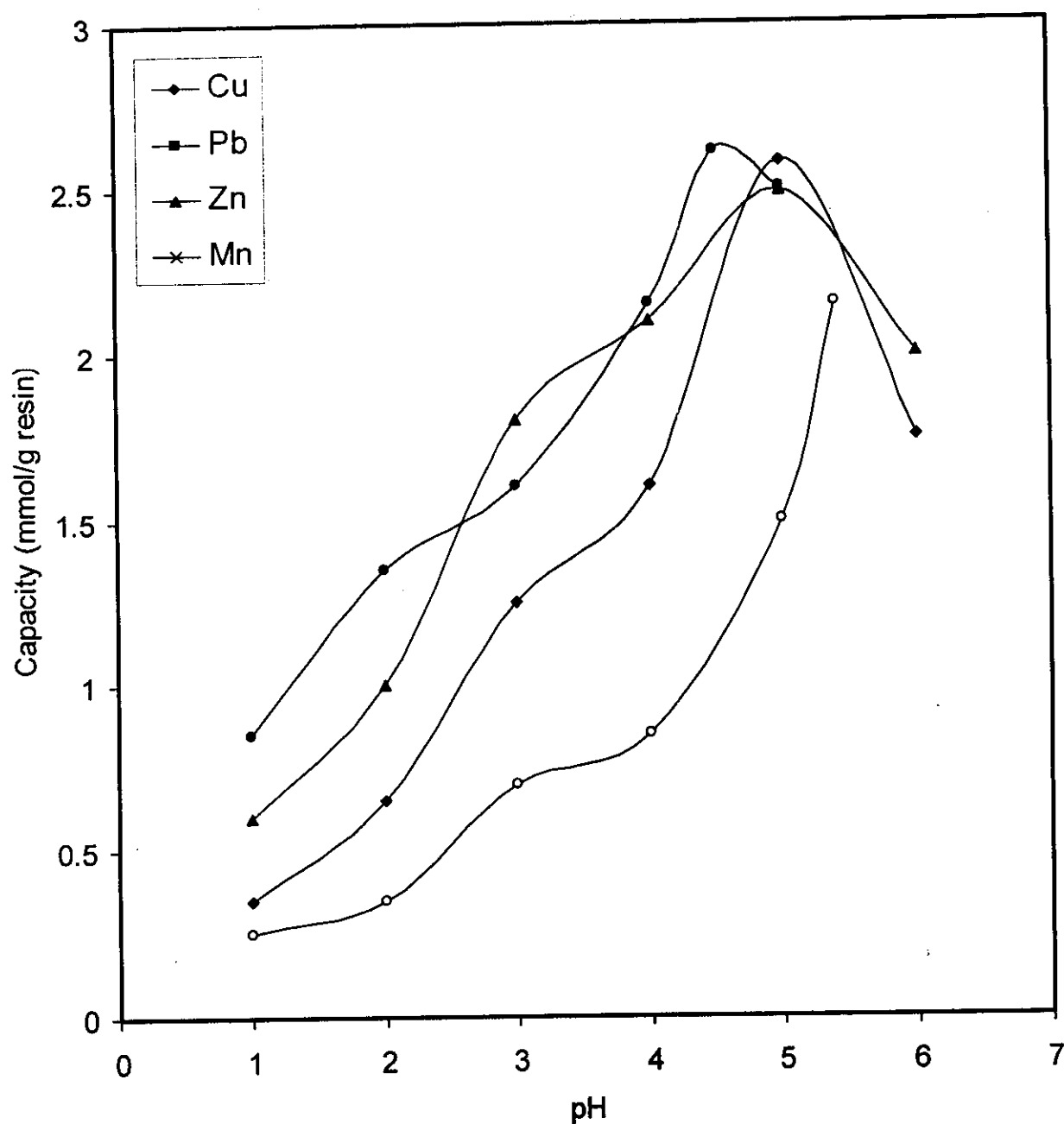
The complexation of heavy metal ions by a chelating resin is strongly dependent on the pH of the medium<sup>(132, 133)</sup>. In preliminary experiment, the uptake behavior of the investigated metal ions ( $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$ ) on (XXXIV) chelating resin at different pH values has been examined by the batch technique, and the results are shown in Table (9), and Figs (25 & 26). In general, the uptake of metal ions increases with increasing pH. High uptake at high pH value implies that metal ions interact preferably with unprotonated amine groups by chelating<sup>(134, 135)</sup>. The total uptake values of  $\text{Hg}^{2+}$  by the resin were higher than that of all other metal ions at lower pH. This can be explained by the higher affinity of  $\text{Hg}^{2+}$  towards (N) donor atom which enables its separation from other metal ions at this pH value<sup>(136)</sup>. Table (9) shows that the (XXXIV) resin uptakes the metal ions according to the following order:



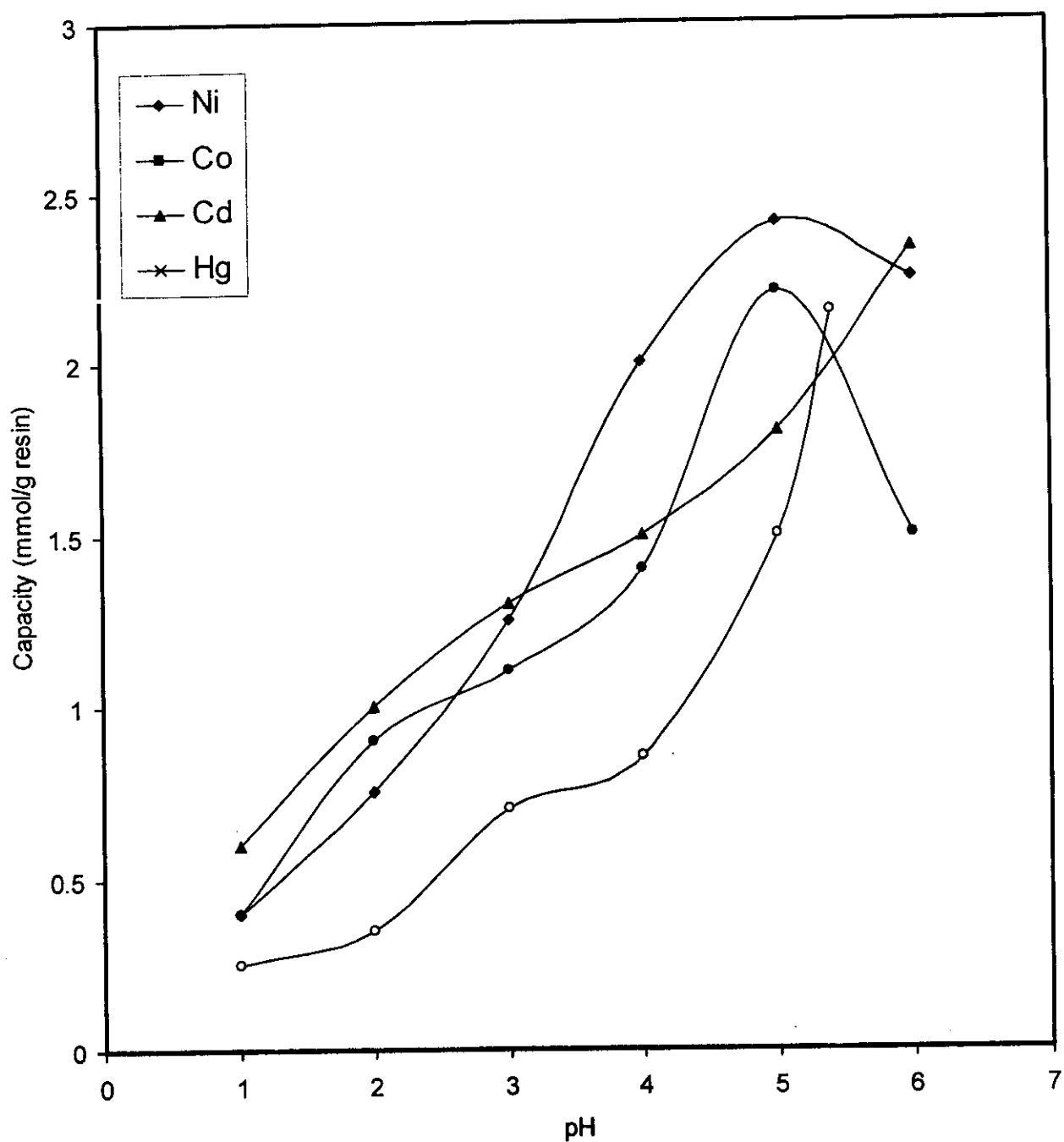
**Table 9.** Effect of pH on the uptake of metal ions for (XXXIV) chelating resin\*.

Metal ion	Optimum pH	Capacity (mmol/g.resin)
$\text{Cu}^{2+}$	5.0	2.58
$\text{Pb}^{2+}$	4.5	2.61
$\text{Zn}^{2+}$	5.0	2.49
$\text{Mn}^{2+}$	5.4	2.15
$\text{Ni}^{2+}$	5.0	2.41
$\text{Co}^{2+}$	5.0	2.21
$\text{Cd}^{2+}$	6.0	2.34
$\text{Hg}^{2+}$	4.9	2.90

\* Resin, 0.1g, Metal ion, 0.005 M; volume of solution, 100ml; time of the reaction, 240 min.



**Fig. (25):** Effect of pH on the uptake of the metal ions ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ ) for (XXXIV). Resin, 0.1g; metal ion, 0.005 M, volume of solution; 100 ml, shaking time, 240 min.



**Fig. (26):** Effect of pH on the uptake of the metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ) for (XXXIV). Resin, 0.1g; metal ion, 0.005 M, volume of solution; 100 ml, shaking time, 240 min.

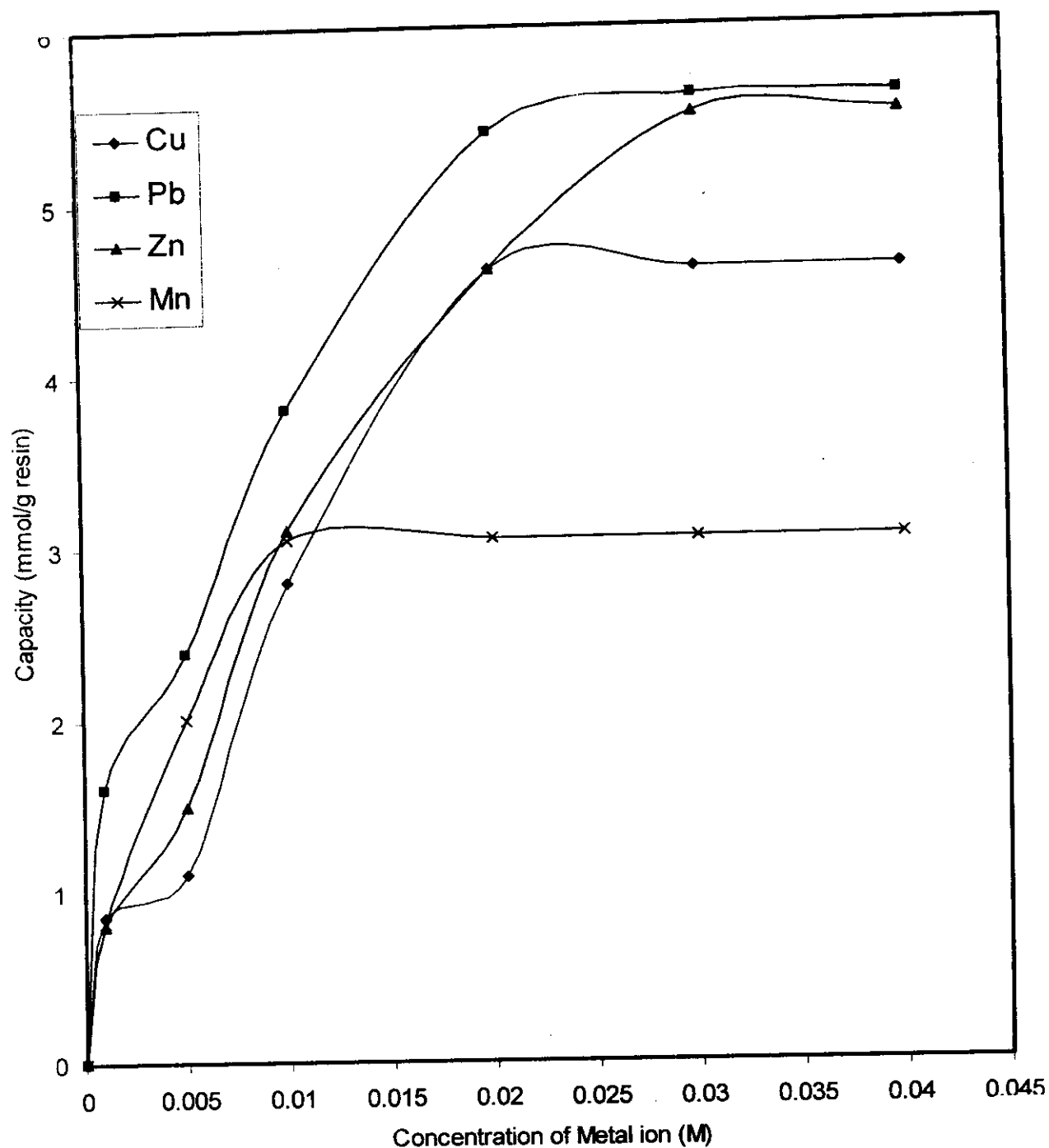
### III.2.3.2 Optimum concentration of metal ions uptake

Uptake isotherms are used to describe the relationship between the amount of uptake and equilibrium concentration of metal ions at constant temperature. The experimental data represented graphically in Figs. (27 & 28) shows the uptake isotherms of the studied metal ions at optimum pH and 28 °C. Inspection of Figs (27 & 28) reveals that the uptake increases with increasing equilibrium concentration until reaching the saturation value, after which the concentration no longer affects the uptake of the metal ion. The capacity of the resin is an important factor to determine how much resin is required to quantitatively remove a specific metal ion from the solution. The loading capacity was determined at optimum pH and the results expressed in (mmol /g resin) are presented in Table (10). The uptake of  $\text{Hg}^{2+}$  by the resin was higher than that of all metal ions at all concentration ranges.

**Table 10.** Effect of concentration on the uptake of metal ions for (XXXIV) chelating resin\*.

Metal ion	Optimum concentration (M)	Capacity (mmol/g resin)
$\text{Cu}^{2+}$	0.02	4.6
$\text{Pb}^{2+}$	0.03	5.6
$\text{Zn}^{2+}$	0.03	5.5
$\text{Mn}^{2+}$	0.01	3.05
$\text{Ni}^{2+}$	0.02	3.53
$\text{Co}^{2+}$	0.02	3.8
$\text{Cd}^{2+}$	0.01	3.615
$\text{Hg}^{2+}$	0.03	6.3

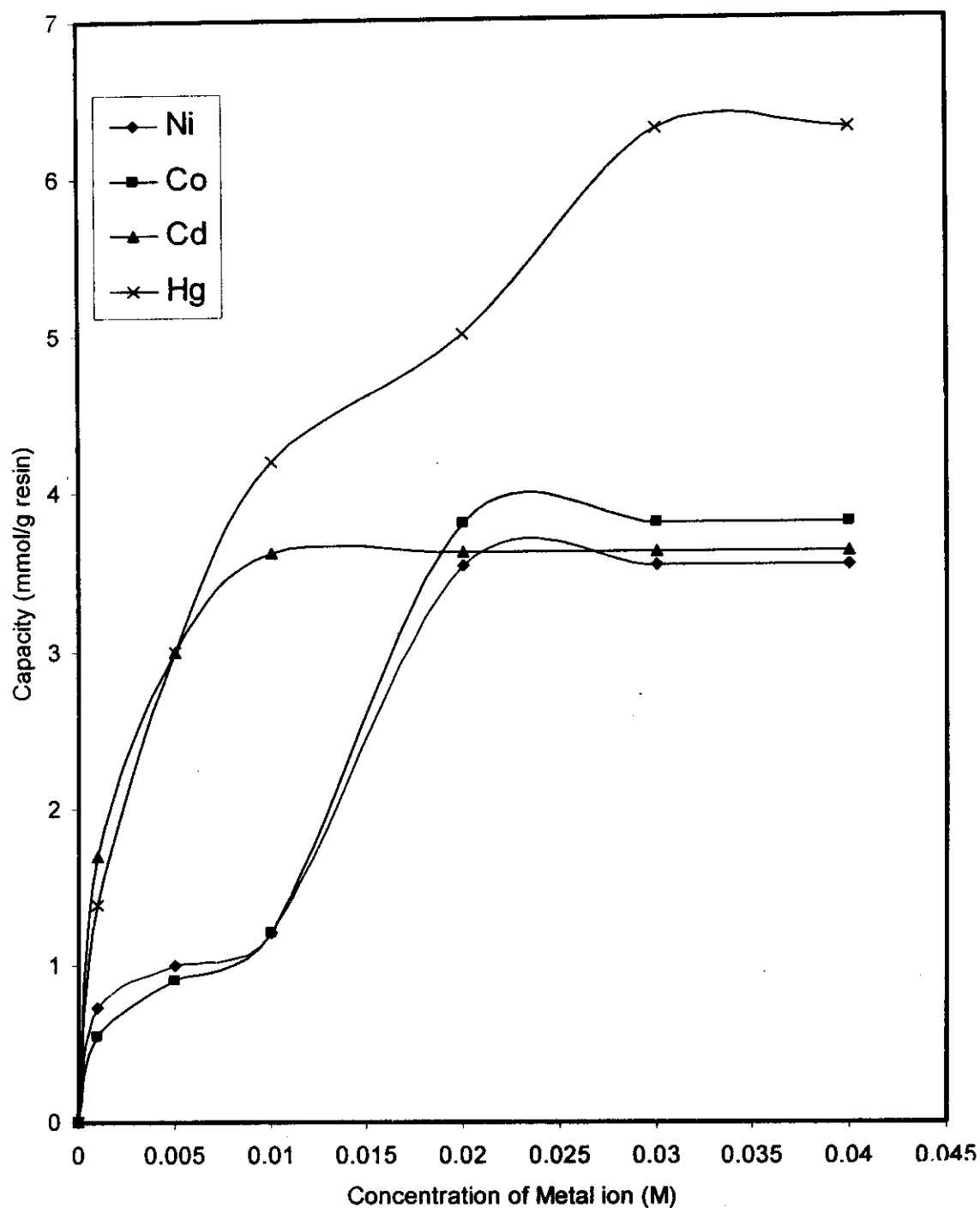
\* Resin, 0.1g, volume of solution, 100ml; time of the reaction, 240 min.



**Fig. (27):** Effect of concentration on the uptake of the metal ions ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ ) for (XXXIV). Resin, 0.1g; volume of solution; 100 ml, shaking time, 240 min.

\*  $\text{Cu}^{2+}$ , pH = 5.0;  $\text{Pb}^{2+}$ , pH = 4.5;  $\text{Zn}^{2+}$ , pH = 5.0;  $\text{Mn}^{2+}$ , pH = 5.4.





**Fig. (28):** Effect of concentration on the uptake of the metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ) for (XXXIV). Resin, 0.1g; volume of solution; 100 ml, shaking time, 240 min.

\*  $\text{Ni}^{2+}$ , pH = 5.0;  $\text{Co}^{2+}$ , pH = 5.0;  $\text{Cd}^{2+}$ , pH = 6.0;  $\text{Hg}^{2+}$ , pH = 4.9.

### III.2.3.3 Effect of shaking time and rate constant studies on metal ions uptake

The kinetics of the resin-metal interaction are of considerable importance if the resin is to be used in dynamic system such as a packed column and a flowing stream. If the complexation is not sufficiently rapid for certain metals, then their concentration on a packed column is unlikely owing to the short contact time between the resin and the solution. In those cases a batch extraction with a large excess of resin should be conducted over an extended period. Kinetic experiments were performed at the optimum pH and optimum concentration of metal ions and the results are illustrated in Table (11), and represented graphically in Fig. (29 & 30). As shown in Table (11) and Figs. (29 & 30), equilibrium was attained within 20 min. for  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$ , 30 min. for  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$  and 40 min for  $\text{Hg}^{2+}$ . This suggests that the uptake occurs mainly on the polymer surface. The uptake capacity of chelating resin for different metal ions shows a maximum value of 6.3 mmol/g for  $\text{Hg}^{2+}$  and a minimum value of 2.7 mmol/g for  $\text{Ni}^{2+}$  and the other metal ions occur in between. This difference in uptake capacity may be attributed to the different stability constants of the formed complexes between the different metal ions and the ligand.

In order to investigate the mechanism of uptake, the rate constant of each metal ion was determined. The pseudo-first order mechanism was applied<sup>(129-131)</sup> as mentioned before.

