



Synthesis and Applications of Polymer Chelating Resins Containing Schiff Base

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In this article, a series of Schiff-base compounds is prepared by condensing aromatic dialdehydes and diamines in the presence of *p*-toluenesulfonic acid as catalyst. The prepared Schiff bases are characterized by CHNS/O, NMR and FTIR techniques. Moreover, analytical applications of Schiff bases as chelating agent was evaluated by loading (20 %) of compounds (B and C) the urethane foams. Furthermore, chelating resins type P1 (B) and P2 (C) are also prepared by loading the Schiff base into polymer backbones. Moreover, the batch process is used to study the ability of these resins in recovering metals ions, such as (Mg²⁺, Pb²⁺, Cu²⁺, Cr³⁺, Ni²⁺, Co²⁺, Cd²⁺ and Ca²⁺). The study is performed by considering the contact time and pH value. Finally, the polymer's maximum loading capacity is in the following sequence: P1 (B) Co²⁺ > Cr³⁺ > Mg²⁺ > Ni²⁺ > Cd²⁺ > Ca²⁺ > Pb²⁺ > Cu²⁺; P2 (C) Mg²⁺ > Cd²⁺ > Ca²⁺ > Co²⁺ > Pb²⁺ > Cu²⁺ > Cr³⁺.

Keywords: Schiff base, Dialdehydes, Diamines, Chelating resin, Metal ions.

INTRODUCTION

Among the different kinds of organic materials, Schiff base or azomethine is a compound containing functional group. Depending on the groups attached to HC=N of Schiff base, these materials are also well-known as (a) imines [1,2]; (b) di-imines when derived from amines and (c) ketamine's when derived from ketones [3]. Schiff-bases have large applications in different fields and have got the wide attention to several researchers, scientists and technologists [4]. Schiff base and their complexes have an essential role in the industrial fields; it can be used as antioxidants and corrosion inhibitors [5].

Chelating resins also (known as specific exchangers, or chelating sorbents) are a subgroup of ion exchange resins, which contain active donor atoms or probes (antenna), such as (P, O, S and N) within their chemical structures. These donor atoms (or probes) are able to coordinate with different metal ions that surrounded them in solution [6]. Chelating resins are capable of recovering many of metallic ions from their aqueous solutions [7]. This can be performed by a batch process or through an extraction column, in which the resin is supported unto silica gel, or glass support [8,9]. The selectivity of these

resins depends mainly on the nature of ligand (antenna) within the resin backbone and pH values of the surrounded medium [10,11]. The uses of the chelating polymers can be summarized as (a) used as protective coatings on the metal's surfaces [12]; (b) utilized in manufacturing the heat resistant fibers used in the semiconductors [13]; (c) used as a membrane in the manufacturing of ionic selective electrodes [14]; (d) can be applied as a green analytical reagent, specifically, involves separating and concentrating of the copper ions from the aqueous solutions, by using the silica gel supported to aurintricarboxylic acid [15]; and (e) used as catalysts for specific chemical reactions such as oxidation, hydrogenation, hydrolysis and as polymeric initiators [16].

EXPERIMENTAL

Preparation the standard metals ions solutions: The standard solutions were prepared by dissolving different metal nitrate (of copper, chromium, magnesium, nickel, cadmium, calcium, lead or copper) in a small amount of water and 2 mL of conc. HNO₃ followed by the addition of demineralized water upto 500 mL.

Preparation of Schiff-base: Into a round bottom flask equipped with a condenser, 0.02 mol of amine dissolved in 15 mL of ethyl alcohol, 0.25 g of *p*-toluene sulphonic acid and 0.01 mol of glyoxal dissolved in 20 mL of ethyl alcohol were added. The reaction mixture was refluxed for 5 h and then cooled to room temperature. The precipitated product was collected and recrystallized from absolute ethanol.

Preparation of polystyrene (Type B): In a small beaker, polystyrene (0.01 mol) is dissolved in 25 mL of absolute ethyl alcohol and then 0.25 g of *p*-toluene sulphonic acid was added. The reaction mixture was then heated with constant stirring for 15 min. Another 20 mL of ethyl alcohol and 10 mL of *ortho*-hydroxybenzaldehyde were added to the reaction vessel. The reaction mixture was refluxed for 8 h followed by cooling to the room temperature. The obtained precipitate was collected as crystals and dried in a vacuum oven.

