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Adsorption of Cd and Pb metal ions onto chelating resin and their application in removal of lead from battery factory wastewaters

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Lead is one of the most used metals in various factory activities. The contamination of soil and water with the metal has become a real or major environmental and public health problem or concern. Therefore, removal this toxic metal from wastewaters is a great challenge to protect environment and people. This study aims to assess adsorbing properties by batch procedure of a chelating ion exchange functionalized by iminodiacetic acid group toward Pb and Cd by varying the concentration of these metals at different contact times and at a given *p*H. In the second step, this adsorbent support is used in dynamic condition in a column for the removal of Pb particularly from effluents from an industrial unit. Finally, the exchange material, packed in bed, is regenerated in order to establish its reusability and efficiency in removing process. The adsorption rate of Pb and Cd onto the chelating adsorbent increases as the initial content and time contact increase and the maximum adsorption capacity is found to be 137.40 and 90.40 mg/g at the plateau of saturation, respectively. In a column, the adsorbing support or material reduce totally the concentration of loaded Pb in effluents during the two first cycles. During the third cycle, the removal power is still good and the content of Pb in the washing is reduced from 22 mg/L to 0.014 mg/L which is lower than the law's discharge levels. The regeneration of the support is achieved by 10 volume bed of 1 M HCl during thirty minutes at least. These results demonstrate clearly the effectiveness of the chelating adsorbent in removing lead from the effluents of the factory and its reusability in numerous cycles after a regeneration stage.

Keywords: Chelating sorbent, Industrial wastewaters, Lead and Cadmium adsorption, Adsorption isotherm, Lead removal

Lead is one the most useful metal in industry particularly in the production and recycling of batteries accumulators or and metal extraction and finishing activities (second fusion) that consume annually nearly 70% of the total production in the world[1]. These activities are the main sources of contamination of employees and environment by this toxic heavy metal pollutant. Pollution by lead wastewaters, discharged directly or indirectly in environment, is growing in developing countries that will affect or cause health hazards in humans[1]. In fact, repeated exposures to lead produce various metal intoxications in numerous organs and tissues particularly neurological, urological and hematological toxicities mainly in human and particularly in children who are more vulnerable[1].

So, to counteract these deleterious effects, the public health and environmental institutions have adopted more stringent constraints legislation on wastewaters containing heavy toxic metal disposal, that inflict industrials and factories their treatments before release them in nature at the requirement levels. Different technologies of treatment have been used and evaluated in removing toxic metals from industrial effluents based on various chemical or physical principles including precipitation by hydroxides, carbonates or sulfides that forming insoluble complex with heavy metal[2], adsorption on kaolinite and montmorillonite[3] and on vegetable matter by products4, bioadsorption on lignin, algae and microbial biomass[5-7], membrane filtration[8] and electrochemical methods such as electrocagulation and electrowinning[9-11].

Among the heavy metal removal technology which has received a great consideration compared to the previous mentioned methods, is the ion exchange process on chelating resin. This method is very simple and effective for removing various heavy metals from solution with a high capacity treatment in addition of its economical importance due its relatively clean and energy efficient and reusability[12]. Chelating resins are ion exchangers with specific functional groups like iminodiacetic acid (IDA), have been widely used to study the adsorption and the recovery of heavy metals from wastewaters[12,13]. The IDA chelating resins have shown particularly higher selectivity for transition metals than alkali metals because this group, in addition of exchange phenomenon, can provide electron pairs to form a stable coordination bond with divalent metals. Therefore, it can be considered as a powerful method in removing metal ion from metal mixtures[12,13]. Effectively, various matrix possessing iminodiacetic acid functional group such as styrene divinyl benzene (Chelex 100, amberlite 748 and Lewatit TP 207 and 208)[14-25], magnetic glycidyl methacrylate (GMA) styrene divinyl benzene[26], polyurethane foam[27] and amino methyl polystyrene (AMPS)[28] were used in numerous studies of adsorption and removal of metals from industrial effluents varying different parameters like *p*H, contact time, temperature and metal ion concentration. In terms of effectiveness, high adsorption capacities and selectivity of the functionalized chelating adsorbing supports towards metal aqueous solutions, leachates or waste effluents have been established.

The objective of this search is to study the adsorption properties of iminodiacetate polystyrene chelating adsorbent toward aqueous divalent metal ions involving Pb(II) and Cd(II) which are predominantly present in the effluents of battery industry and lead refining activities from an implanted unit at Sétif (East part region of Algeria). The adsorption approach was carried out in batch and in uncompetitive mode by using synthetic aqueous solutions at different contact times by varying the concentration of these metals at an optimal pH. In column, the adsorption was performed using the aqueous effluents from this factory by loading the adsorbing medium bed under hydrodynamic conditions. Finally, a regeneration attempt of the chelating support by sorption/desorption process was conducted in order to assess its reusability in removal of heavy metals particularly lead from this effluents.