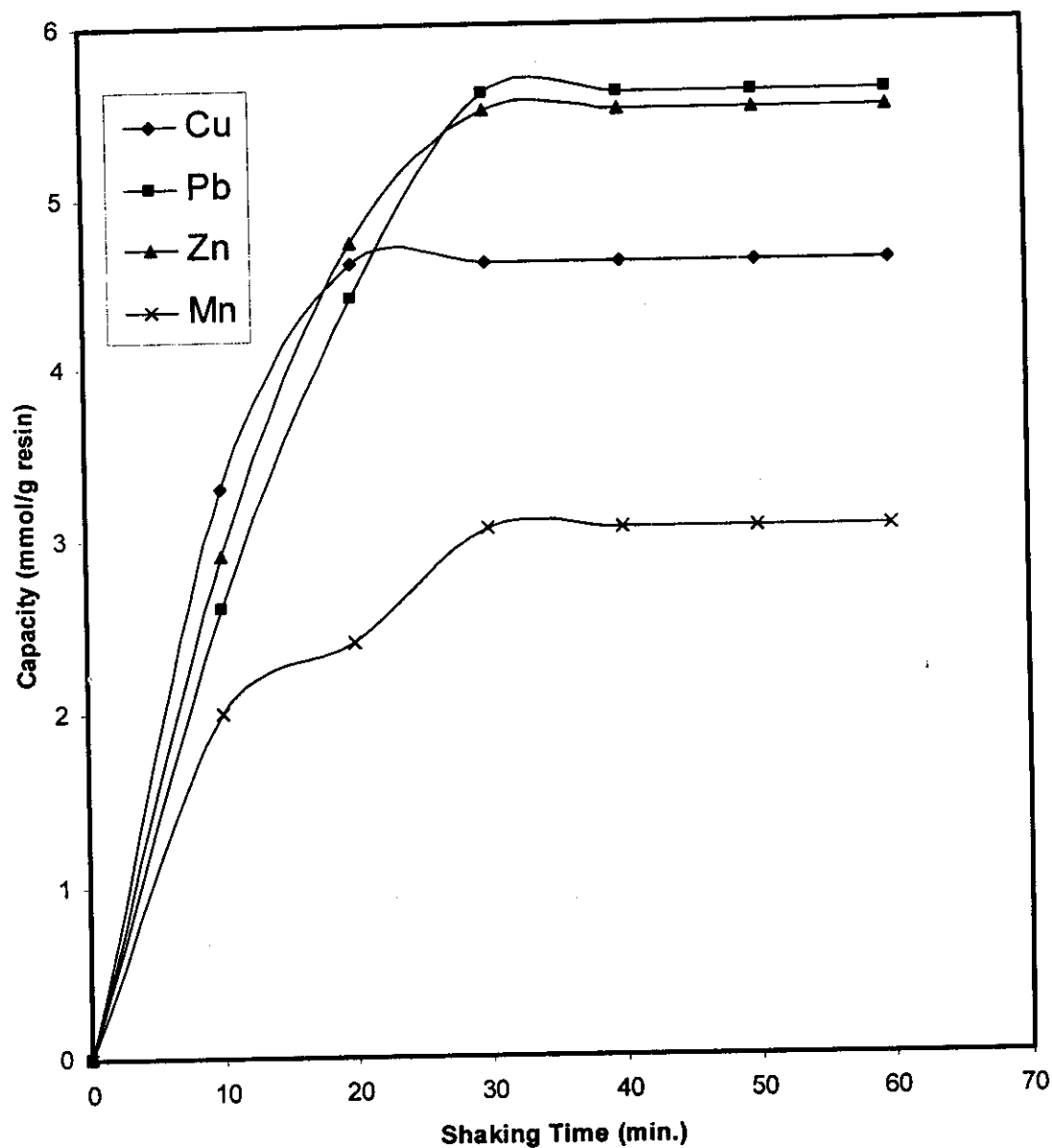
The plots of  $\ln(a-x)$  with versus time for selected metal ions " $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ " under investigation on resin (XXXIV) are shown in Figs. (31 & 32). The straight line plots Figs. (31 & 32) of  $\ln(a-x)$  versus time for different metal ions indicate

the validity of Eq. (3) and the process follow first order rate kinetics for all metals. The rate constant ( $k$ ) values were calculated from the slopes of these plots and are given in Table (5).

**Table 11.** Effect of shaking time on the uptake of metal ions for (XXXIV) chelating resin\*.

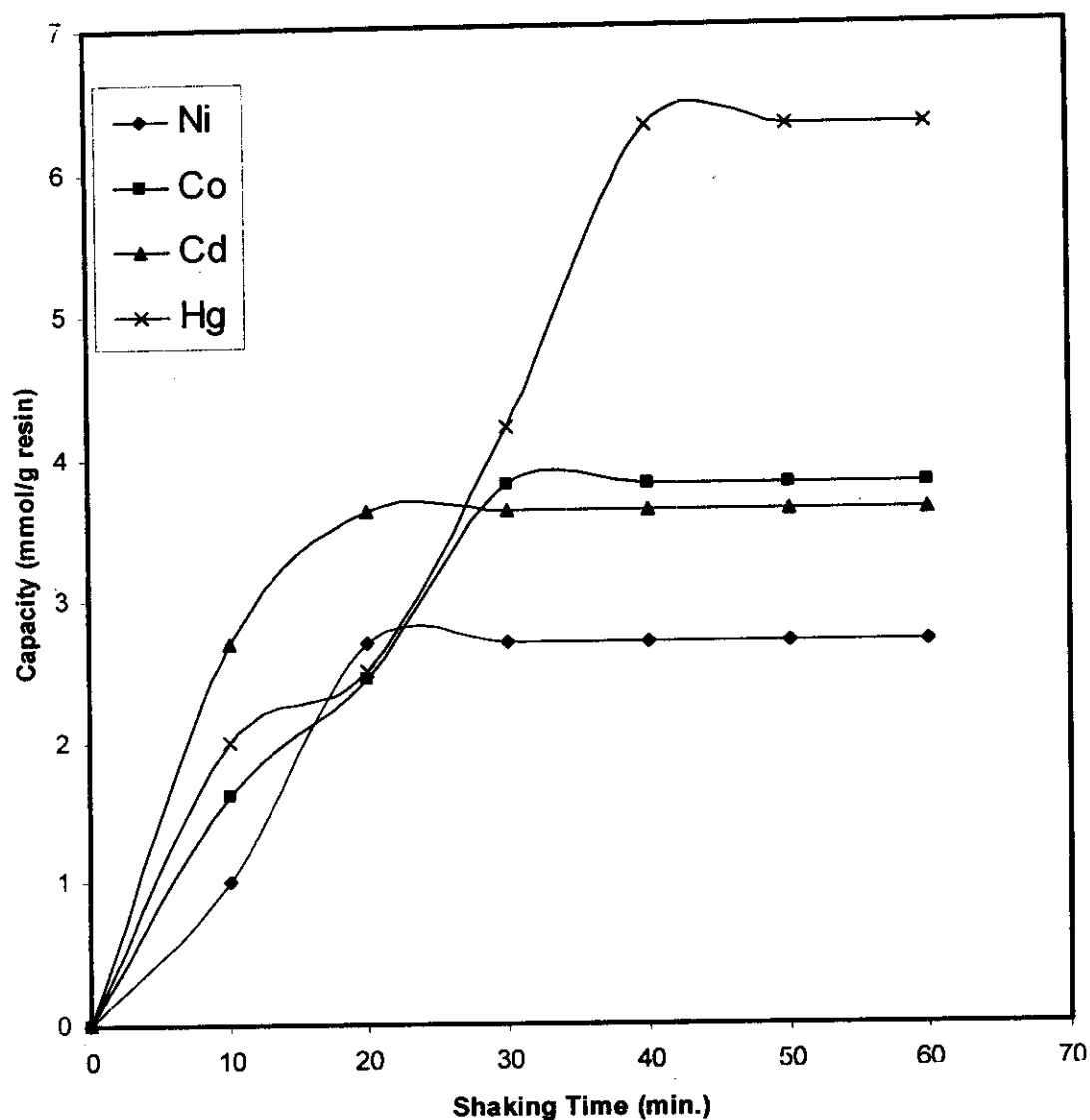
Time (min.)	Capacity (mmol. Metal ion/g resin)							
	$\text{Cu}^{2+}$	$\text{Pb}^{2+}$	$\text{Zn}^{2+}$	$\text{Mn}^{2+}$	$\text{Ni}^{2+}$	$\text{Co}^{2+}$	$\text{Cd}^{2+}$	$\text{Hg}^{2+}$
0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	3.3	2.6	2.9	2.0	1.0	1.62	2.7	2.0
20	4.6	4.4	4.73	2.4	2.7	2.45	3.615	2.5
30	4.6	5.6	5.5	3.05	2.7	3.8	3.615	4.2
40	4.6	5.6	5.5	3.05	2.7	3.8	3.615	6.3
50	4.6	5.6	5.5	3.05	2.7	3.8	3.615	6.3
60	4.6	5.6	5.5	3.05	2.7	3.8	3.615	6.3

\* Resin, 0.1g; volume of solution, 100 ml.



**Fig. (29):** Effect of shaking time on the uptake of the metal ions ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ ) for (XXXIV). Resin, 0.1g; volume of solution; 100 ml.

\*  $\text{Cu}^{2+}$ , pH = 5.0, M = 0.02;  $\text{Pb}^{2+}$ , pH = 4.5, M = 0.03;  $\text{Zn}^{2+}$ , pH = 5.0, M = 0.03;  
 $\text{Mn}^{2+}$ , pH = 5.4, M = 0.01.



**Fig. (30):** Effect of shaking time on the uptake of the metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ) for (XXXIV). Resin, 0.1g; volume of solution; 100 ml.

\*  $\text{Ni}^{2+}$ , pH = 5.0, M = 0.02;  $\text{Co}^{2+}$ , pH = 5.0, M = 0.02;  $\text{Cd}^{2+}$ , pH = 6.0, M = 0.01;  $\text{Hg}^{2+}$ , pH = 4.9, M = 0.03.

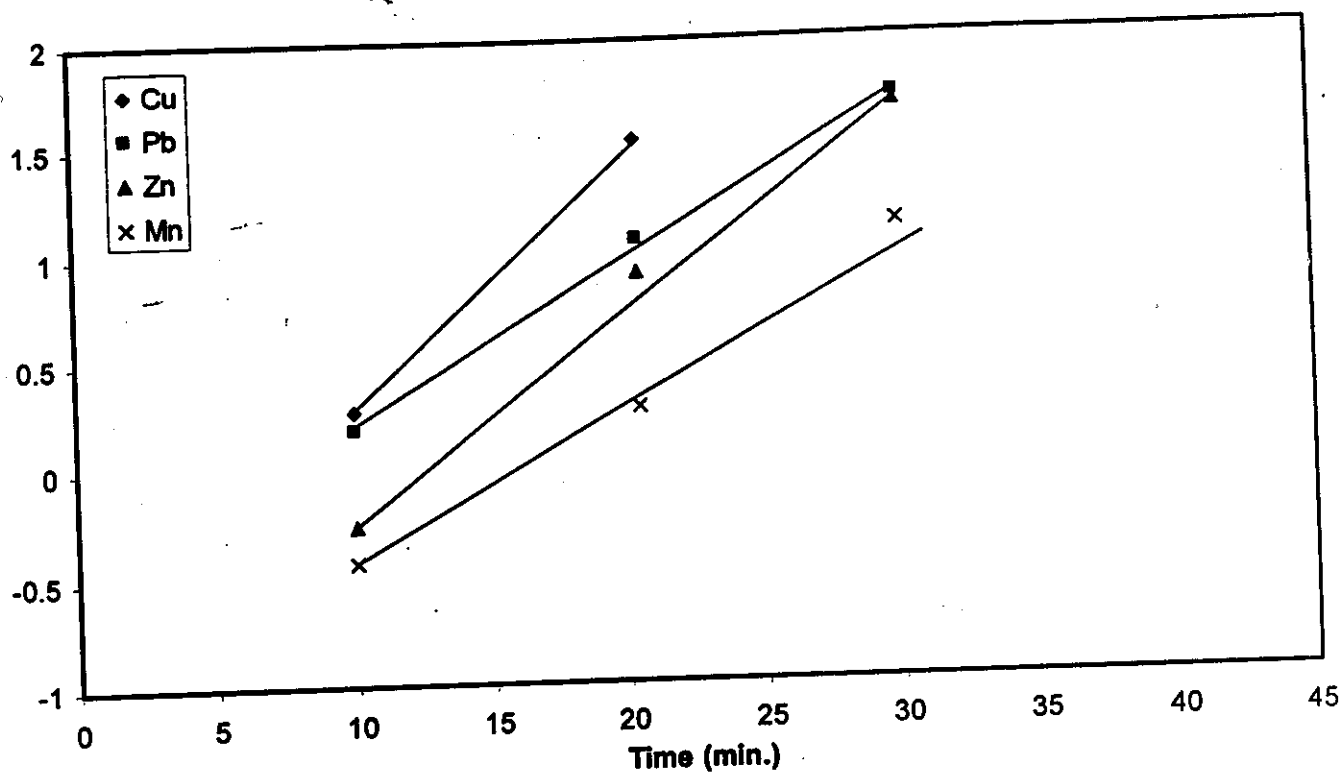


Fig. (31): Effect of rate constant on the uptake of the metal ions ( $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ ) for (XXXIV) resin.

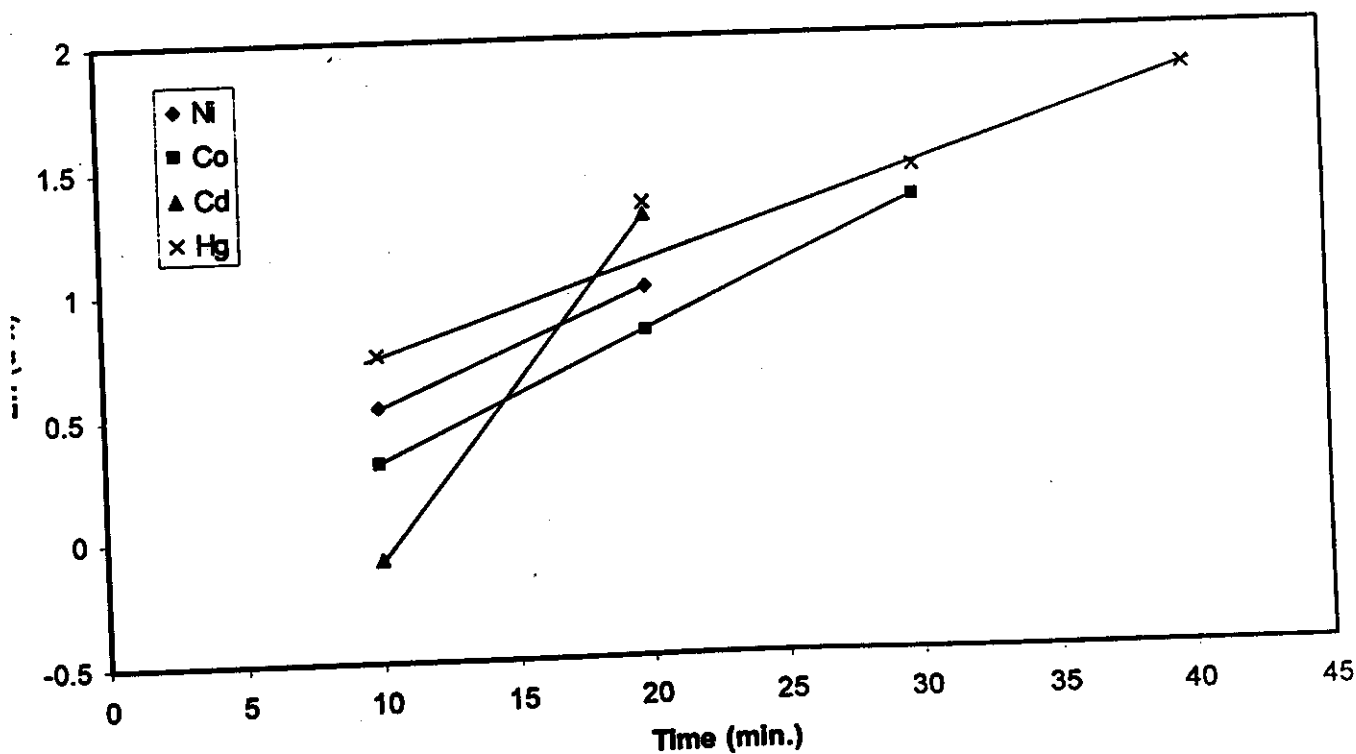


Fig. (32): Effect of rate constant on the uptake of the metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ) for (XXXIV) resin.

### III.3. Uptake of metal ions using column technique:

#### III.3.1 Uptake of metal ions by chelating resin containing o.phenylene diamine ligand (XXXII)

##### III.3.1.1 Uptake of $\text{Hg}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Hg}^{2+}$  by a solution containing 2567.6 mg/l of  $\text{Hg}^{2+}$  (0.0128 M) at pH 5.1. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (33). The break-through curve obtained Fig. (33a) indicates that using flow rate of 1.0 ml/min,  $\text{Hg}^{2+}$  starts to break-through at 190 ml of effluent and complete break-through is achieved at about 390 ml of effluent. Calculating the total amount of  $\text{Hg}^{2+}$  uptakes, showed that 5.673 mmol  $\text{Hg}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (6.1 mmol  $\text{Hg}^{2+}$ /g resin), the efficiency of the column using this flow rate is 93 %.  $\text{Hg}^{2+}$  was found completely eluted with 30 ml 2M  $\text{HNO}_3$ .

The effect of repeated use of the chelating resin on the sorption ability for  $\text{Hg}^{2+}$  was investigated in column operation. The break-through curves of the regenerated resin are shown in Fig. (33). Also the capacity of the regenerated resin is reported in Table (12).

In the common water treatment system with ion-exchange or chelating resin columns, complete elution of metals is not attempted in order to avoid unnecessary consumption of eluent and chemical disintegration of the resin beads. For treatment of commercially available thiol-containing chelating resins on which  $\text{Hg}^{2+}$  is uptakes, ignition and disposal in deep wells are inevitable because  $\text{Hg}^{2+}$  cannot be flushed out of the resin by any means <sup>(137)</sup>. Treatment by ignition and disposal in

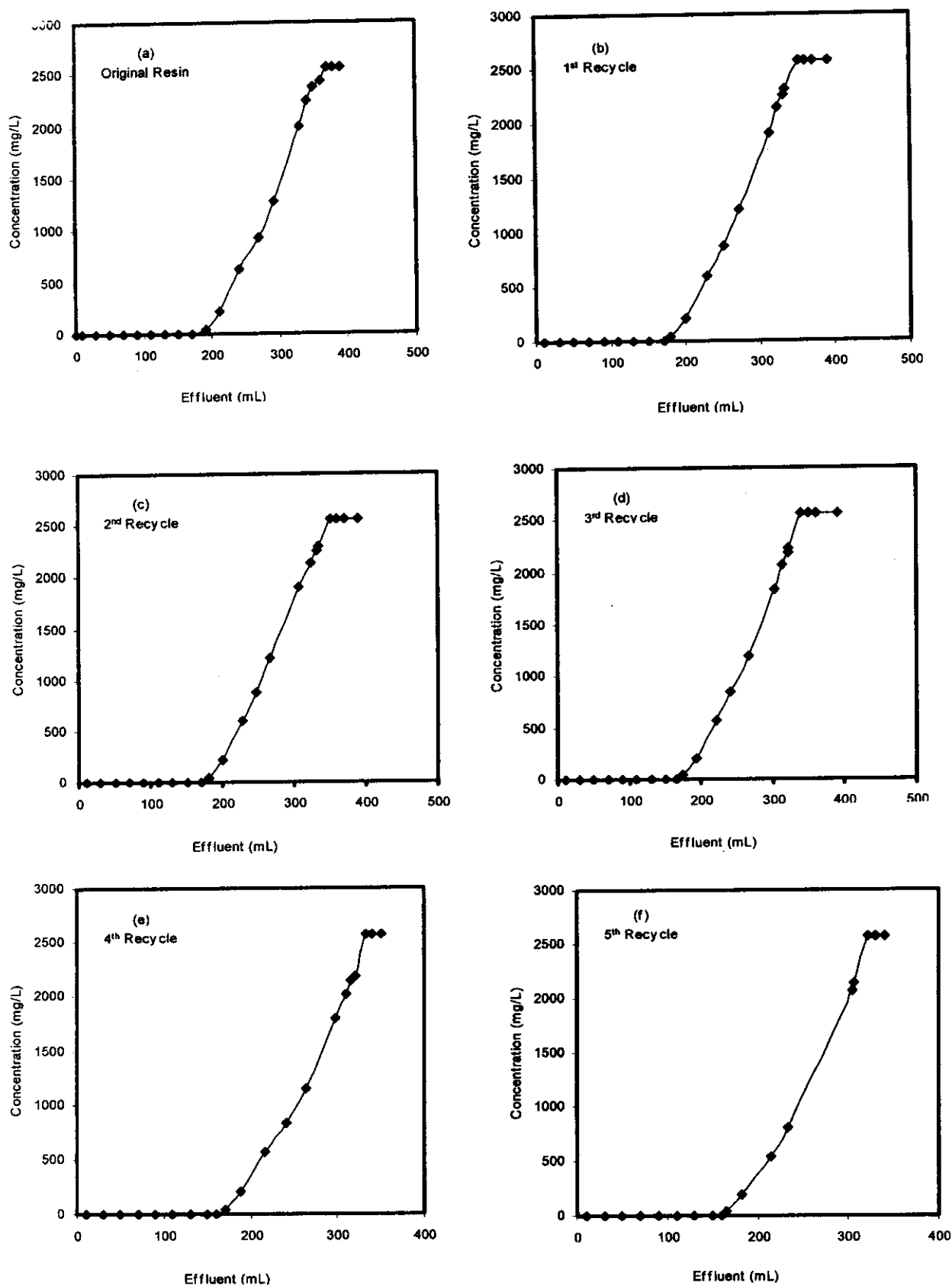


wells are undesirable not only because of economical loss, but also because of air and underground strata may occur. The ease of recovery of the (XXXII) chelating resin is one of the favorable features of its practical use.

Table 12: Metal ions sorption capacity of chelating resin (XXXII) regenerated with 2 M  $\text{HNO}_3$ .