Preparation of chelate resin (P1) with metal ions: Into a round bottom flask provided with dropping funnel, magnetic stirrer, condenser and inlet-outlet N₂ tube, 0.01 mol; 2.5 g of Schiff base and the same amount of phenol were added. Then 50 mL of formaldehyde was added to the reaction vessel followed by adjusting the pH by adding sodium hydroxide solution (5 mL; 5 %) until pH = 9.5. Then, the reaction was then refluxed with stirring for 8 h.

After completion of the reaction, a soft jelly substance was formed and then treated with phosphoric acid until reached pH = 7.0-7.5. The solvent was removed by evaporation and the final product was dried at 120 °C for 2 h for further curing. The obtained resin was grinded, washed thoroughly with distilled water and dried. Consequently, Fig. 1 shows the proposed structure of the chelate resin P1 (C).

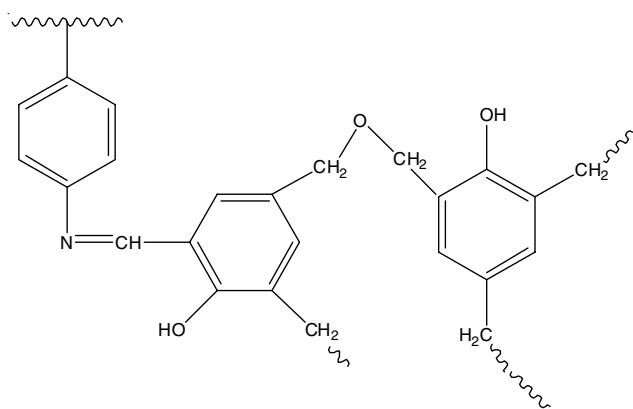


Fig. 1. Speculative chemical structure of P1 (C)

Preparation of chelate resin (P2) with polystyrene (Type B): Polystyrene (Type B) (0.01 mol; 2.4 g), phenol (0.05 mol; 0.47 g) and 50 mL of formaldehyde was added to the reaction vessel. The pH of the reaction mixture was adjusted by adding sodium hydroxide solution (5 mL; 5 %) until pH becomes 9.5. The reaction was then refluxed with stirring for 6 h. After completion of the reaction, a soft jelly substance was formed and then treated with phosphoric acid until pH = 7.0-7.5. The solvent was removed by evaporation and the final product then dried at 120 °C for 2 h for further curing. The obtained resin was grinded, washed thoroughly with distilled water and then dried. Fig. 2 illustrates the suggested chemical structure of chelate resin P3 (B).

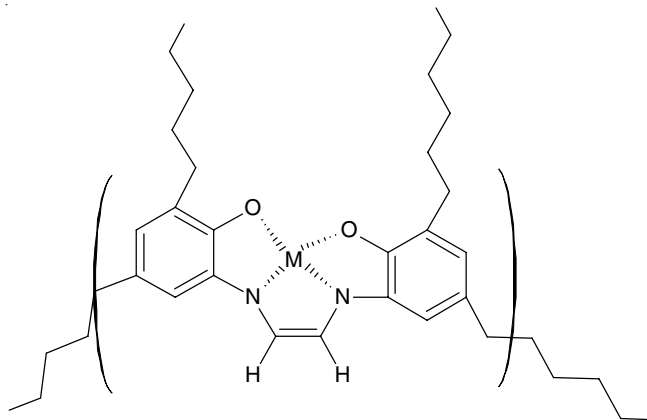


Fig. 2. Suggested chemical structure of the chelate resin P3 (B)

RESULTS AND DISCUSSION

¹H NMR study: ¹H NMR spectra showed a singlet peak at $\delta = 2.5$ ppm belongs to the protons of non-deuterium DMSO traces exists in the deuterium one. Another singlet peak at $\delta = 3.3$ ppm due to the presence of traces of water in the DMSO solvent. Proton NMR spectra for monomer (M) revealed a singlet peak at $\delta = 5.67$ ppm, which correspond to the hydroxyl proton and a singlet at $\delta = 8.36$ ppm is related to the Schiff base proton. Doublet located at $\delta = 6.78$ - 6.79 ppm was attributed to the proton at position-4 of benzene ring. On the other hand, the proton adjacent to carbon that bears hydroxyl group presented a doublet at $\delta = 7.13$ - 7.14 ppm. Triplet peaks at $\delta = 6.99$ ppm, $\delta = 7.19$ ppm belong to the protons at positions (2 and 3) of the benzene ring.