No. of regycle	Capacity (mmol-Metal ion/g-resin) %						
	$\text{Hg}^{2+}$	$\text{Cu}^{2+}$	$\text{Pb}^{2+}$	$\text{Zn}^{2+}$	$\text{Cd}^{2+}$	$\text{Ni}^{2+}$	$\text{Mn}^{2+}$
0	100*	100*	100*	100*	100*	100*	100*
1	95	98	99	98	98	99	99
2	95	98	98	98	97	97	99
3	92	95	96	95	97	93	97
4	90	92	93	93	94	93	96
5	87	89	88	89	80	90	92

- \*  $\text{Hg}^{2+}$ ; Sorption capacity of the original chelating resin was 5.673 mmol/g resin
- \*  $\text{Cu}^{2+}$ ; Sorption capacity of the original chelating resin was 2.46 mmol/g resin
- \*  $\text{Pb}^{2+}$ ; Sorption capacity of the original chelating resin was 3.87 mmol/g resin
- \*  $\text{Zn}^{2+}$ ; Sorption capacity of the original chelating resin was 3.645 mmol/g resin
- \*  $\text{Cd}^{2+}$ ; Sorption capacity of the original chelating resin was 3.696 mmol/g resin
- \*  $\text{Ni}^{2+}$ ; Sorption capacity of the original chelating resin was 2.268 mmol/g resin
- \*  $\text{Mn}^{2+}$ ; Sorption capacity of the original chelating resin was 2.72 mmol/g resin

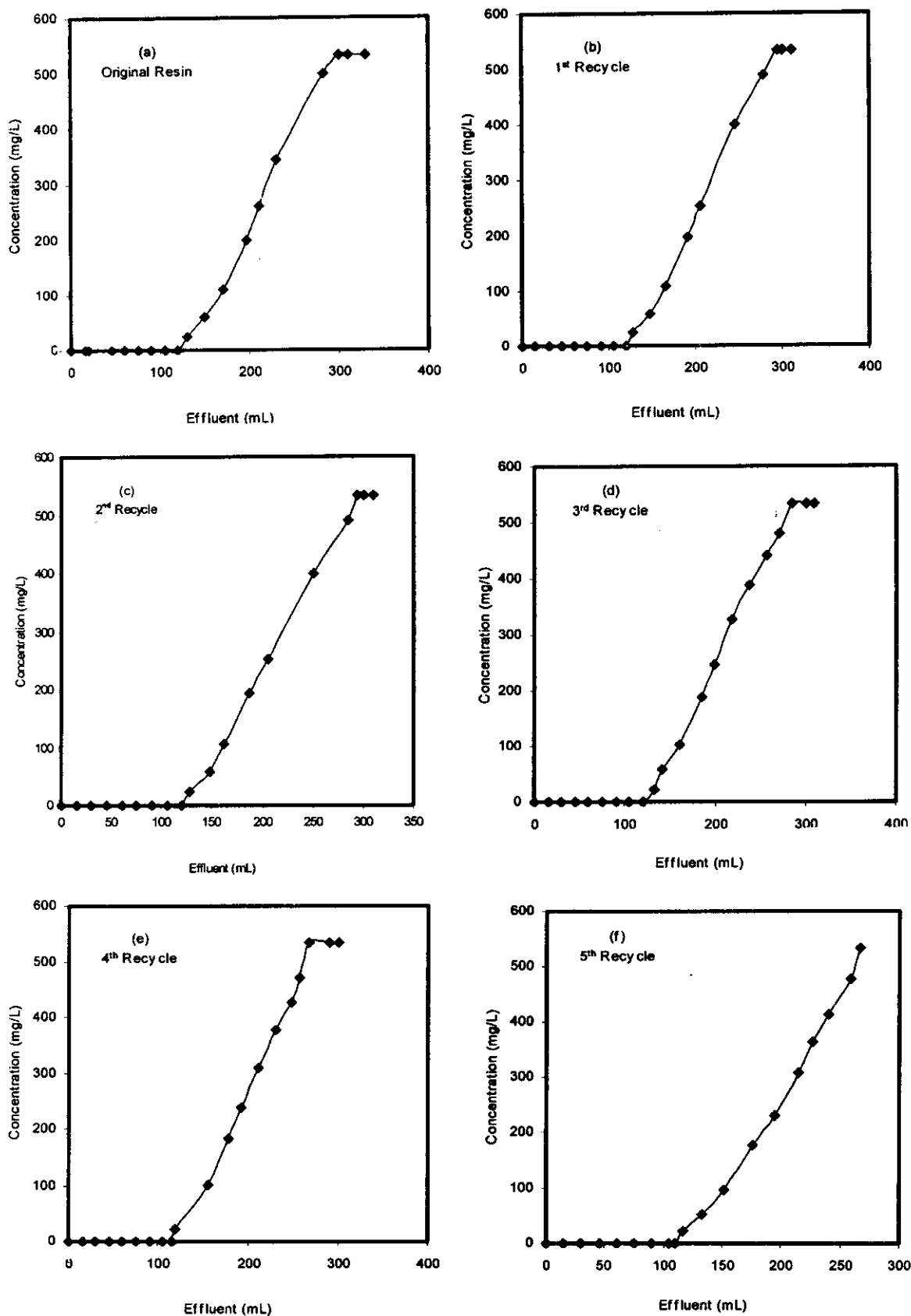


**Fig. (33):** Break-through curves for  $\text{Hg}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Hg}^{2+}$ , 2567.6 mg/L (0.0128 M). Flow rate, 1ml/min., pH value, 5.

### III.3.1.2 Uptake of $\text{Cu}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Cu}^{2+}$  by a solution containing 533.7 mg/l of  $\text{Cu}^{2+}$  (0.0084M) at pH 4.5. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (34). The break-through curve obtained Fig. (34a) indicates that using flow rate of 1.0 ml/min.  $\text{Cu}^{2+}$  starts to break-through at 130 ml of effluent and complete break-through is achieved of at about 300 ml of effluent. Calculating the total amount of  $\text{Cu}^{2+}$  uptakes, showed that 2.46 mmol  $\text{Cu}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (3.0 mmol  $\text{Cu}^{2+}$ /g resin), the efficiency of the column using this flow rate is 82 %.

The elution of  $\text{Cu}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Cu}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (34). Also the capacity of the regenerated resin is reported in Table (12).

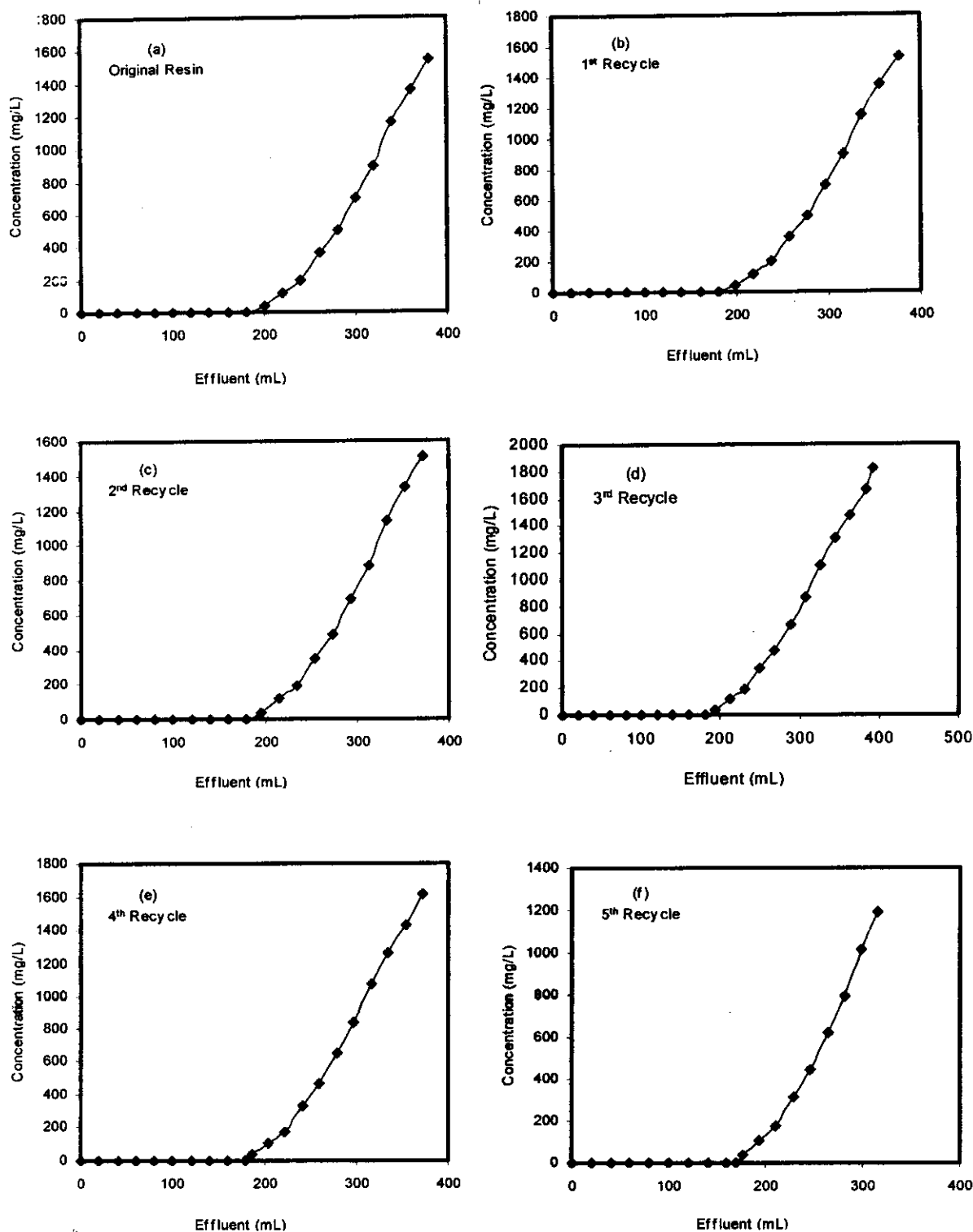


**Fig. (34):** Break-through curves for  $\text{Cu}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Cu}^{2+}$ , 533.7 mg/L (0.0084 M). Flow rate, 1ml/min., pH value, 4.5.

### III.3.1.3 Uptake of $\text{Pb}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Pb}^{2+}$  by a solution containing 1823.3 mg/l of  $\text{Pb}^{2+}$  (0.0088M) at pH 4.3. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (35). The break-through curve obtained Fig. (35a) indicates that using flow rate of 1.0 ml/min.  $\text{Pb}^{2+}$  starts to break-through at 200 ml of effluent and complete break-through is achieved of at about 410 ml of effluent. Calculating the total amount of  $\text{Pb}^{2+}$  uptakes, showed that 3.87 mmol  $\text{Pb}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (4.5 mmol  $\text{Pb}^{2+}$ /g resin), the efficiency of the column using this flow rate is 86 %.

The elution of  $\text{Pb}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Pb}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (35). Also the capacity of the regenerated resin is reported in Table (12).

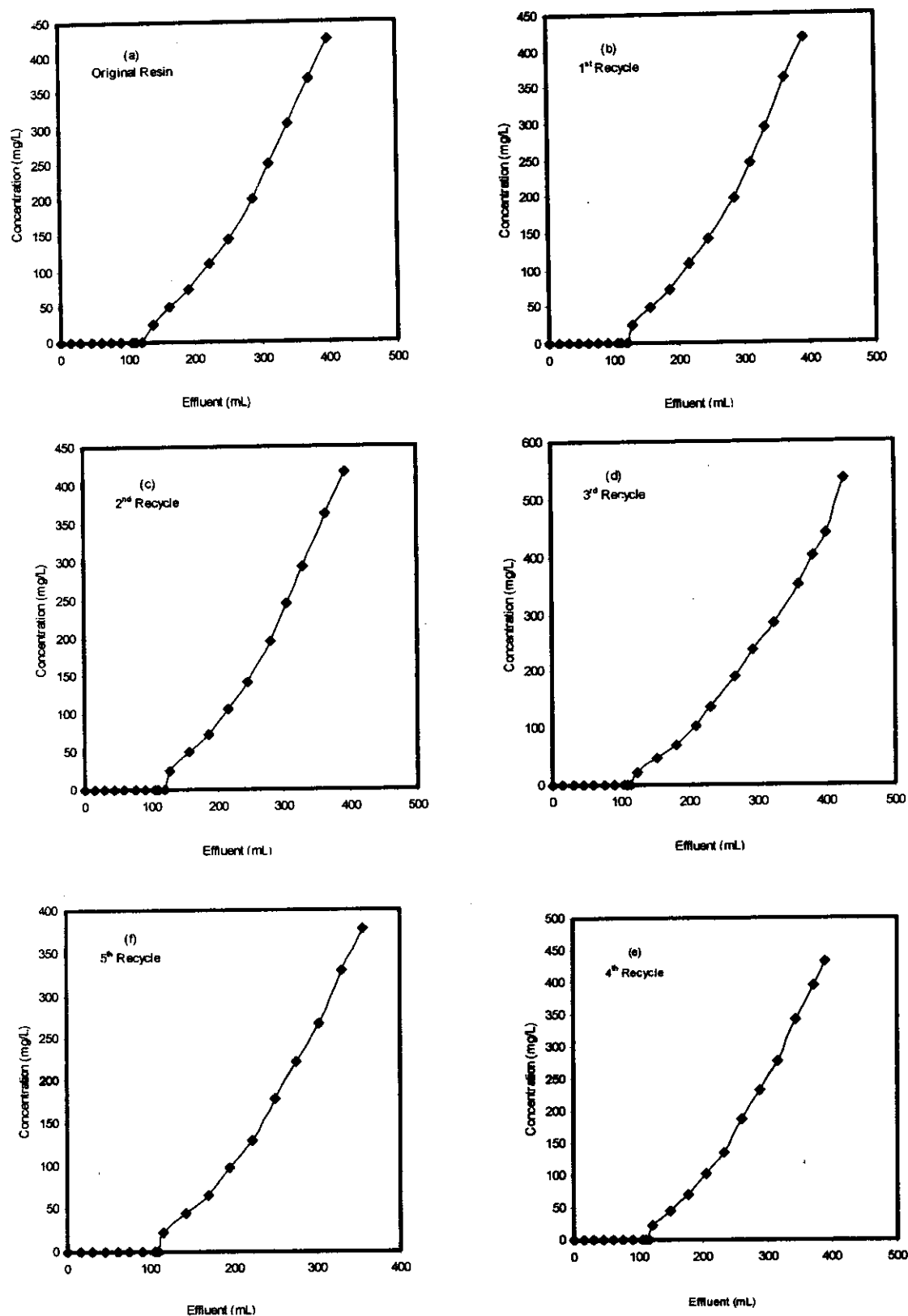


**Fig. (35):** Break-through curves for  $Pb^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $Pb^{2+}$ , 1823.3 mg/L (0.0088 M). Flow rate, 1ml/min., pH value, 4.3.

#### **III.3.1.4 Uptake of $\text{Zn}^{2+}$ ion:**

Column uptake tests were carried out for the removal of  $\text{Zn}^{2+}$  by a solution containing 536.0 mg/l of  $\text{Zn}^{2+}$  (0.0082 M) at pH 5.1. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (36). The break-through curve obtained Fig. (36a) indicates that using flow rate of 1.0 ml/min.  $\text{Zn}^{2+}$  starts to break-through at 130 ml of effluent and complete break-through is achieved at about 450 ml of effluent. Calculating the total amount of  $\text{Zn}^{2+}$  uptakes, showed that 3.645mmol  $\text{Zn}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (4.5 mmol  $\text{Zn}^{2+}$ /g resin), the efficiency of the column using this flow rate is 81 %.

The elution of  $\text{Zn}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Zn}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (36). Also the capacity of the regenerated resin is reported in Table (12).



**Fig. (36):** Break-through curves for  $\text{Zn}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Zn}^{2+}$ , 536.0 mg/L (0.0082 M). Flow rate, 1ml/min., pH value, 5.1.



### III.3.1.5 Uptake of $\text{Cd}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Cd}^{2+}$  by a solution containing 1056.6 mg/l of  $\text{Cd}^{2+}$  (0.0094 M) at pH 6.2. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (37). The break-through curve obtained Fig. (37a) indicates that using flow rate of 1.0 ml/min.  $\text{Cd}^{2+}$  starts to break-through at 120 ml of effluent and complete break-through is achieved of at about 360 ml of effluent. Calculating the total amount of  $\text{Cd}^{2+}$  uptakes, showed that 3.696 mmol  $\text{Cd}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (4.4 mmol  $\text{Cd}^{2+}$ /g resin), the efficiency of the column using this flow rate is 84 %.

The elution of  $\text{Cd}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Cd}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (37). Also the capacity of the regenerated resin is reported in Table (12).

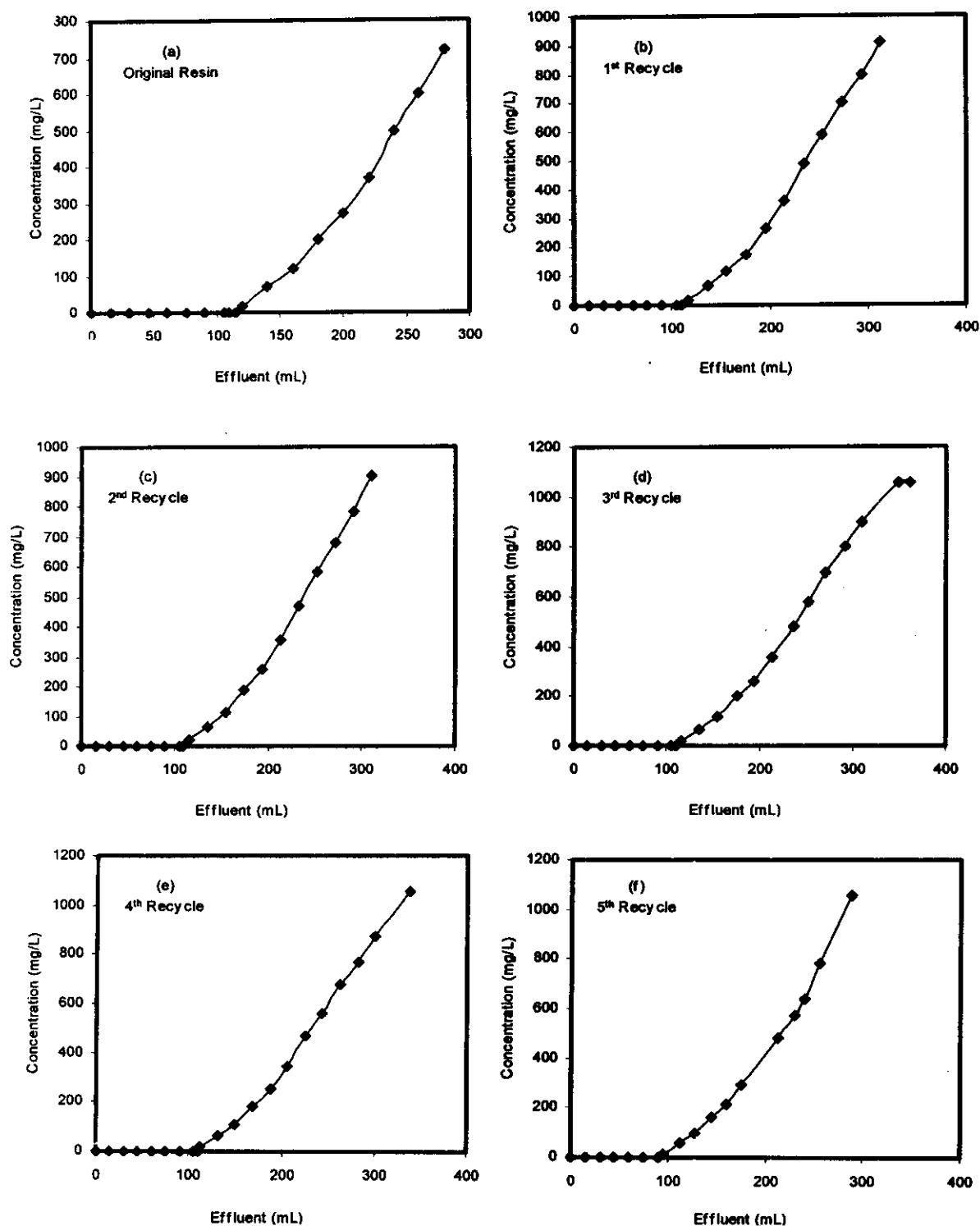


Fig. (37): Break-through curves for  $\text{Cd}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Cd}^{2+}$ , 1056.6 mg/L (0.0094 M). Flow rate, 1ml/min., pH value, 6.2.

### III.3.1.6 Uptake of $\text{Ni}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Ni}^{2+}$  by a solution containing 551.9 mg/l of  $\text{Ni}^{2+}$  (0.0094 M) at pH 4.9. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (38). The break-through curve obtained Fig. (38a) indicates that using flow rate of 1.0 ml/min.  $\text{Ni}^{2+}$  starts to break-through at 180 ml of effluent and complete break-through is achieved at about 370 ml of effluent. Calculating the total amount of  $\text{Ni}^{2+}$  uptakes, showed that 2.268 mmol  $\text{Ni}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (2.7 mmol  $\text{Ni}^{2+}$ /g resin), the efficiency of the column using this flow rate is 84 %.

The elution of  $\text{Ni}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Ni}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (38). Also the capacity of the regenerated resin is reported in Table (12).