Infrared spectra for the prepared Schiff-bases: All the synthesized Schiff-bases revealed a strong to medium peaks at 1658-1608 cm⁻¹ attributed to the stretching vibration of the azomethine linkages. Disappearing of the symmetric and asymmetric peaks at 3400-3300 cm⁻¹ related to the amine groups of the primary amine, peaks of C-H aldehyde at 2720 cm⁻¹ and peaks corresponding to the carbonyl group at 1710-1685 cm⁻¹ were clearly observed.

Infrared spectra of chelating resins P1 (B) and P2 (C): IR spectra of the resins exhibited an absorption band at 2950-2920 cm⁻¹ and an absorption band at 3461-3406 cm⁻¹ correspond to the stretching vibrations of CH₂ aliphatic and hydroxyl groups, respectively. Table-1 summarizes the key absorption peaks of chelating resins P1 (B) and P2 (C).

Chelation efficiency of P1 (B): Batch process has been used to study the analytical efficiency of resin P1 (B) towards a number of metallic ions such as Ca²⁺, Cd²⁺, Co²⁺, Ni²⁺, Cr³⁺, Cu²⁺, Pb²⁺ and Mg²⁺. The studied ions (Cd²⁺, Co²⁺, Ni²⁺, Cr³⁺, Cu²⁺ and Pb²⁺) presented a high response towards chelate resin.

Effect of contact time on the maximum loading capacity of P1 (B): It is observed that by increasing the contact time for the solutions of the ions, the resin loading capacity became higher. The ions (Ca²⁺, Cd²⁺, Co²⁺, Ni²⁺, Cr³⁺, Cu²⁺, Pb²⁺ and Mg²⁺) reached to the equilibrium after about 8 h from their existing in solution together with the chelate resin. The increase in the loading capacity then went down gradually until reaching the higher contact time (24 h). Table-2 shows the effect of contact time on the loading capacity of P1 (B) with metallic ions at specific pH.

TABLE-1
INFRARED SPECTRAL DATA (ν_{\max}) OF THE FUNCTIONAL GROUPS OF THE PREPARED FOAMS

Code	IR ν (cm^{-1})				
	OH	CH ₂ aliphatic	C=C aromatic	C=N	C-N
P1(B)	3406.05	2920.03	1481.23	1602.74	1276.79
P2(C)	3461.99	2950.01	1496.66	1610.45	1257.50

TABLE-2
NUMBER OF MILLIGRAMS OF IONS (Mg^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Cr^{3+} , Cu^{2+} and Pb^{2+}) RECOVERED BY (0.1 g) OF RESIN P1 (B) AS A FUNCTION OF TIME AT DIFFERENT pH VALUES

Ions	pH	Loading capacity (mg/g resin)					
		Contact time (h)					
		0.5	1	3	6	8	24
Ca^{2+}	2	7.5	7.6	7.8	8.2	8.7	10.1
	4	7.7	7.8	8.1	8.8	9.4	10.4
	6	7.9	7.9	8.6	9.0	9.9	10.7
	8	7.9	8.0	8.9	9.6	10.0	11.2
Cr^{3+}	2	18.7	18.7	18.8	19.0	19.6	19.9
	4	19.0	19.2	19.5	19.8	20.1	20.4
Pb^{2+}	2	3.9	4.1	4.4	4.9	5.2	5.7
	4	4.9	5.0	5.4	6.1	6.6	6.9
	5.5	5.3	5.7	5.9	6.4	6.9	7.3
Cu^{2+}	2	2.7	2.8	3.0	3.6	4.1	5.0
	4	3.0	3.3	3.8	4.4	4.9	5.3
	6	3.8	3.9	4.2	4.8	5.5	6.0
Mg^{2+}	2	9.2	9.3	9.9	10.6	11.8	12.1
	4	9.3	9.3	10.4	10.9	12.0	12.4
	6	9.5	9.5	10.9	11.4	12.7	13.3
Cd^{2+}	2	7.3	7.5	8.1	9.3	9.9	10.2
	4	7.3	7.7	8.5	10.0	10.8	11.5
	6	7.5	7.9	9.0	10.2	10.9	11.7
Ni^{2+}	2	7.6	8.2	8.8	9.6	10.4	10.9
	4	7.7	8.5	9.2	10.7	10.5	11.0
	6	7.9	8.8	10.0	10.9	11.3	11.8
	8	8.1	9.0	10.7	11.2	11.9	12.6
Co^{2+}	2	17.9	18.0	18.7	19.4	20.2	20.5
	4	18.1	18.6	18.9	19.8	21.3	21.7
	6	18.4	18.5	19.1	20.0	21.6	22.0

Effect of pH on the efficiency of P1 (B): The experiments showed that the pH value has a significant effect on the loading efficiency of the resin under study and with almost all of the studied ions. The maximum loading capacity for the resin P1 (B) appeared to be at higher pH value and at almost all contact times. Figs. 3-8 show the effect of pH on the loading capacity of P1 (B) towards the ions and at different contact times.

Conclusion

In this work, a number of experiments have been carried out. In the first part, we conducted preparation of the following;

firstly, a preparation of a series of Schiff-bases compounds from the reaction of an aromatic dialdehyde and di-amine. Secondly, preparation of chelate resins by loading (20 %) of compounds (B and C) the urethane foams. Lastly, chelating resins type P1 (B) and P2 (C) were prepared by loading the Schiff base ligands into polymer backbones. The infrared spectra for the prepared Schiff-bases and the chelating resins (P1 (B) and P2 (C)) have been described. Finally, the efficiency of the prepared chelating resins was studied. It is observed that by increasing the contact time for the solutions of the ions under study, the resin loading capacity became higher.

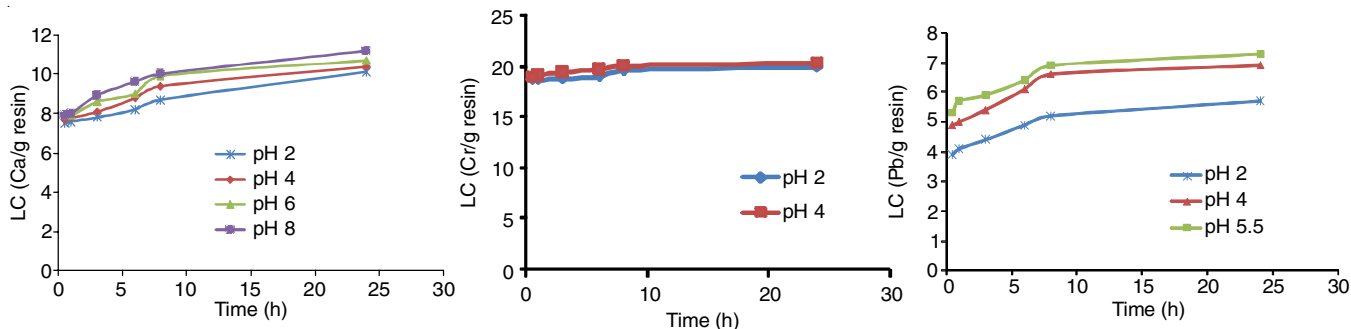


Fig. 3. Impact of contact times on the loading capacity of P1 (B) with metallic ions (Ca^{2+} , Cr^{3+} and Pb^{2+}) at a specific pH value