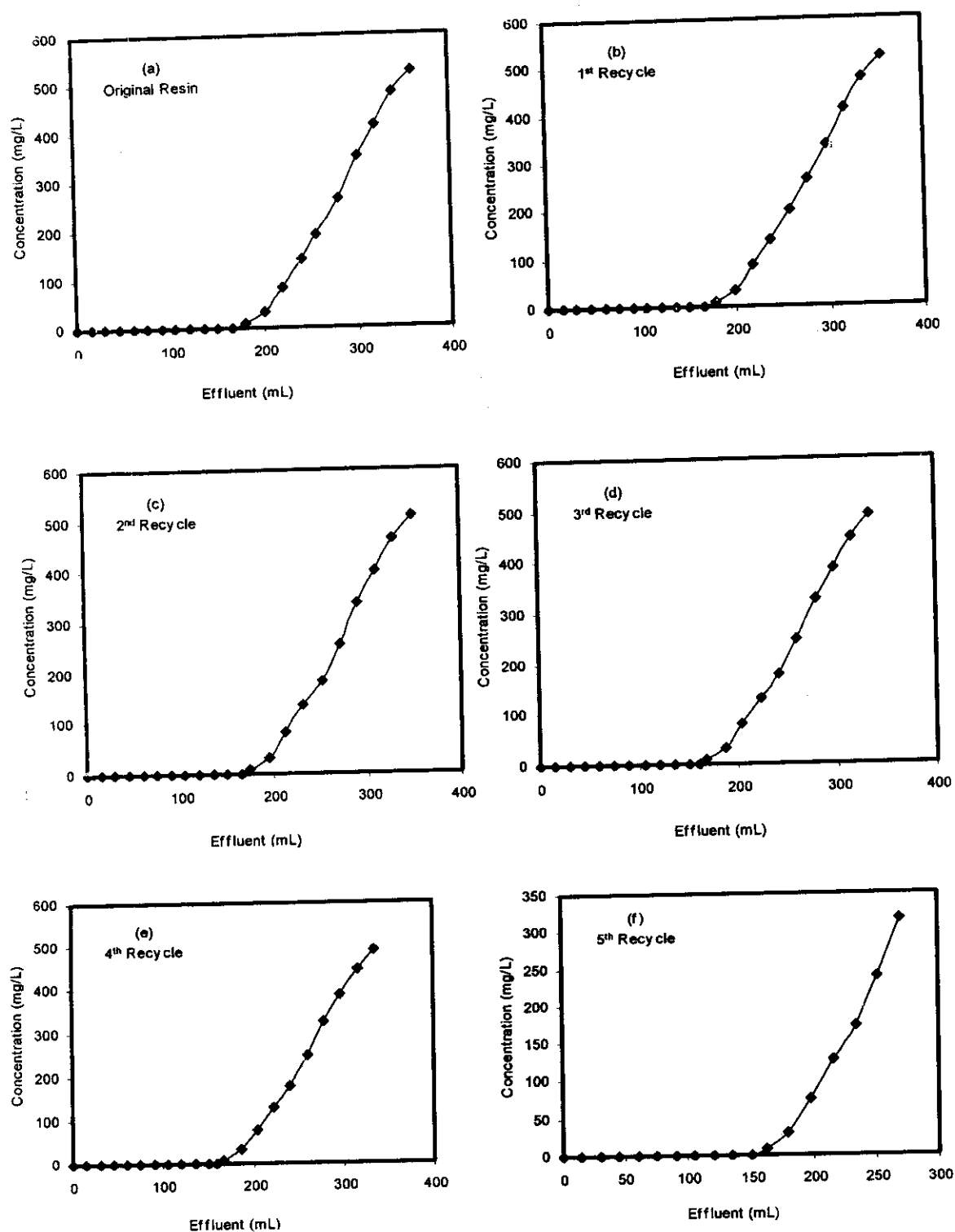
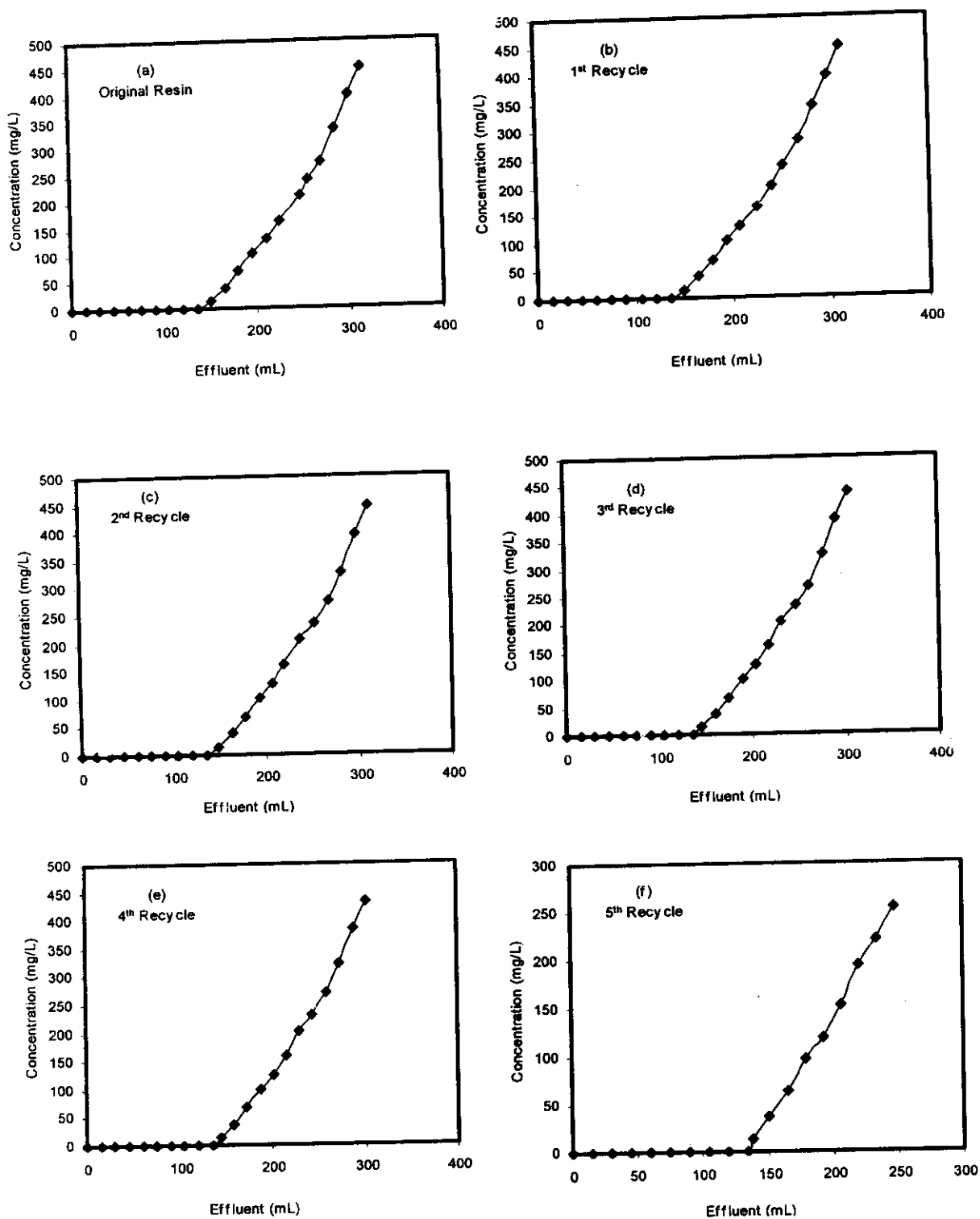


Fig. (38): Break-through curves for  $\text{Ni}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Ni}^{2+}$ , 551.9 mg/L (0.0094 M). Flow rate, 1ml/min., pH value, 4.9.

### III.3.1.7 Uptake of $\text{Mn}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Mn}^{2+}$  by a solution containing 516.4 mg/l of  $\text{Mn}^{2+}$  (0.0094 M) at pH 5.7. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (39). The break-through curve obtained Fig. (39a) indicates that using flow rate of 1.0 ml/min.  $\text{Mn}^{2+}$  starts to break-through at 150 ml of effluent and complete break-through is achieved at about 340 ml of effluent. Calculating the total amount of  $\text{Mn}^{2+}$  uptakes, showed that 2.72 mmol  $\text{Mn}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (3.2 mmol  $\text{Mn}^{2+}$ /g resin), the efficiency of the column using this flow rate is 85 %.

The elution of  $\text{Mn}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Mn}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (39). Also the capacity of the regenerated resin is reported in Table (12).

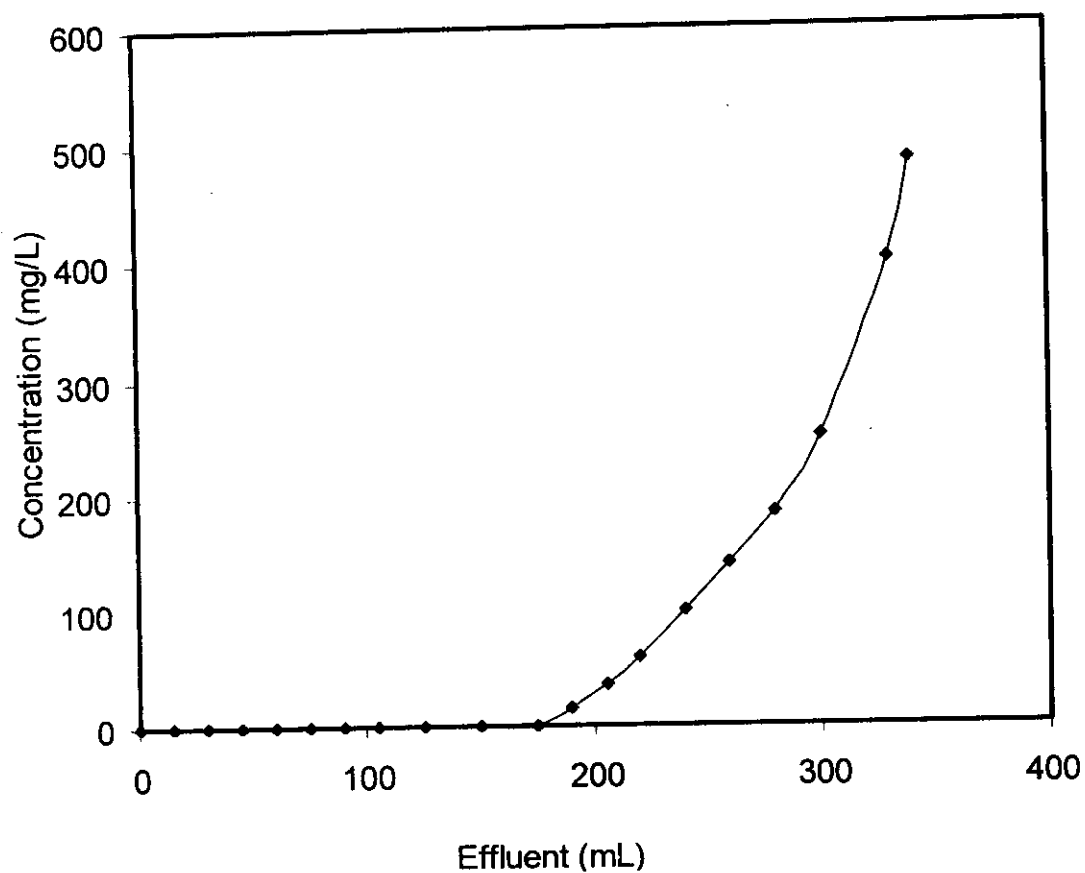


**Fig. (39):** Break-through curves for  $\text{Mn}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Mn}^{2+}$ , 516.4 mg/L (0.0094 M). Flow rate, 1ml/min., pH value, 5.7.

### III.3.1.8 Uptake of $\text{Co}^{2+}$ ion:

Chelating resin was also found effective in column operation for the removal of  $\text{Co}^{2+}$ . Column uptake tests were carried out for the removal of  $\text{Co}^{2+}$  by a solution containing 530.4 mg/l of  $\text{Co}^{2+}$  (0.009 M) at pH 4.8. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (40). The break through curve obtained Fig. (40). Indicates that using flow rate of 1.0 ml/min,  $\text{Co}^{2+}$  starts to break-through at 190 ml of effluent and complete break-through is achieved of at about 360 ml of effluent. Calculating the total amount of  $\text{Co}^{2+}$  uptakes, showed that 3.008 mmol  $\text{Co}^{2+}$  /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (3.2 mmol  $\text{Co}^{2+}$ /g resin), the efficiency of the column using this flow rate is 94%.

The recovery of  $\text{Co}^{2+}$  still remained incomplete this is presumably because  $\text{Co}^{2+}$  is partially oxidized on the chelating resin giving a much more stable ( $\text{Co}^{3+}$ -resin) complex <sup>(138)</sup>.



**Fig. (40):** Break-through curve for  $\text{Co}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Co}^{2+}$ , 530.4 mg/L (0.009 M). Flow rate, 1ml/min., pH value, 4.8.



### **III.3.2 Uptake of metal ions by chelating resin containing $\alpha$ -amino phenol ligand (XXXIII)**

#### **III.3.2.1 Uptake of $\text{Hg}^{2+}$ ion:**

Column uptake tests were carried out for the removal of  $\text{Hg}^{2+}$  by a solution containing 2567.6 mg/l of  $\text{Hg}^{2+}$  (0.0128 M) at pH 5.0. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (41). The break-through curve obtained Fig. (41a) indicates that using flow rate of 1.0 ml/min,  $\text{Hg}^{2+}$  starts to break-through at 190 ml of effluent and complete break-through is achieved at about 430 ml of effluent. Calculating the total amount of  $\text{Hg}^{2+}$  uptakes, showed that 5.4 mmol  $\text{Hg}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (6.0 mmol  $\text{Hg}^{2+}$ /g resin), the efficiency of the column using this flow rate is 90 %.  $\text{Hg}^{2+}$  was found completely eluted with 30 ml 2M  $\text{HNO}_3$ .

The effect of repeated use of the chelating resin on the sorption ability for  $\text{Hg}^{2+}$  was investigated in column operation. The break-through curves of the regenerated resin are shown in Fig. (41). Also the capacity of the regenerated resin is reported in Table (13).

**Table 13:** Metal ions sorption capacity of chelating resin (XXXIII) regenerated with 2 M  $\text{HNO}_3$ .

No. of recycle	Capacity (mmol. Metal ion /g resin) %						
	$\text{Hg}^{2+}$	$\text{Cu}^{2+}$	$\text{Pb}^{2+}$	$\text{Zn}^{2+}$	$\text{Cd}^{2+}$	$\text{Ni}^{2+}$	$\text{Mn}^{2+}$
0	100*	100*	100*	100*	100*	100*	100*
1	97	99	98	99	98	99	99
2	96	97	95	96	98	97	97
3	92	96	93	96	97	97	97
4	88	94	90	92	92	93	94
5	88	91	88	89	90	91	91

\*  $\text{Hg}^{2+}$ ; Sorption capacity of the original chelating resin was 5.4 mmol/g resin

\*  $\text{Cu}^{2+}$ ; Sorption capacity of the original chelating resin was 3.872 mmol/g resin

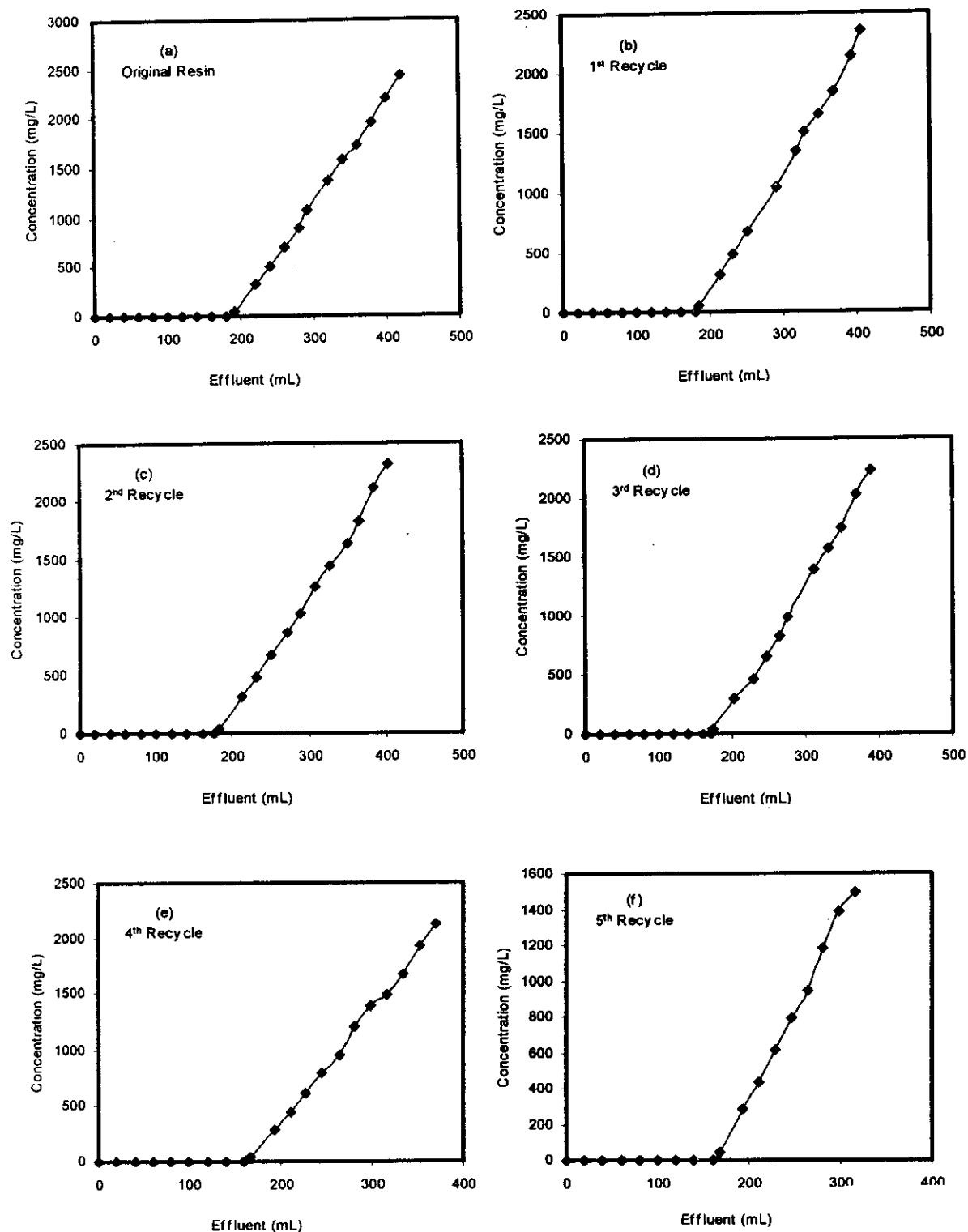
\*  $\text{Pb}^{2+}$ ; Sorption capacity of the original chelating resin was 2.7 mmol/g resin

\*  $\text{Zn}^{2+}$ ; Sorption capacity of the original chelating resin was 3.995 mmol/g resin

\*  $\text{Cd}^{2+}$ ; Sorption capacity of the original chelating resin was 2.886 mmol/g resin

\*  $\text{Ni}^{2+}$ ; Sorption capacity of the original chelating resin was 2.58 mmol/g resin

\*  $\text{Mn}^{2+}$ ; Sorption capacity of the original chelating resin was 2.465 mmol/g resin

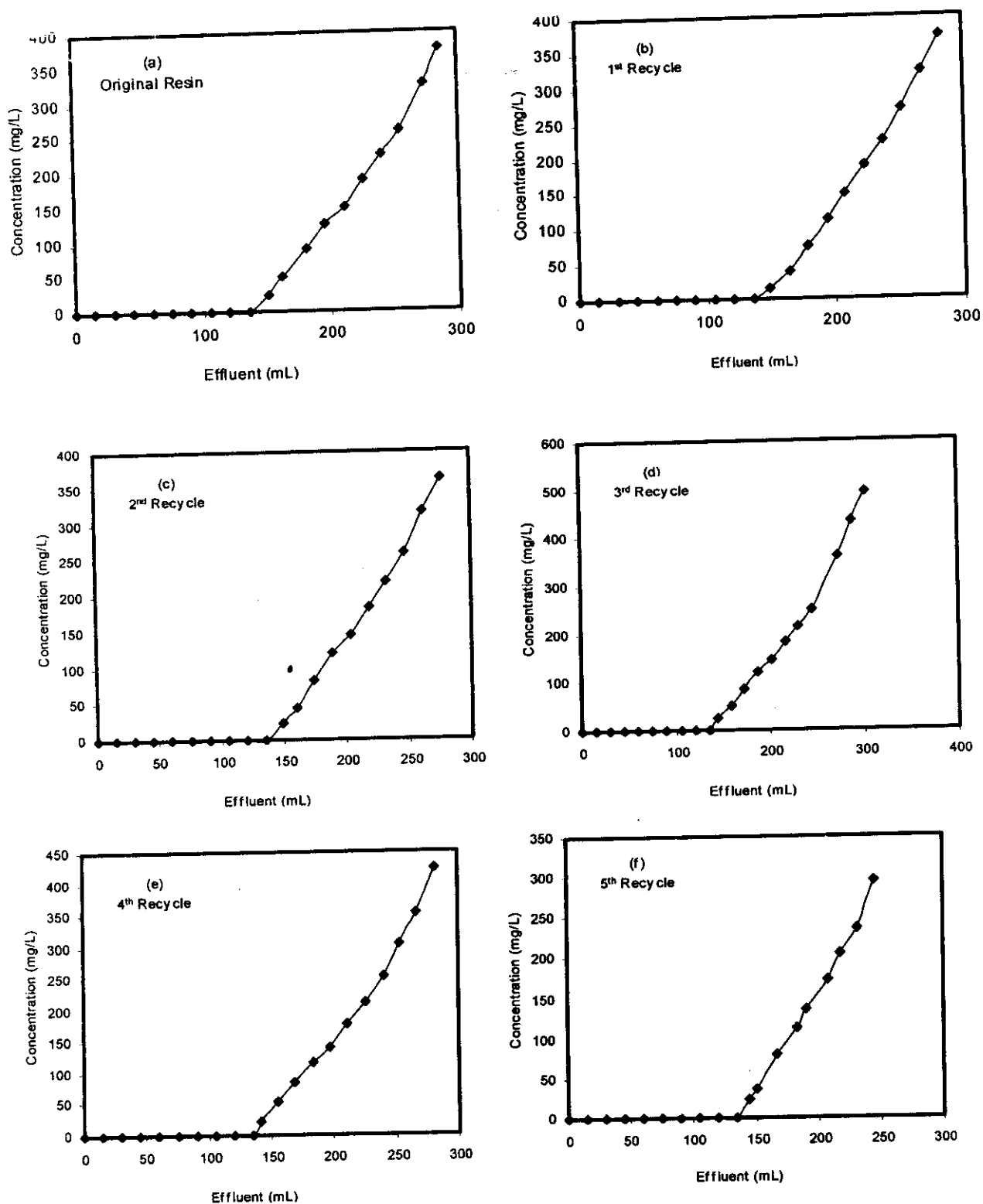


**Fig. (41):** Break-through curves for  $\text{Hg}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Hg}^{2+}$ , 2567.6 mg/L (0.0128 M). Flow rate, 1ml/min., pH value, 5.0.

### III.3.2.2 Uptake of $\text{Cu}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Cu}^{2+}$  by a solution containing 533.7 mg/l of  $\text{Cu}^{2+}$  (0.0084 M) at pH 4.7. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (42). The break-through curve obtained Fig. (42a) indicates that using flow rate of 1.0 ml/min.  $\text{Cu}^{2+}$  starts to break-through at 150 ml of effluent and complete break-through is achieved at about 320 ml of effluent. Calculating the total amount of  $\text{Cu}^{2+}$  uptakes, showed that 3.872mmol  $\text{Cu}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (4.4 mmol  $\text{Cu}^{2+}$ /g resin), the efficiency of the column using this flow rate is 88 %.

The elution of  $\text{Cu}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Cu}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (42). Also the capacity of the regenerated resin is reported in Table (13).



**Fig. (42):** Break-through curves for  $\text{Cu}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Cu}^{2+}$ , 533.7 mg/L (0.0084 M). Flow rate, 1ml/min., pH value, 4.7.

### III.3.2.3 Uptake of $\text{Pb}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Pb}^{2+}$  by a solution containing 1823.3 mg/l of  $\text{Pb}^{2+}$  (0.0088 M) at pH 4.3. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (43). The break-through curve obtained Fig. (43a) indicates that using flow rate of 1.0 ml/min.  $\text{Pb}^{2+}$  starts to break-through at 190 ml of effluent and complete break-through is achieved of at about 380 ml of effluent. Calculating the total amount of  $\text{Pb}^{2+}$  uptakes, showed that 2.7 mmol  $\text{Pb}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (3.0 mmol  $\text{Pb}^{2+}$ /g resin), the efficiency of the column using this flow rate is 90 %.

The elution of  $\text{Pb}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Pb}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (43). Also the capacity of the regenerated resin is reported in Table (13).

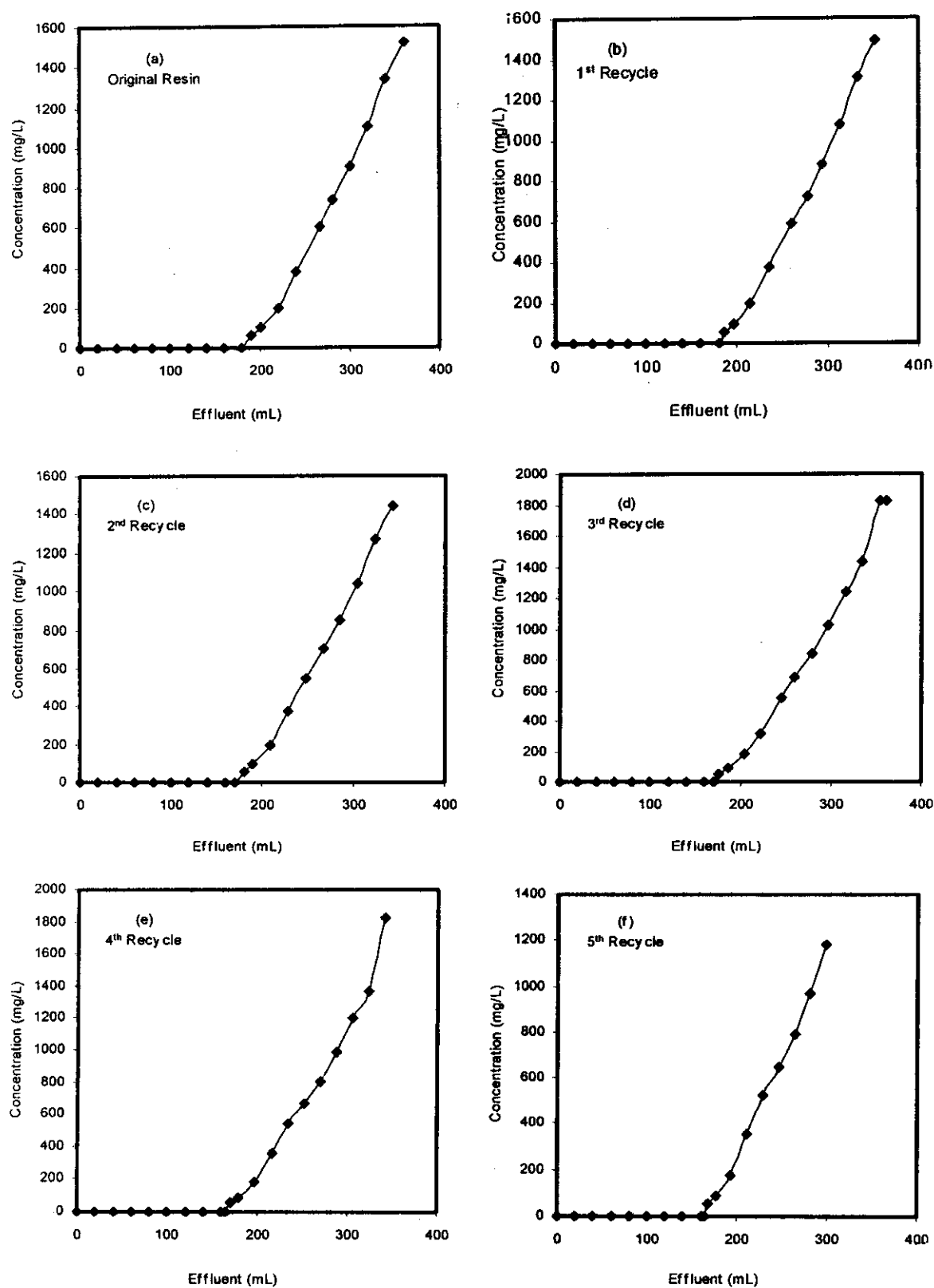


Fig. (43): Break-through curves for  $Pb^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $Pb^{2+}$ , 1823.3 mg/L (0.0088 M). Flow rate, 1ml/min., pH value, 4.3.

### III.3.2.4 Uptake of $\text{Zn}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Zn}^{2+}$  by a solution containing 536.0 mg/l of  $\text{Zn}^{2+}$  (0.0082 M) at pH 5.0. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (44). The break-through curve obtained Fig. (44a) indicates that using flow rate of 1.0 ml/min.  $\text{Zn}^{2+}$  starts to break-through at 150 ml of effluent and complete break-through is achieved at about 470 ml of effluent. Calculating the total amount of  $\text{Zn}^{2+}$  uptakes, showed that 3.995 mmol  $\text{Zn}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (4.7 mmol  $\text{Zn}^{2+}$ /g resin), the efficiency of the column using this flow rate is 85 %.

The elution of  $\text{Zn}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Zn}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (44). Also the capacity of the regenerated resin is reported in Table (13).



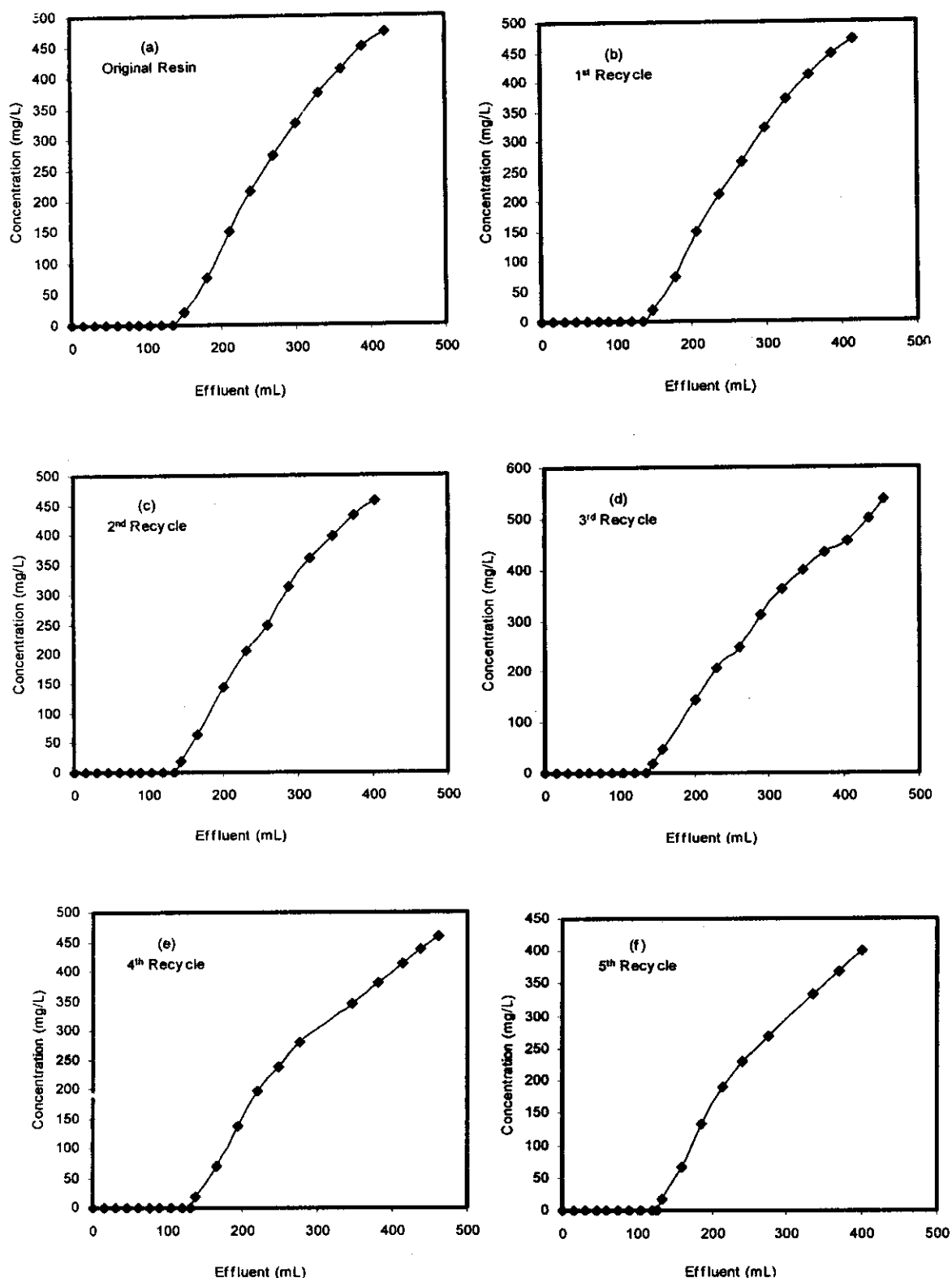
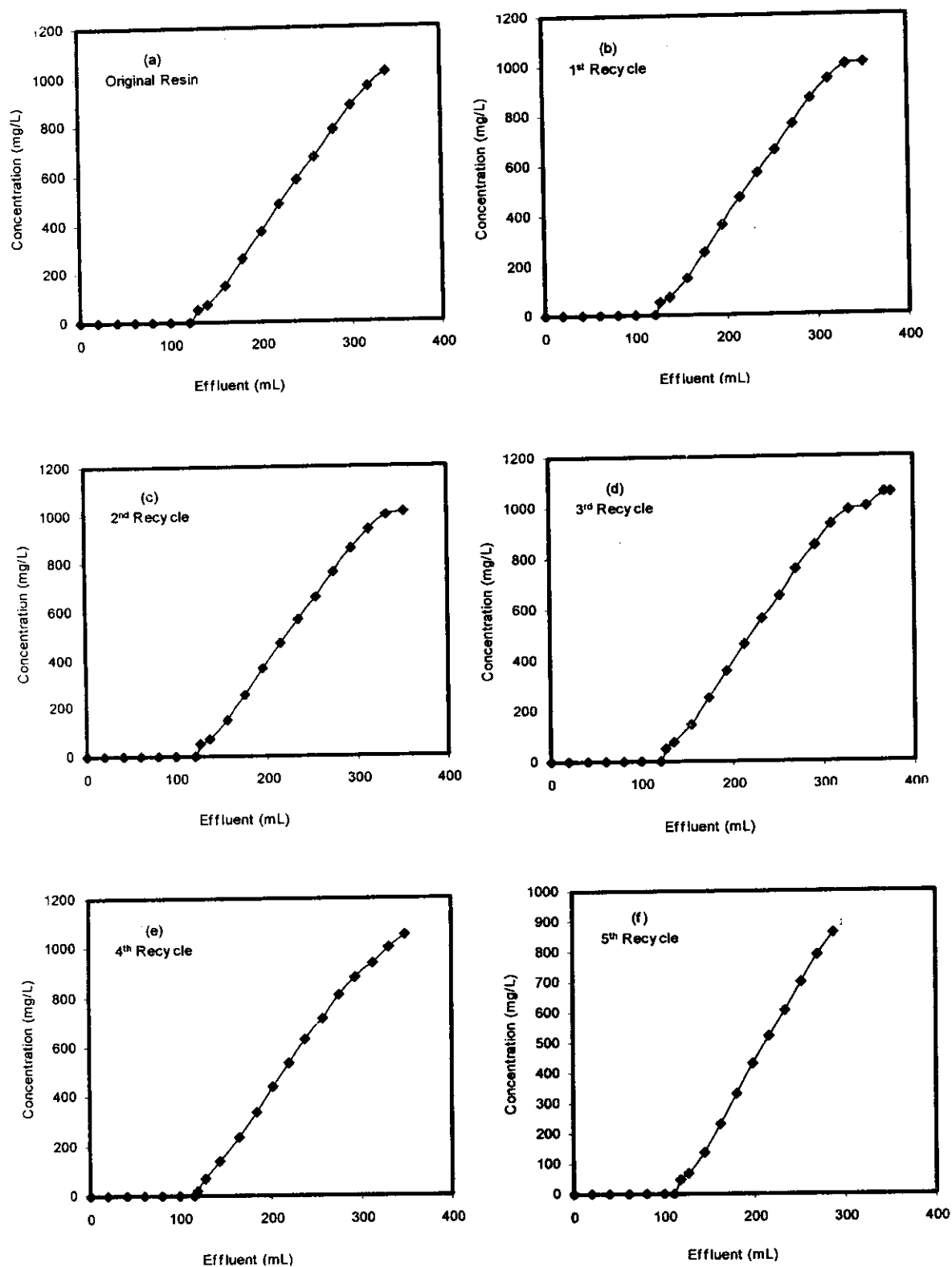


Fig. (44): Break-through curves for  $\text{Zn}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Zn}^{2+}$ , 536.0 mg/L (0.0082 M). Flow rate, 1ml/min., pH value, 5.0.

### III.3.2.5 Uptake of $\text{Cd}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Cd}^{2+}$  by a solution containing 1056.6 mg/l of  $\text{Cd}^{2+}$  (0.0094 M) at pH 5.7. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (45). The break-through curve obtained Fig. (45a) indicates that using flow rate of 1.0 ml/min.  $\text{Cd}^{2+}$  starts to break-through at 130 ml of effluent and complete break-through is achieved at about 380 ml of effluent. Calculating the total amount of  $\text{Cd}^{2+}$  uptakes, showed that 2.886 mmol  $\text{Cd}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (3.7 mmol  $\text{Cd}^{2+}$ /g resin), the efficiency of the column using this flow rate is 78 %.

The elution of  $\text{Cd}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Cd}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (45). Also the capacity of the regenerated resin is reported in Table (13).

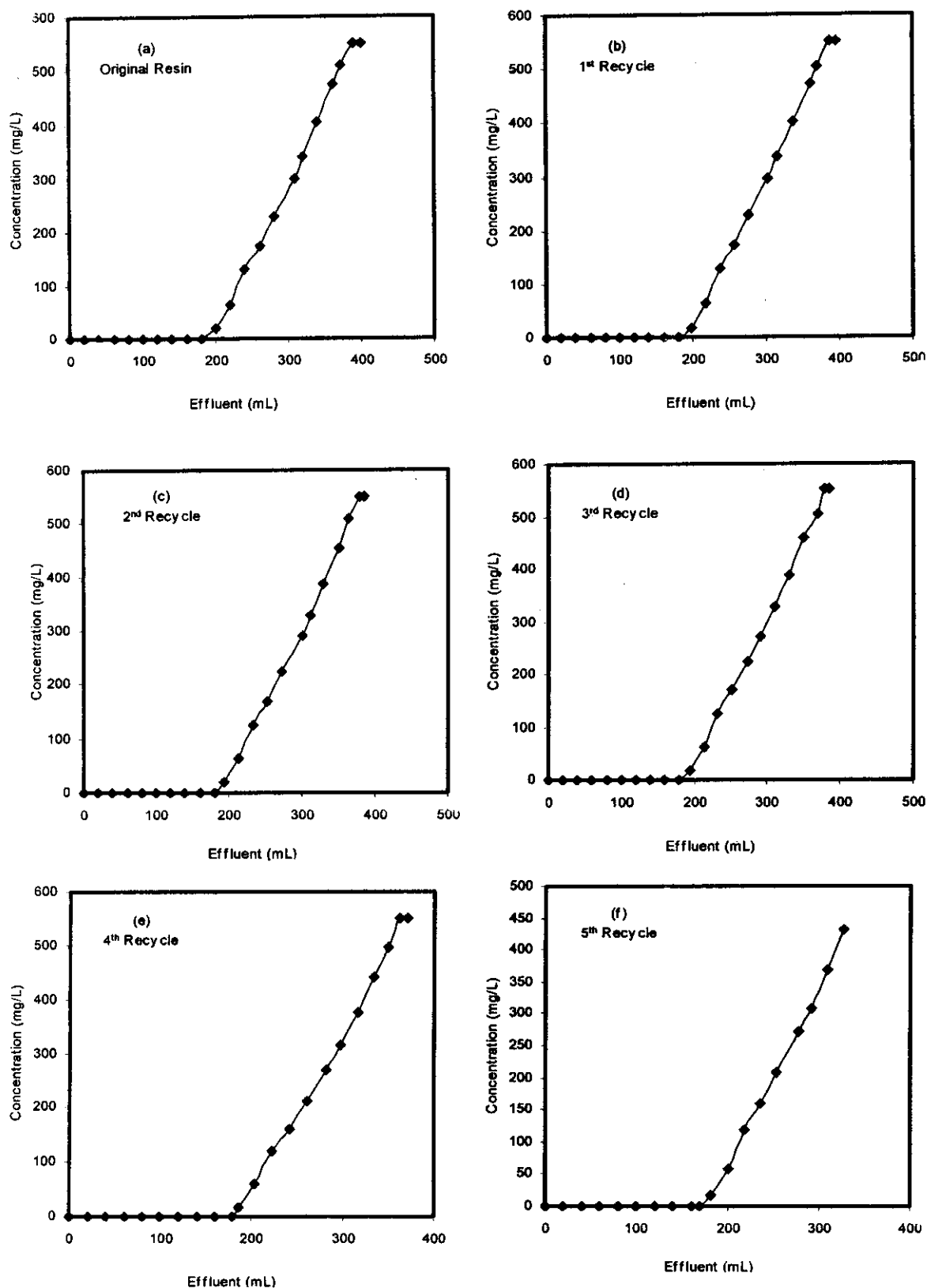


**Fig. (45):** Break-through curves for  $\text{Cd}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Cd}^{2+}$ , 1056.6 mg/L (0.0094 M). Flow rate, 1ml/min., pH value, 5.7.

### III.3.2.6 Uptake of $\text{Ni}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Ni}^{2+}$  by a solution containing 551.9 mg/l of  $\text{Ni}^{2+}$  (0.0094 M) at pH 4.9. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (46). The break-through curve obtained Fig. (46a) indicates that using flow rate of 1.0 ml/min.  $\text{Ni}^{2+}$  starts to break-through at 200 ml of effluent and complete break-through is achieved at about 390 ml of effluent. Calculating the total amount of  $\text{Ni}^{2+}$  uptakes, showed that 2.58 mmol  $\text{Ni}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (3.0 mmol  $\text{Ni}^{2+}$ /g resin), the efficiency of the column using this flow rate is 86 %.

The elution of  $\text{Ni}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Ni}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (46). Also the capacity of the regenerated resin is reported in Table (13).



**Fig. (46):** Break-through curves for  $\text{Ni}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Ni}^{2+}$ , 551.9 mg/L (0.0094 M). Flow rate, 1ml/min., pH value, 4.9.

### III.3.2.7 Uptake of $\text{Mn}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Mn}^{2+}$  by a solution containing 516.4 mg/l of  $\text{Mn}^{2+}$  (0.0094M) at pH 5.6. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (47). The break-through curve obtained Fig. (47a) indicates that using flow rate of 1.0 ml/min.  $\text{Mn}^{2+}$  starts to break-through at 140 ml of effluent and complete break-through is achieved at about 350 ml of effluent. Calculating the total amount of  $\text{Mn}^{2+}$  uptakes, showed that 2.465 mmol  $\text{Mn}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (2.97 mmol  $\text{Mn}^{2+}$ /g resin), the efficiency of the column using this flow rate is 83 %.