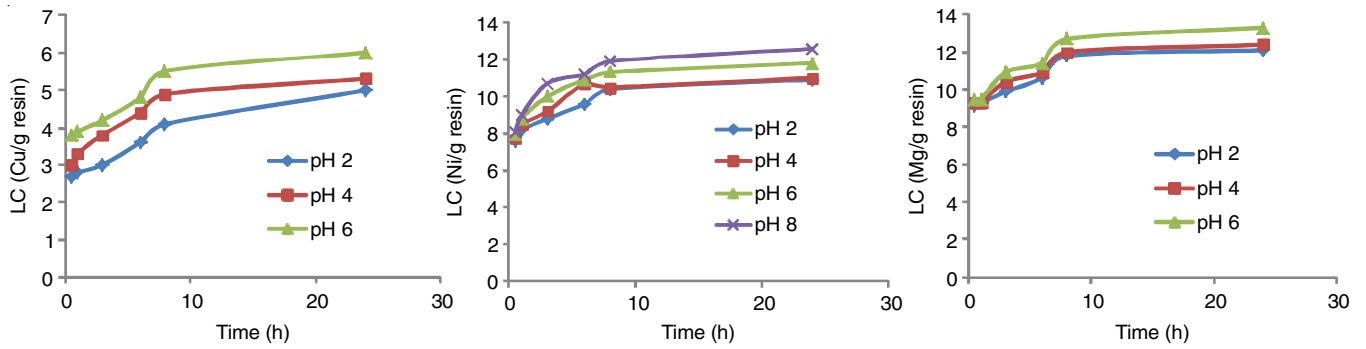


Fig. 4. Effect of contact times on the loading capacity of P1 (B) with metallic ions (Cu^{2+} , Ni^{2+} and Mg^{2+}) at a specific pH value

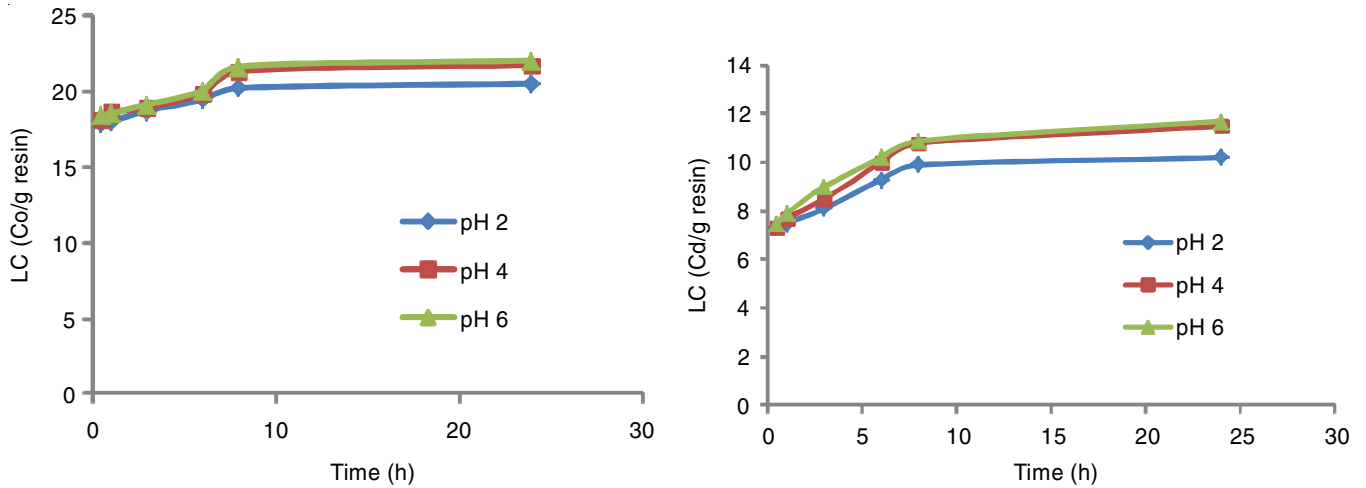


Fig. 5. Effect of contact times on the loading capacity of P1 (B) with metallic ions (Co^{2+} and Cd^{2+}) at a specific pH

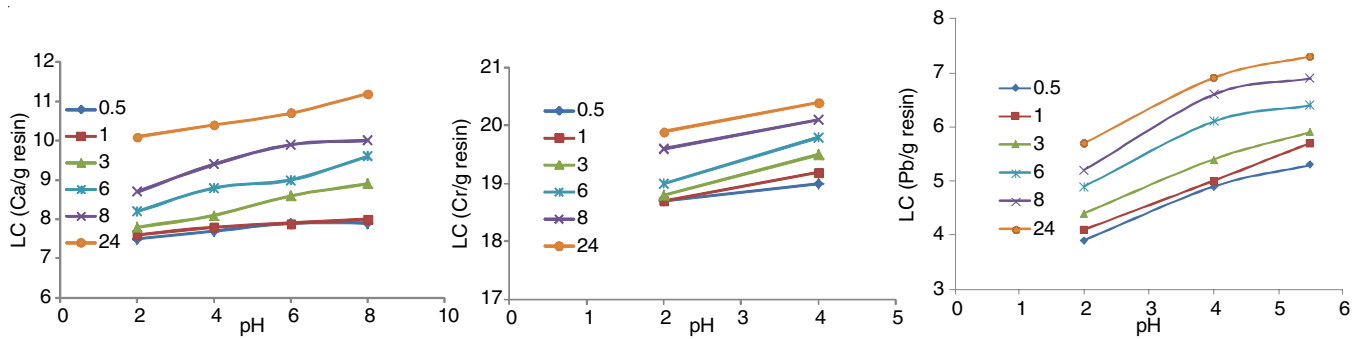


Fig. 6. Effect of pH values on the loading capacity of P1 (B) towards the ions (Ca^{2+} , Cr^{3+} and Pb^{2+}) under investigation at different contact times