The elution of  $\text{Mn}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Mn}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (47). Also the capacity of the regenerated resin is reported in Table (13).

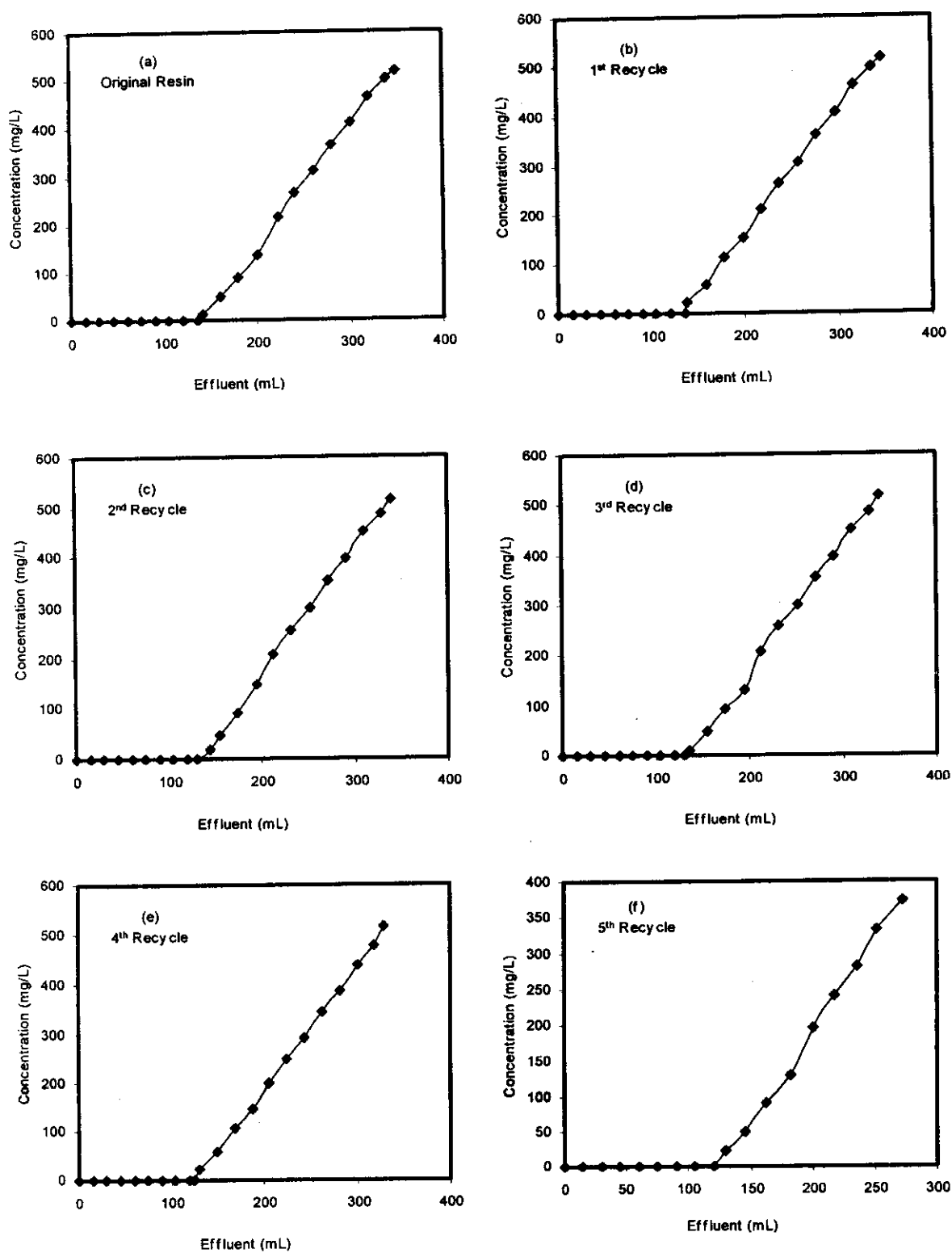


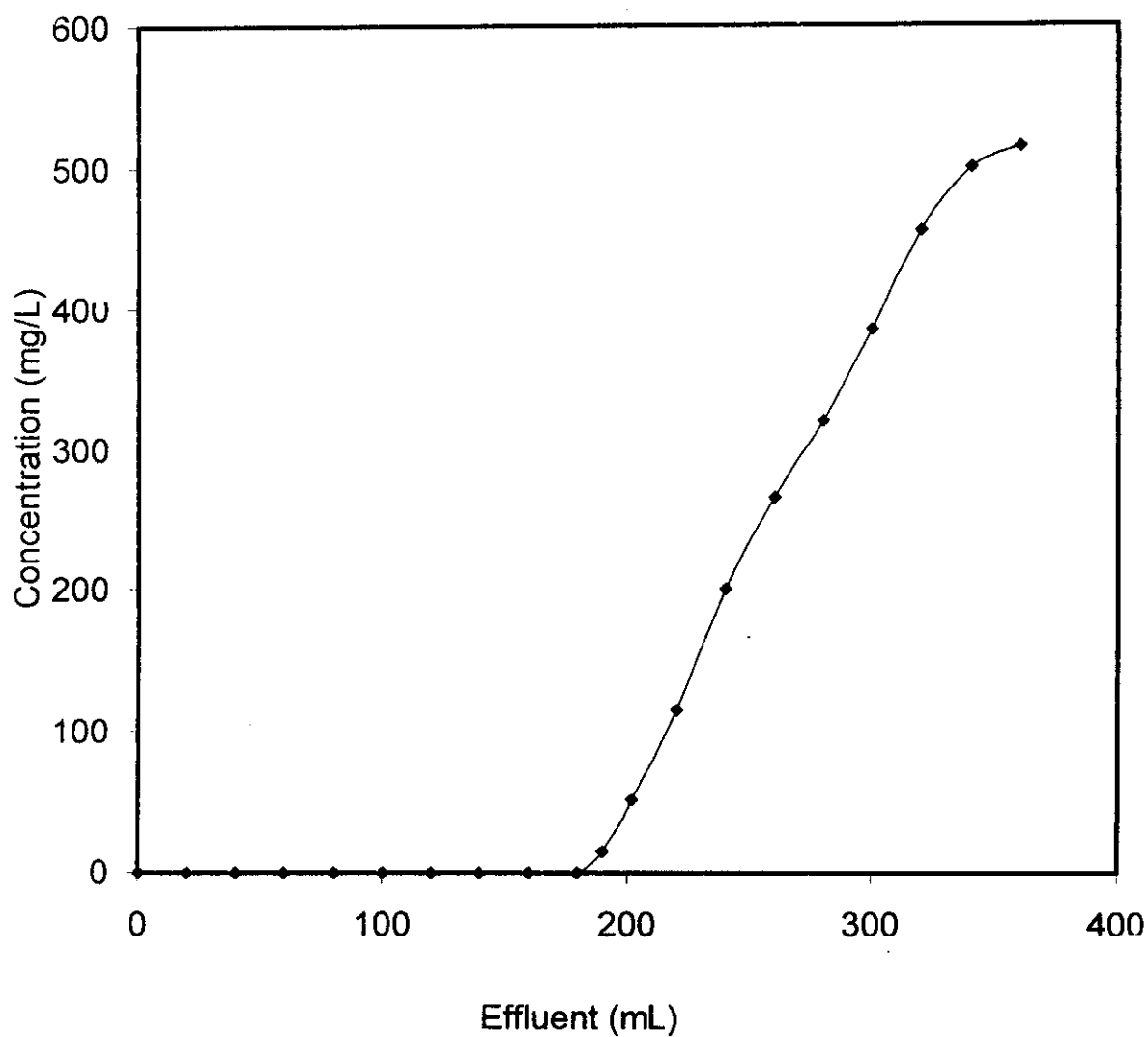
Fig. (47): Break-through curves for  $\text{Mn}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Mn}^{2+}$ , 516.4 mg/L (0.0094 M). Flow rate, 1ml/min., pH value, 5.6.

### III.3.2.8 Uptake of $\text{Co}^{2+}$ ion:

Chelating resin was also found effective in column operation for the removal of  $\text{Co}^{2+}$ . Column uptake tests were carried out for the removal of  $\text{Co}^{2+}$  by a solution containing 530.4 mg/l of  $\text{Co}^{2+}$  (0.009 M) at pH 4.5. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (48). The break through curve obtained Fig. (48). Indicates that using flow rate of 1.0 ml/min,  $\text{Co}^{2+}$  starts to break-through at 190 ml of effluent and complete break-through is achieved of at about 380 ml of effluent. Calculating the total amount of  $\text{Co}^{2+}$  uptakes, showed that 2.91 mmol  $\text{Co}^{2+}$  /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (3.0 mmol  $\text{Co}^{2+}$ /g resin), the efficiency of the column using this flow rate is 97%.

The recovery of  $\text{Co}^{2+}$  still remained incomplete this is presumably because  $\text{Co}^{2+}$  is partially oxidized on the chelating resin giving a much more stable ( $\text{Co}^{3+}$ -resin) complex <sup>(138)</sup>.





**Fig. (48):** Break-through curve for  $\text{Co}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Co}^{2+}$ , 530.4 mg/L (0.009 M). Flow rate, 1 ml/min., pH value, 4.5.

### **III.3.3 Uptake of metal ions by chelating resin containing 4-amino antipyrine ligand (XXXIV)**

#### **III.3.3.1 Uptake of $\text{Hg}^{2+}$ ion:**

Column uptake tests were carried out for the removal of  $\text{Hg}^{2+}$  by a solution containing 2567.6 mg/l of  $\text{Hg}^{2+}$  (0.0128 M) at pH 4.9. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (49). The break-through curve obtained Fig. (49a) indicates that using flow rate of 1.0 ml/min,  $\text{Hg}^{2+}$  starts to break-through at 200 ml of effluent and complete break-through is achieved at about 480 ml of effluent. Calculating the total amount of  $\text{Hg}^{2+}$  uptakes, showed that 6.048 mmol  $\text{Hg}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (6.3 mmol  $\text{Hg}^{2+}$ /g resin), the efficiency of the column using this flow rate is 96 %.  $\text{Hg}^{2+}$  was found completely eluted with 30 ml 2M  $\text{HNO}_3$ .

The effect of repeated use of the chelating resin on the sorption ability for  $\text{Hg}^{2+}$  was investigated in column operation. The break-through curves of the regenerated resin are shown in Fig. (49). Also the capacity of the regenerated resin is reported in Table (14).

**Table 14:** Metal ions sorption capacity of chelating resin (XXXIV) regenerated with 2 M HNO<sub>3</sub>.

No. of recycle	Capacity (mmol. Metal ion /g resin) %						
	Hg <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cd <sup>2+</sup>	Ni <sup>2+</sup>	Mn <sup>2+</sup>
0	100*	100*	100*	100*	100*	100*	100*
1	98	99	97	98	98	99	99
2	97	98	97	97	97	99	99
3	95	96	95	94	95	96	97
4	91	95	91	91	91	92	92
5	86	89	90	89	90	90	92

\* Hg<sup>2+</sup>; Sorption capacity of the original chelating resin was 6.048 mmol/g resin

\* Cu<sup>2+</sup>; Sorption capacity of the original chelating resin was 4.186 mmol/g resin

\* Pb<sup>2+</sup>; Sorption capacity of the original chelating resin was 5.208 mmol/g resin

\* Zn<sup>2+</sup>; Sorption capacity of the original chelating resin was 4.895 mmol/g resin

\* Cd<sup>2+</sup>; Sorption capacity of the original chelating resin was 2.964 mmol/g resin

\* Ni<sup>2+</sup>; Sorption capacity of the original chelating resin was 3.212 mmol/g resin

\* Mn<sup>2+</sup>; Sorption capacity of the original chelating resin was 2.806 mmol/g resin

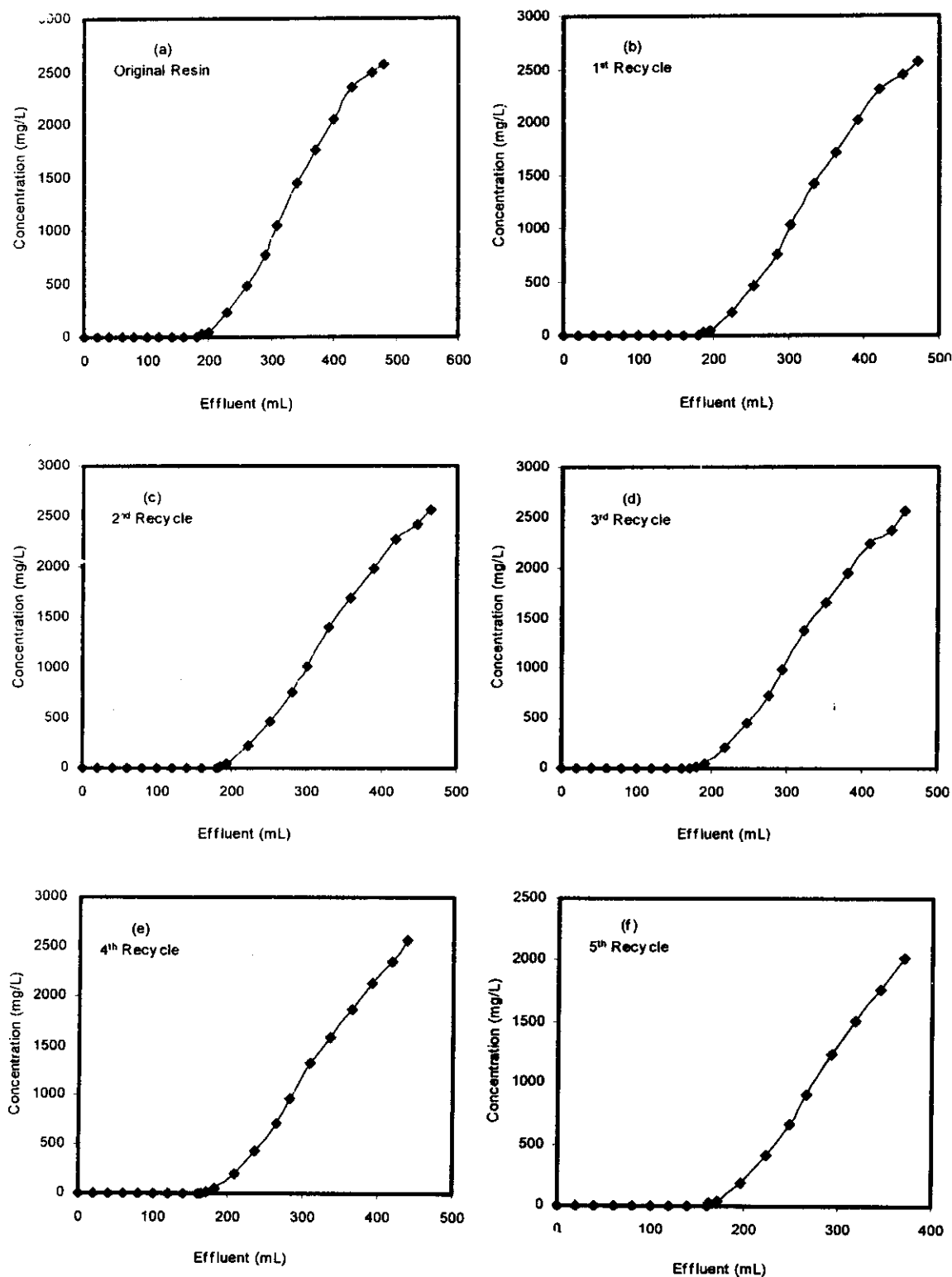
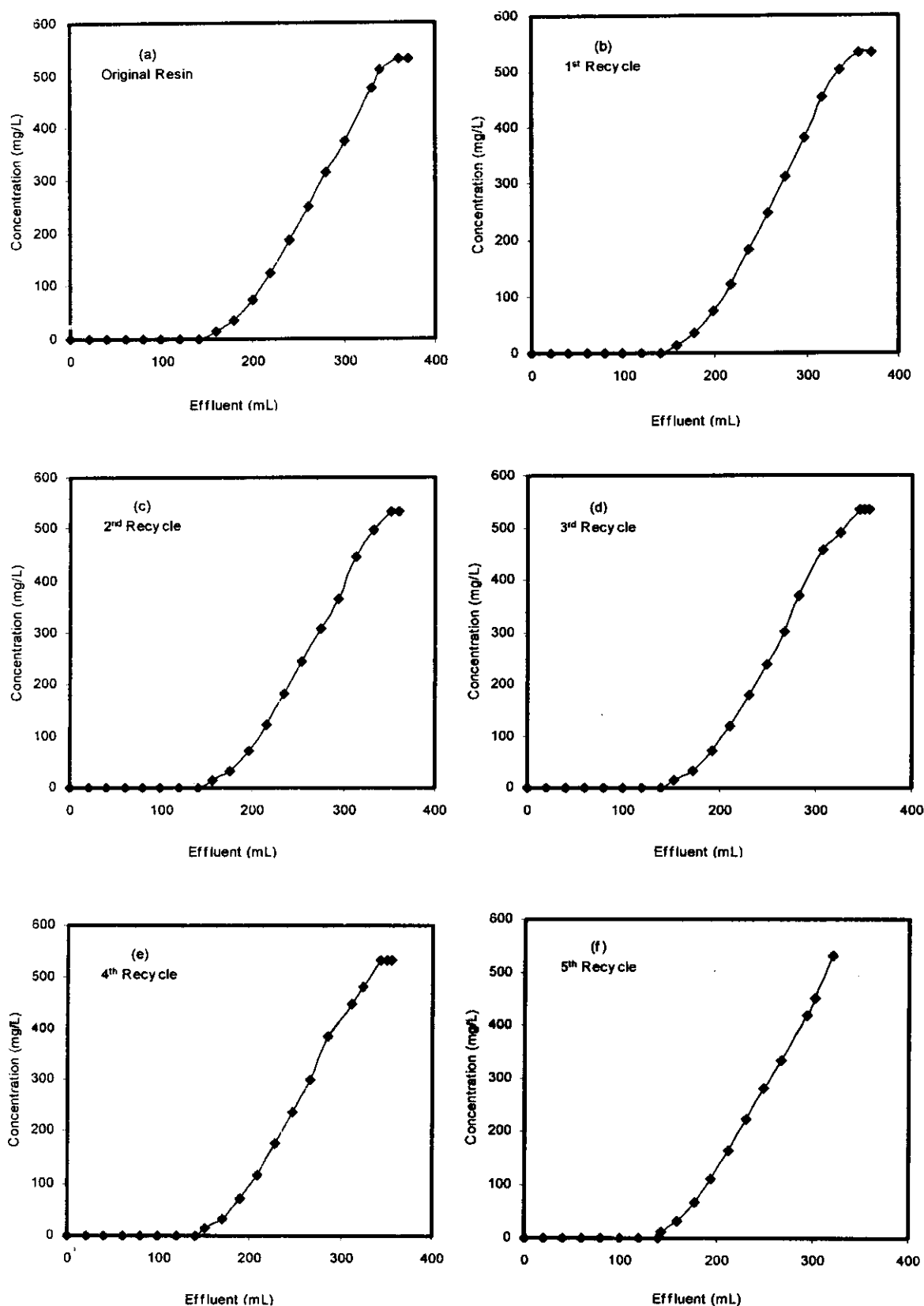


Fig. (49): Break-through curves for  $\text{Hg}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Hg}^{2+}$ , 2567.6 mg/L (0.0128 M). Flow rate, 1ml/min., pH value, 4.9.

### III.3.3.2 Uptake of $\text{Cu}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Cu}^{2+}$  by a solution containing 533.7 mg/l of  $\text{Cu}^{2+}$  (0.0084M) at pH 5.0. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (50). The break-through curve obtained Fig. (50a) indicates that using flow rate of 1.0 ml/min.  $\text{Cu}^{2+}$  starts to break-through at 160 ml of effluent and complete break-through is achieved of at about 360 ml of effluent. Calculating the total amount of  $\text{Cu}^{2+}$  uptakes, showed that 4.186 mmol  $\text{Cu}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (4.6 mmol  $\text{Cu}^{2+}$ /g resin), the efficiency of the column using this flow rate is 91 %.

The elution of  $\text{Cu}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Cu}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (50). Also the capacity of the regenerated resin is reported in Table (14).