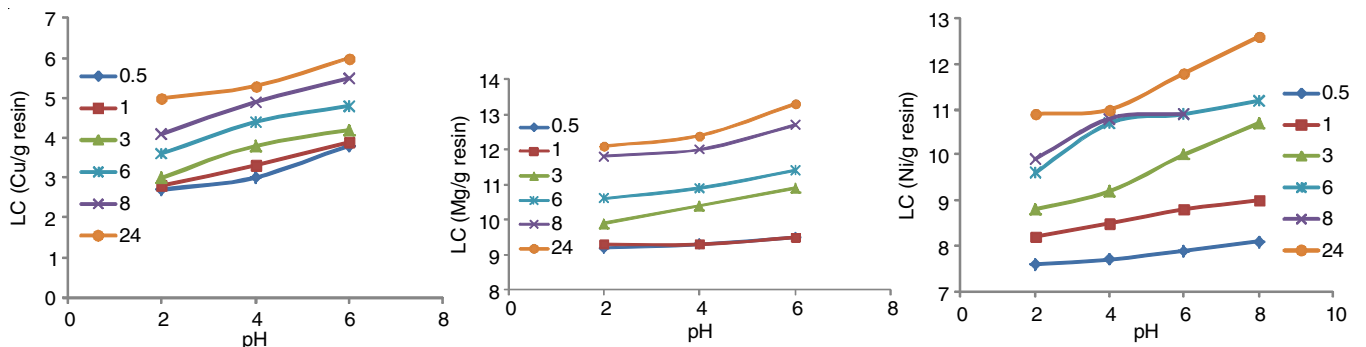


Fig. 7. Effect of pH values on the loading capacity of P1 (B) towards the ions (Cu^{2+} , Mg^{2+} and Ni^{2+}) under investigation at different contact times

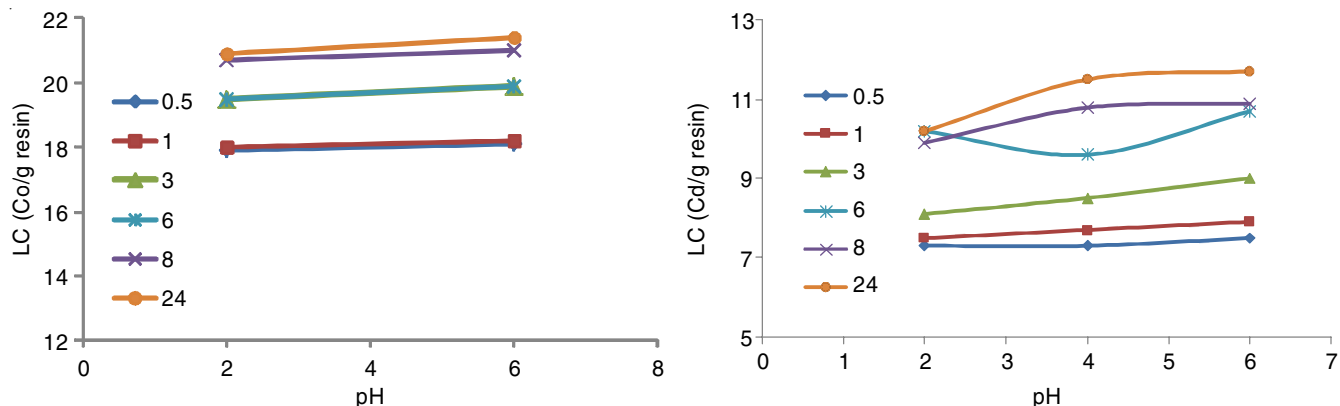


Fig. 8. Effect of pH values on the loading capacity of P1 (B) towards the ions (Co^{2+} and Cd^{2+}) under investigation at different contact times

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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