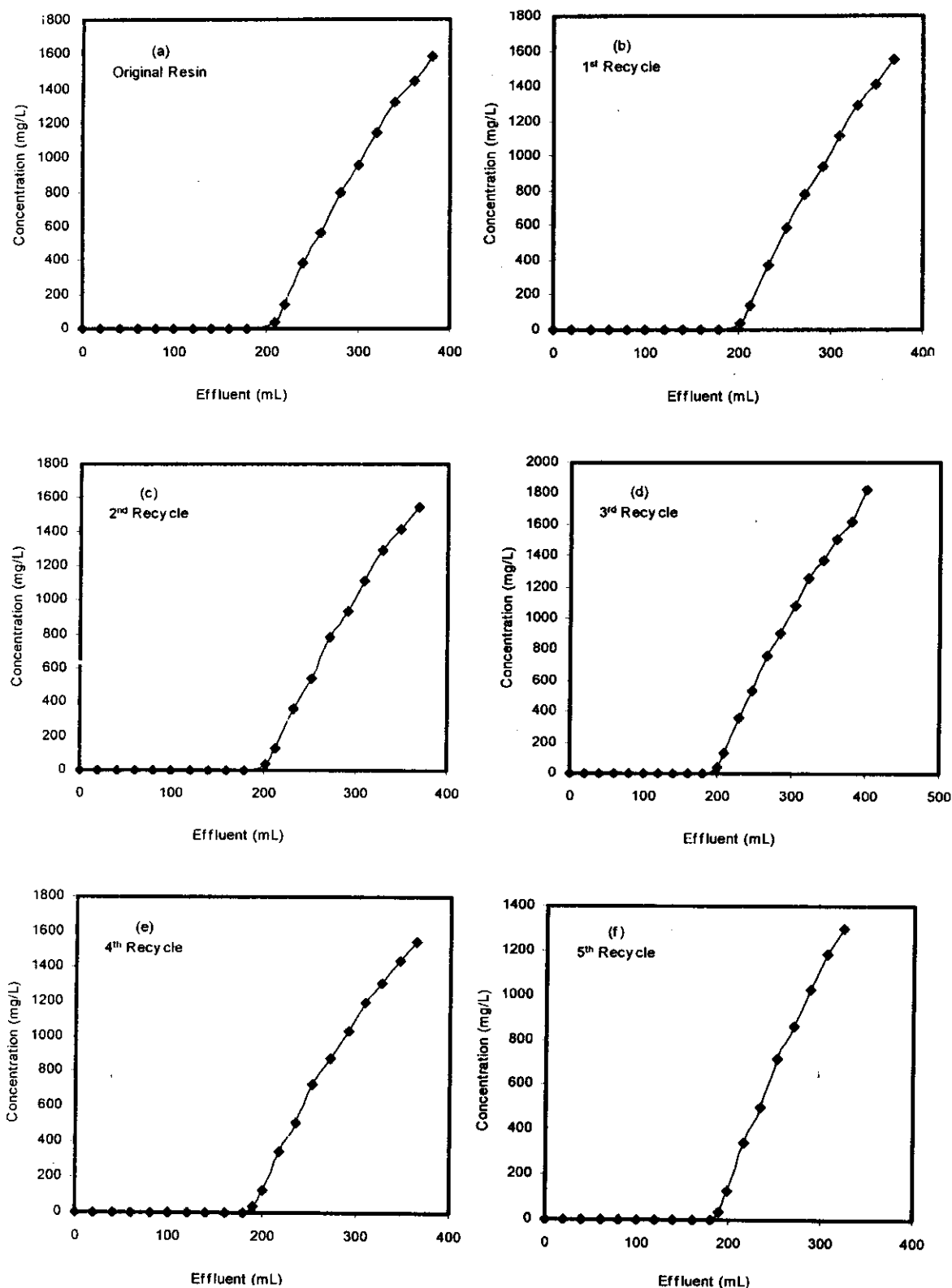


**Fig. (50):** Break-through curves for  $\text{Cu}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Cu}^{2+}$ , 533.7 mg/L (0.0084 M). Flow rate, 1ml/min., pH value, 5.0.

### III.3.3.3 Uptake of $\text{Pb}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Pb}^{2+}$  by a solution containing 1823.3 mg/l of  $\text{Pb}^{2+}$  (0.0088M) at pH 4.5. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (51). The break-through curve obtained Fig. (51a) indicates that using flow rate of 1.0 ml/min.  $\text{Pb}^{2+}$  starts to break-through at 210 ml of effluent and complete break-through is achieved of at about 420 ml of effluent. Calculating the total amount of  $\text{Pb}^{2+}$  uptakes, showed that 5.208 mmol  $\text{Pb}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (5.6 mmol  $\text{Pb}^{2+}$ /g resin), the efficiency of the column using this flow rate is 93 %.

The elution of  $\text{Pb}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Pb}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (51). Also the capacity of the regenerated resin is reported in Table (14).



**Fig. (51):** Break-through curves for  $\text{Pb}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Pb}^{2+}$ , 1823.3 mg/L (0.0088 M). Flow rate, 1ml/min., pH value, 4.5.



#### III.3.3.4 Uptake of $\text{Zn}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Zn}^{2+}$  by a solution containing 536.0 mg/l of  $\text{Zn}^{2+}$  (0.0082 M) at pH 5.0. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (52). The break-through curve obtained Fig. (52a) indicates that using flow rate of 1.0 ml/min.  $\text{Zn}^{2+}$  starts to break-through at 150 ml of effluent and complete break-through is achieved of at about 510 ml of effluent. Calculating the total amount of  $\text{Zn}^{2+}$  uptakes, showed that 4.895 mmol  $\text{Zn}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (5.5 mmol  $\text{Zn}^{2+}$ /g resin), the efficiency of the column using this flow rate is 89 %.

The elution of  $\text{Zn}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Zn}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (52). Also the capacity of the regenerated resin is reported in Table (14).

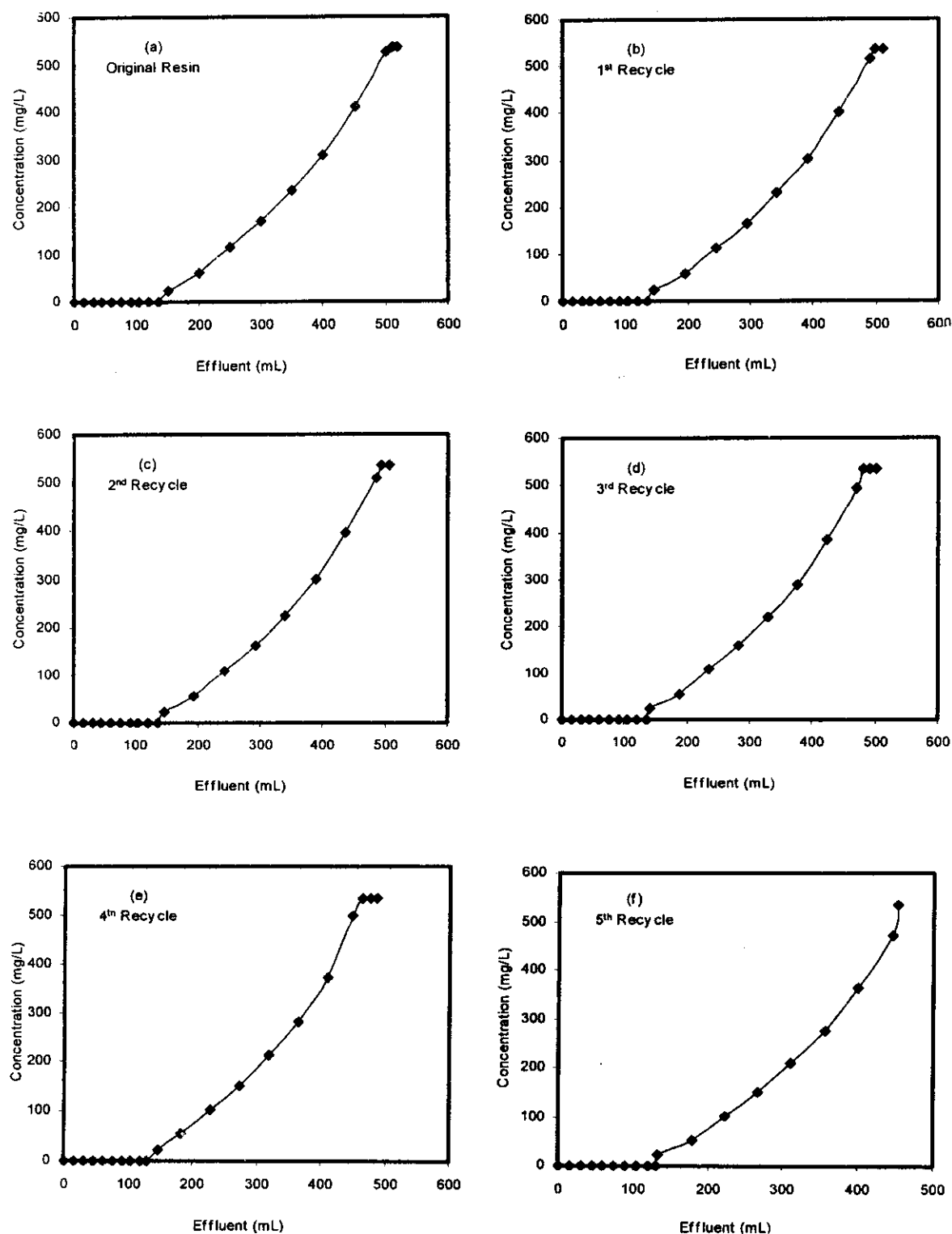


Fig. (52): Break-through curves for  $\text{Zn}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Zn}^{2+}$ , 536.0 mg/L (0.0082 M). Flow rate, 1ml/min., pH value, 5.0.

### III.3.3.5 Uptake of $\text{Cd}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Cd}^{2+}$  by a solution containing 1056.6 mg/l of  $\text{Cd}^{2+}$  (0.0094 M) at pH 6.0. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (53). The break-through curve obtained Fig. (53a) indicates that using flow rate of 1.0 ml/min.  $\text{Cd}^{2+}$  starts to break-through at 140 ml of effluent and complete break-through is achieved at about 420 ml of effluent. Calculating the total amount of  $\text{Cd}^{2+}$  uptakes, showed that 2.964 mmol  $\text{Cd}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (3.615 mmol  $\text{Cd}^{2+}$ /g resin), the efficiency of the column using this flow rate is 82 %.

The elution of  $\text{Cd}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Cd}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (53). Also the capacity of the regenerated resin is reported in Table (14).

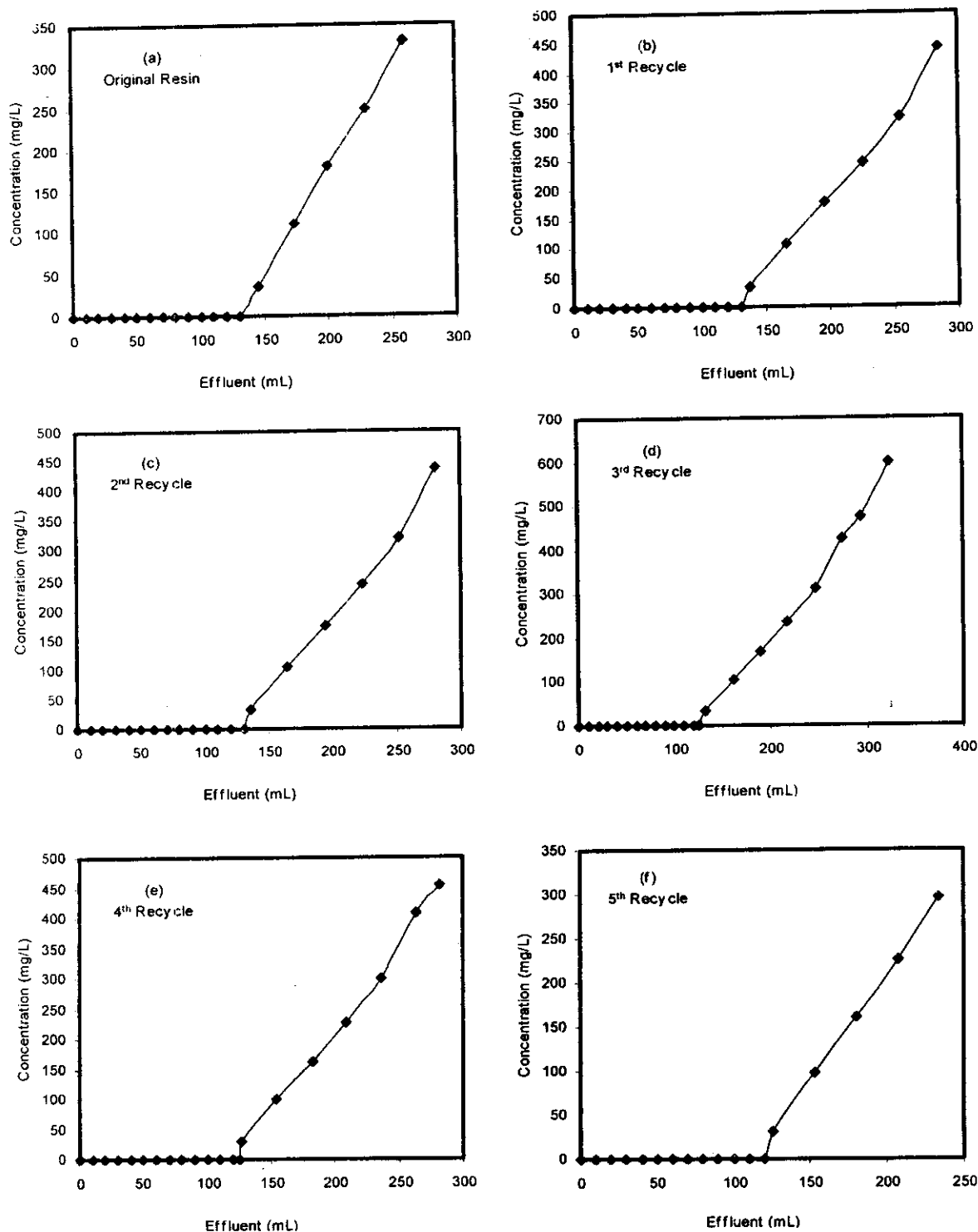


Fig. (53): Break-through curves for  $\text{Cd}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Cd}^{2+}$ , 1056.6 mg/L (0.0094 M). Flow rate, 1ml/min., pH value, 6.0.

### III.3.3.6 Uptake of $\text{Ni}^{2+}$ ion:

Column uptake tests were carried out for the removal of  $\text{Ni}^{2+}$  by a solution containing 551.9 mg/l of  $\text{Ni}^{2+}$  (0.0094M) at pH 5.0. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (54). The break-through curve obtained Fig. (54a) indicates that using flow rate of 1.0 ml/min.  $\text{Ni}^{2+}$  starts to break-through at 200 ml of effluent and complete break-through is achieved of at about 410 ml of effluent. Calculating the total amount of  $\text{Ni}^{2+}$  uptakes, showed that 3.212 mmol  $\text{Ni}^{2+}$ /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (3.53 mmol  $\text{Ni}^{2+}$ /g resin), the efficiency of the column using this flow rate is 91 %.

The elution of  $\text{Ni}^{2+}$  uptakes on the resin was completed by passing 20 ml of 2 M  $\text{HNO}_3$  solution through the column at the a flow rate of 0.25 ml/min. The effect of repeated use of the chelating resins on the sorption ability for  $\text{Ni}^{2+}$  was investigated in column operation. The break through curves of the regenerated resin are shown in Fig. (54). Also the capacity of the regenerated resin is reported in Table (14).

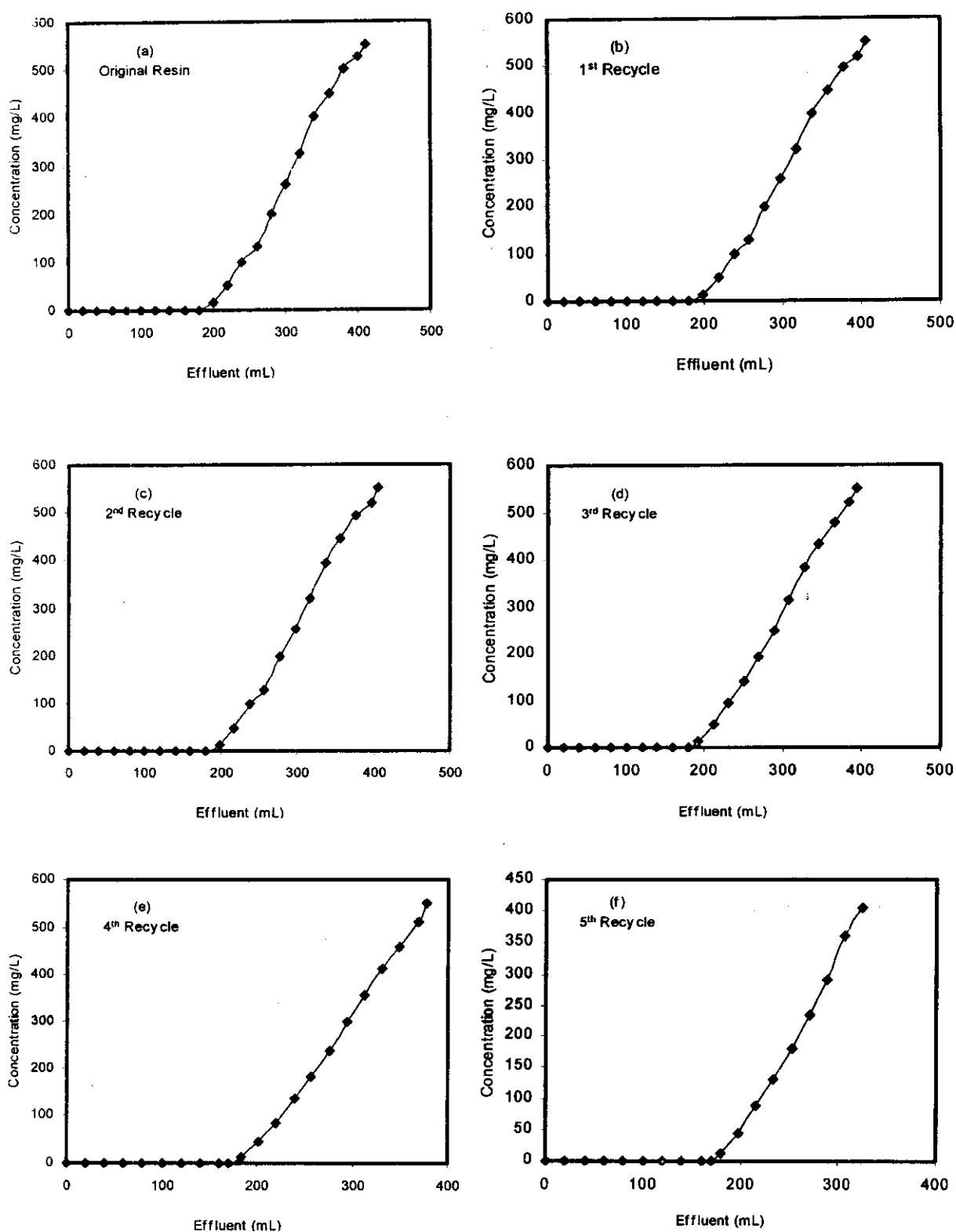
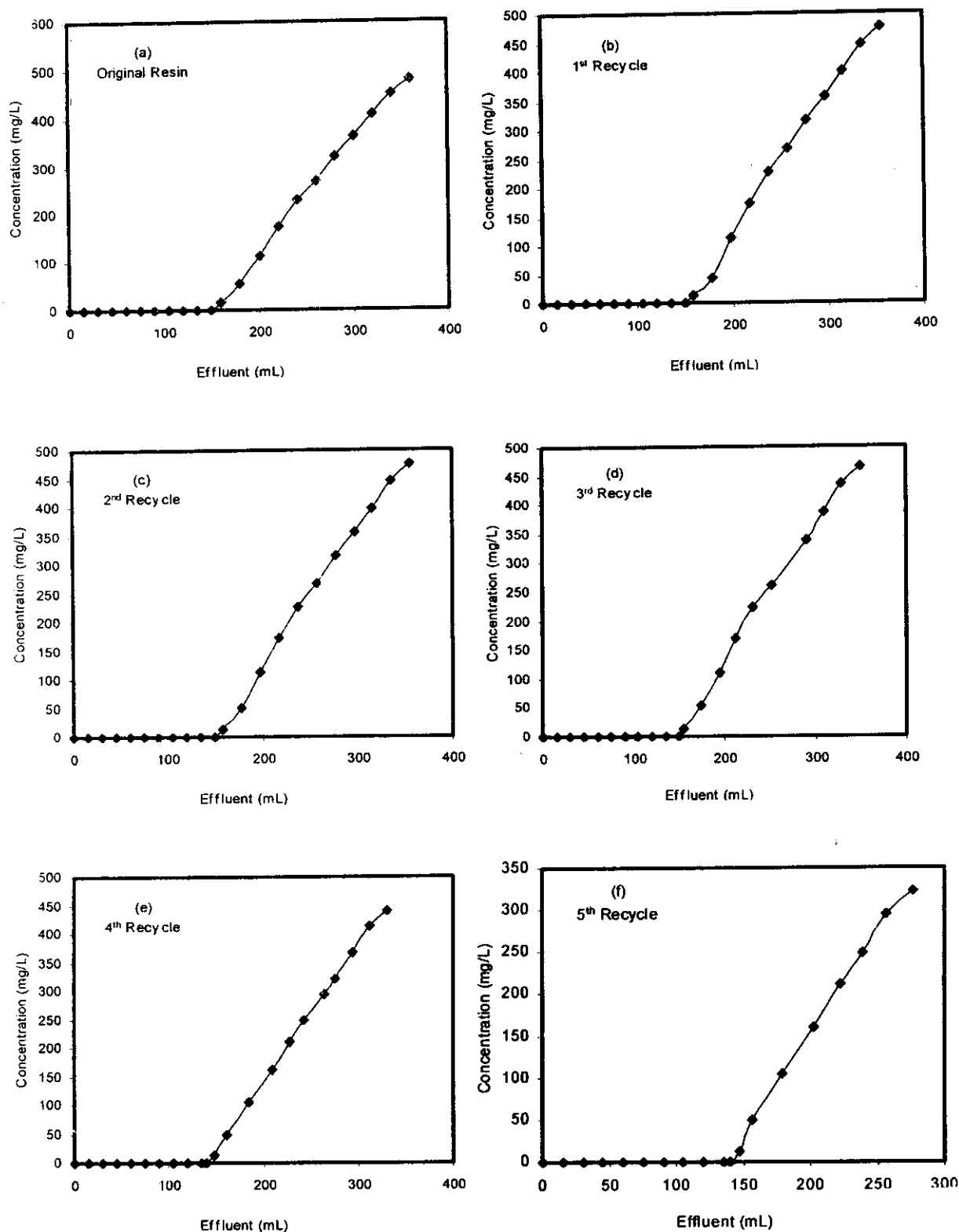


Fig. (54): Break-through curves for  $\text{Ni}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Ni}^{2+}$ , 551.9 mg/L (0.0094 M). Flow rate, 1ml/min., pH value, 5.0.



**Fig. (55):** Break-through curves for  $Mn^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $Mn^{2+}$ , 516.4 mg/L (0.0094 M). Flow rate, 1ml/min., pH value, 5.4.

### III.3.3.8 Uptake of $\text{Co}^{2+}$ ion:

Chelating resin was also found effective in column operation for the removal of  $\text{Co}^{2+}$ . Column uptake tests were carried out for the removal of  $\text{Co}^{2+}$  by a solution containing 530.4 mg/l of  $\text{Co}^{2+}$  (0.009 M) at pH 5.0. The solution continuously passed through a column packed with 1.0 g of the resin at a rate of 1.0 ml/min. The break-through curves are presented in Fig. (56). The break through curve obtained Fig. (56). Indicates that using flow rate of 1.0 ml/min,  $\text{Co}^{2+}$  starts to break-through at 200 ml of effluent and complete break-through is achieved of at about 410 ml of effluent. Calculating the total amount of  $\text{Co}^{2+}$  uptakes, showed that 3.648 mmol  $\text{Co}^{2+}$  /g resin was uptakes. Comparing this value with the calculated equilibrium value in batch method (3.8 mmol  $\text{Co}^{2+}$ /g resin), the efficiency of the column using this flow rate is 96%.

The recovery of  $\text{Co}^{2+}$  still remained incomplete this is presumably because  $\text{Co}^{2+}$  is partially oxidized on the chelating resin giving a much more stable ( $\text{Co}^{3+}$ -resin) complex <sup>(138)</sup>.



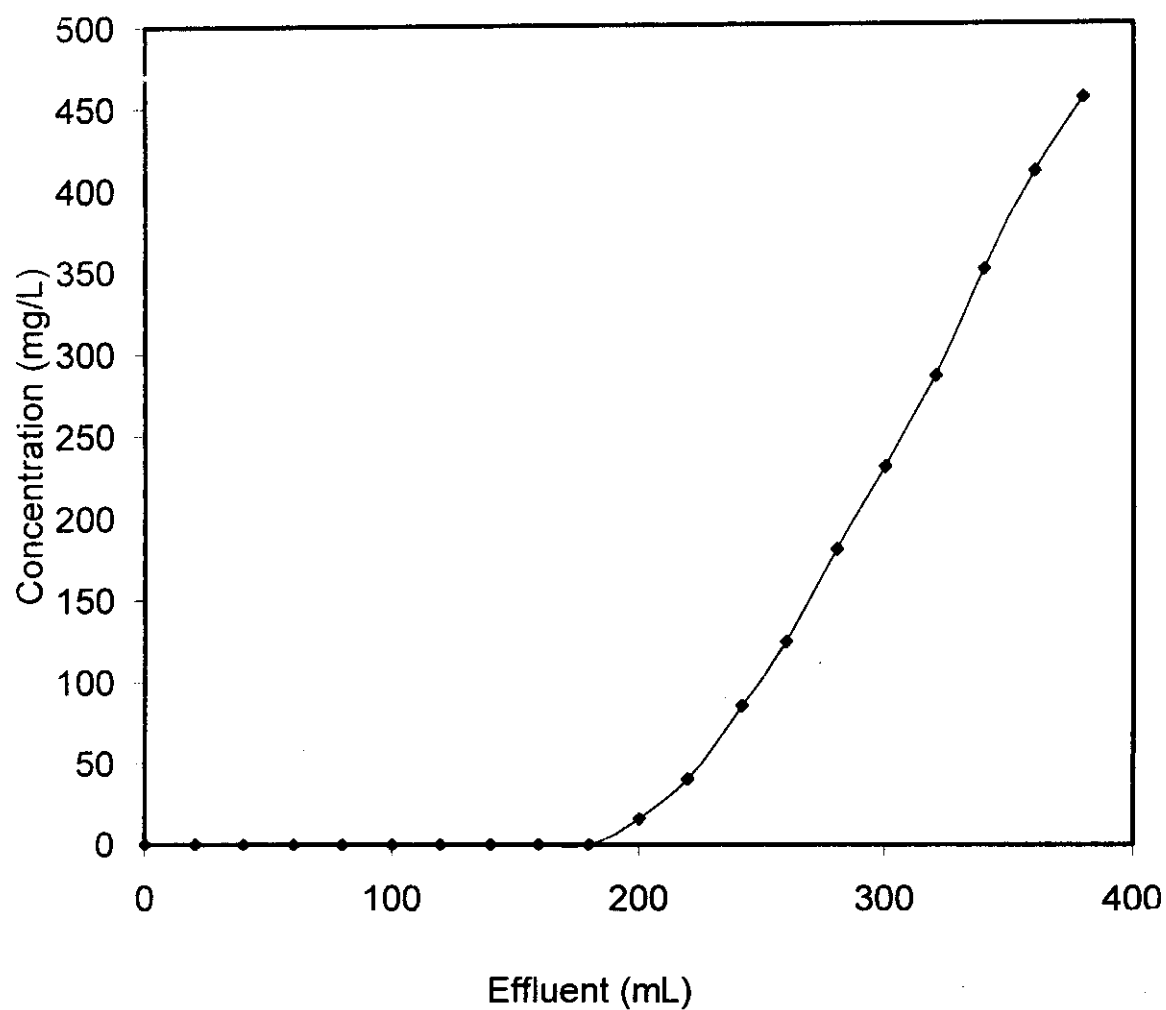


Fig. (56): Break-through curve for  $\text{Co}^{2+}$ . Amount of resin, 1.0g. Initial concentration of  $\text{Co}^{2+}$ , 530.4 mg/L (0.009 M). Flow rate, 1ml/min., pH value, 5.0.

### III.4 The effect of ionic radius and type of chelating resin on the uptake of mixture of metal

The effect of ionic radius and type of chelating resin on the uptake of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  ions can be obtained from the comparison shown in Table (15) and Fig. (57). From the given data in Table (15), the following points can be abstracted:

- 1-  $\text{Co}^{2+}$  (0.65 Å) is too small and can easily diffuse through the resins, whereas  $\text{Hg}^{2+}$  is too big (0.96 Å) and faces a very higher resistance solution inside its diffusion through the resins.

So, we can say that, as the ionic radius increases the uptake of metal ions through the resins decrease.

- 2- The chelating resins was highly effective for the uptake of metal ions, and the capacity increased according to the following:



The factor affecting on the efficiency of resin is the coordination groups content "composition factor". For (XXXII) resin, it have two amino groups, but (XXXIII) resin have one amino group and one hydroxyl group, because that amino group is more efficiency in coordinated with metal ions than hydroxyl group, we showed that the efficiency of (XXXII) resin is more than that of (XXXIII). But in case of (XXXIV) resin it have one amino group with one oxygen and two nitrogen atoms, each of them have lone pair of electrons which can be donated to form chelation with different metal ions, therefore (XXXIV) resin is the highest efficiency for uptaking metal ions.

According to the above, we can arrange the efficiency of the resins in the following order:



In Egypt, the concentration of total heavy metal ions in wastewater is severely controlled by law environment 4 (1994) to be 5 mg/l. The results presented here indicate the practical applicability of the chelating resin (XXXII), (XXXIII) and (XXXIV) for the final stage of waste water treatment, after the general procedure for removal of meal ions.

**Table 15:** Effect of each ionic radius and the type of chelating resin on uptake of metal ions.

Metal ions	Ionic radius	Capacity (mmol. metal ion/g resin)		
		(XXXII)	(XXXIII)	(XXXIV)
$\text{Cu}^{2+}$	0.73	1.3	1.19	1.4
$\text{Zn}^{2+}$	0.74	0.702	0.647	0.910
$\text{Ni}^{2+}$	0.69	1.33	1.28	1.49
$\text{Co}^{2+}$	0.65	1.469	1.381	1.72
$\text{Cd}^{2+}$	0.95	0.502	0.424	0.583
$\text{Hg}^{2+}$	0.96	0.333	0.307	0.346

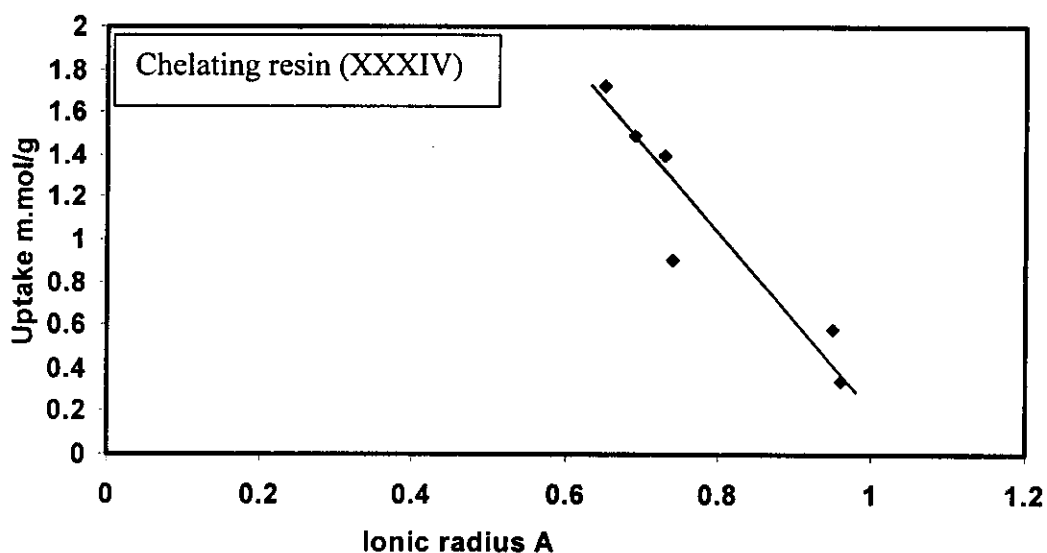
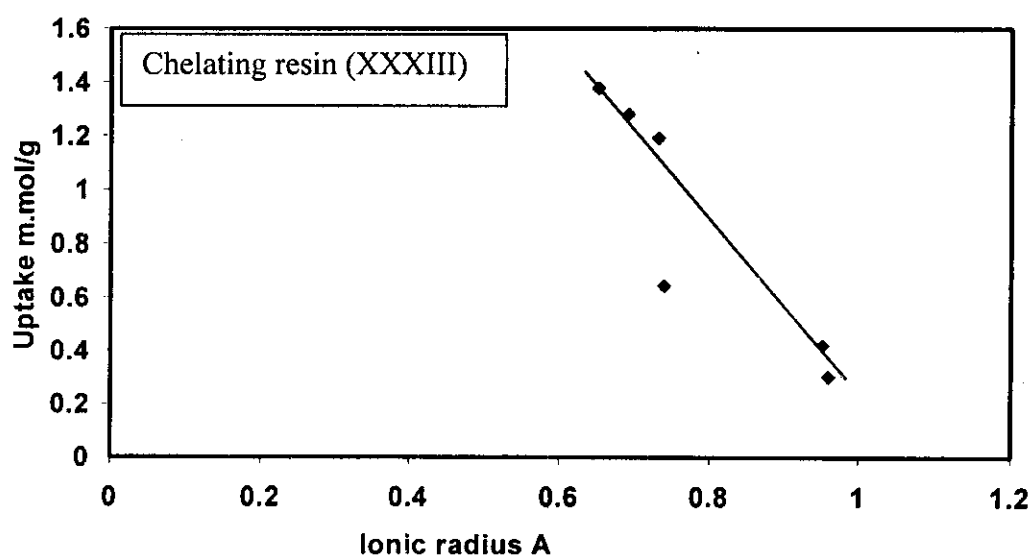
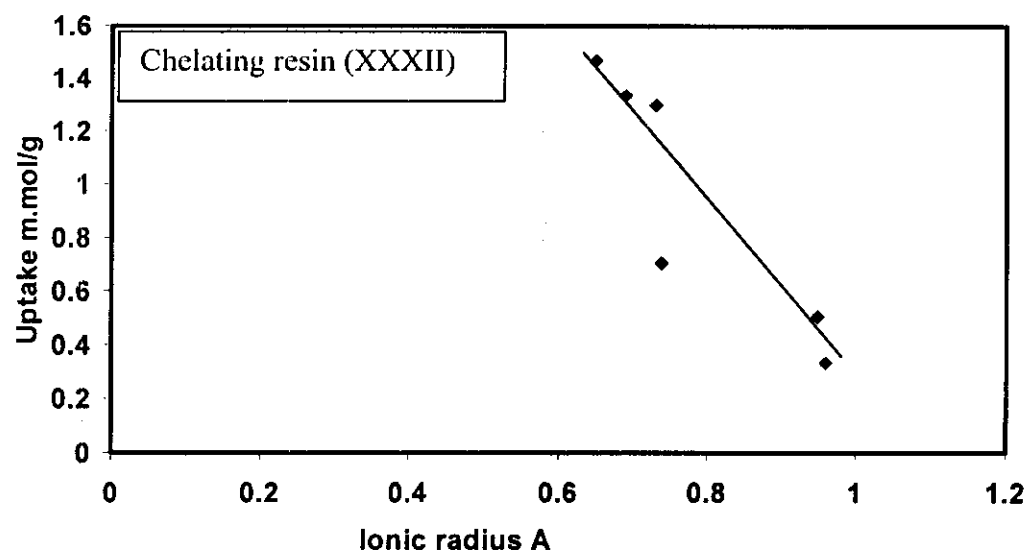


Fig. (57): Effect of each ionic radius and the type of chelating resin on uptake of metal ions.

### **III.5 Proposed flow-sheet for wastewater treatment:**

#### **Reaction tank:**

In the first treatment stage, the pH of wastewater in the reaction tank is adjusted over pH range 8.0-8.5 by dosing sodium hydroxide. In this pH range, the metal ions precipitate as insoluble hydroxides, and organic polyelectrolyte (coagulant) such as is added to stimulate flock formation and improve its setting characteristics (Fig. 58).

#### **Clarifier:**

The wastewater treated in the reaction tank will settle in the clarifier, the clean effluent will overflow and the sludge will be drawn off regularly for dewatering.

#### **Sludge handling:**

The sludge from the bottom of the clarifier drawn off and piped to the dewatering station. The sludge is collected in bags made of special purpose materials, allowed to drip dry and removed for disposal in an approved manner.

#### **Adjusting tank:**

Clear pre-treated effluent will overflow from the clarifier to the adjusting tank, and the pH of the pretreated water is adjusted to 7.0 by dosing sulphuric acid.

#### **Chelating resin column:**

In the stage, pretreated water is pumped into the chelating resin column where uptake of industrial metal ions takes place at pH 7.0. The final effluent will be partially reused or discharged as required, and in accordance with the current regulations for the limit of release or reuse.

In industrial wastewater treatment it is more economic to use the equalizer instead of reaction tank, clarifier and adjusting tank. In equalizing tank pH adjustment as well as the precipitation of heavy metal hydroxides take place Fig. (59) illustrates the simplified flow sheet of industrial wastewater treatment.

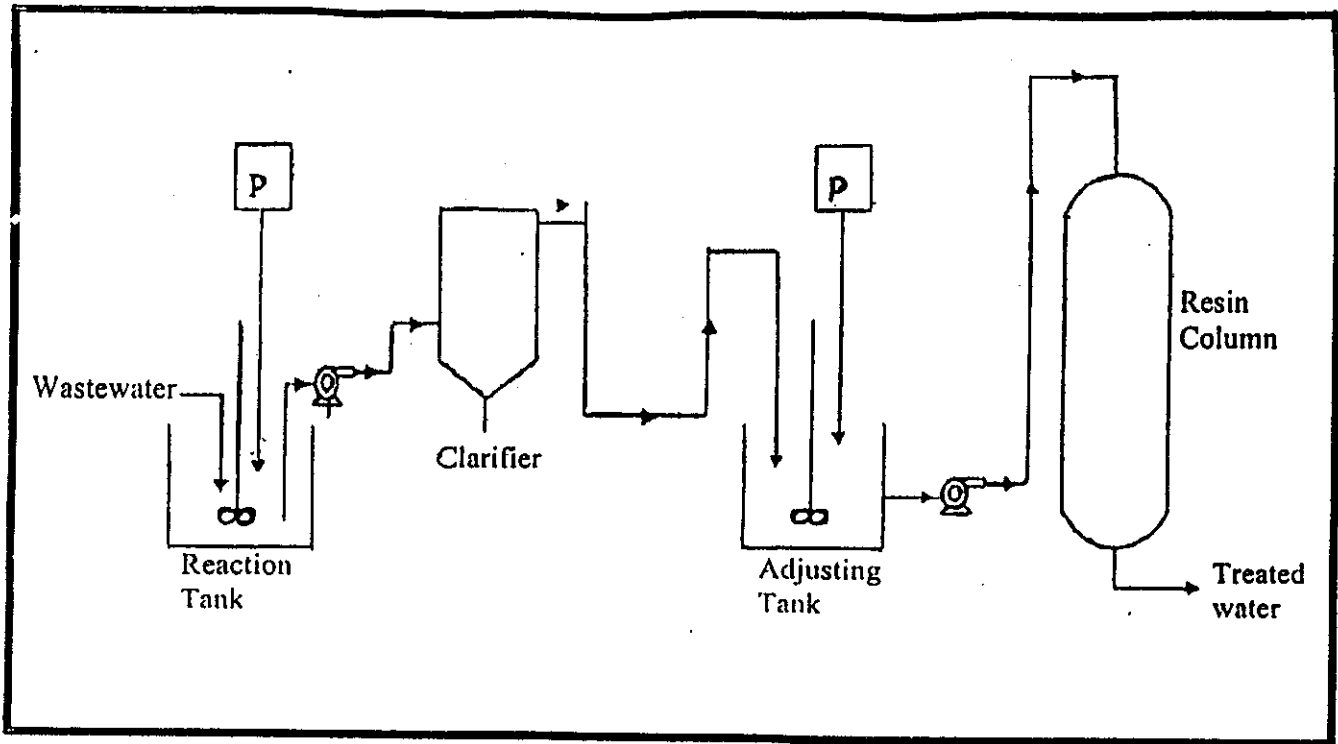


Fig. (58): Proposed flow sheet of wastewater treatment

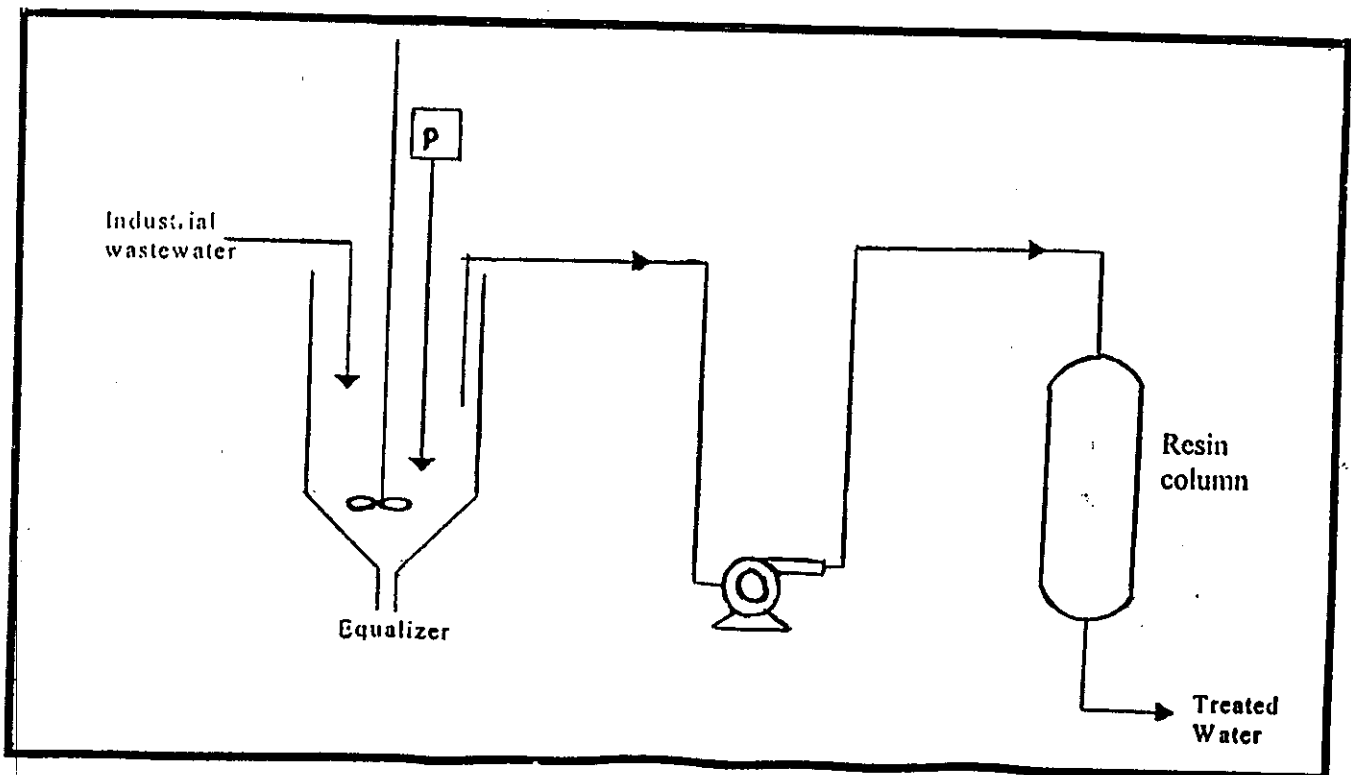


Fig. (59): Simplified flow sheet of industrial wastewater treatment.