Experimental Section

All chemicals used in this study were of analytical grade. Solutions of lead nitrate [Pb (NO3)$_2$] and cadmium nitrate [Cd $(NO_3)_2.4H_2O$], purchased from PROLABO (French), were prepared by dilution with double deionized water (20µs cm^{-1}) obtained from ENPEC (Algeria) from a mother solution at a given molarities. Macroporous cationic exchanger chelating resins Amberlite IRC 748 functionalized by iminodiacetic acid groups (IDA) in hydrogen form was acquired from Rohm and Haas company product (USA). The macro reticular structure of this resin ensures its stability in aggressive medium and confers its usability in selective adsorption and removal of heavy metals from waste effluents in a wide range of *p*H at an effective flow rate.

Atomic absorption spectrophotometer (AAS) Perkin-Elmer 3110 AAA model working with an air acetylene flame was used to estimate the content of metals solutions. The *p*H measurement was determined by a glass electrode (Hanna HI 9321), FT-IR spectrophotometer (Shimadzu) was employed to assess the characteristic spectra of complexes metal-chelating resin. A plastic column (1.14×13 cm) with a maximum gel bed volume (10 mL) with two porous filters and a peristaltic pump from LKB were used in the packed bed in adsorption and desorption trials of waste effluents and support regeneration.

Methods

Characterization of the IDA chelating resin

The functional groups of the dried native and metal complexes IDA chelating resins were characterized by Fourier transform infra red spectroscopy (FT-IR) in the range of 4000-500 cm^{-1} by pellet KBr method.

Adsorption isotherms

Prior to use, the chelating adsorbent beads were washed with 1M NaOH, 1M HCl and *n*-hexane to remove possible organic and inorganic residues or impurities of synthesis. Then, it was washed with deionized water (ENPEC, Algeria) extensively during three times, and was converted to Na^+ from by column flushing with 1M NaCl for 12 h[12]. Finally, the resin was rewashed with deionized water and dried in vacuum oven at 60°C until its use**.**

In a preliminary approach, the effect of contact time on the ion exchange of the heavy metal by the chelating resin Amberlite 748 was ascertained by column process. The pre-washed resin in sodium form (0.025 g) was equilibrated separately with 10 mL of 4×10^{-3} mol.L^{-1} lead and cadmium metal solutions at optimum adjusted *p*H (5.10) in a stopped glass tube during various incubation times varying in the range between 90 and 1440 min. under constant shaking at room temperature. The remaining concentrations in filtrate supernatant of the metal ions at equilibrium were measured by atomic absorption spectrophotometry. The adsorbed content of metal ion onto the resin was calculated as the difference between the initial and residual concentrations of the solution metals before and after adsorption procedure respectively. All the experiments were performed in duplicate and the results are the average values.

The adsorption isotherms were performed by column process at an optimum *p*H value and room temperature (25°C) by keeping the resin mass at constant value (0.025 g) during adsorption and adding 10 mL at a various initial concentrations of lead and cadmium metal solutions from 0.5×10^{-3} to 10^{-2} M. The residual contents, in supernatant, of the metal ions at equilibrium were measured as previously cited. The adsorbed amount of metal ion at the chelating adsorbent interface was deduced indirectly by subtraction the remaining concentrations in adsorption assay supernatant from the initial one. All the experiments were achieved in duplicate and the results are the average values.

The adsorption capacity expressed in $mg.g^{-1}$(Qe) and the removal percentage (% R), at equilibrium, of lead and cadmium at interface were calculated from equations 1 and 2 below:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad \dots (1)$$

$$\%R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad \dots (2)$$

where C_0 and C_e expressed in mmole/L or mg/L are the initial and equilibrium concentrations of metal ions in aqueous solution respectively and V the volume of solution in mL and m the weight or mass of chelating resin in g.

The adsorption isotherm curves were established by plotting the adsorbed heavy metal ions level against the remaining or free one in solution and consequently the affinity constants were evaluated by Langmuir model according to the equation 3 below.

$$\frac{\theta}{1-\theta} = K_a . C_e \quad \dots (3)$$

where θ ($mol.L^{-1}$) and 1- θ represent the covered and uncovered surface respectively, K_a is the constant affinity of the chelating ion exchange ($L.mol^{-1}$) and C_e is the equilibrium (remaining or free) concentration of metal ions in aqueous phase ($mol.L^{-1}$). This isotherm can be fitted to a linear form and therefore the affinity constant (K_a) can be determined from the slope of a plot of $\frac{\theta}{1-\theta}$ versus C_e.

Trial removal of lead from industrial effluents by column

The actual waste effluents used in the experiments was obtained from battery factory and lead finishing unit ENPEC (Entreprise Nationale des Produits Electro Chimiques), Sétif, Algeria. The chemical composition of the waste waters after a neutralizing treatment by calcium hydroxide (Ca $(OH)_2$) was characterized by *p*H of 5,10 with a high level of lead in the range of 22 mg/L. The other metals were present in a very low content that vary between 0.001 mg/L for Nickel, Selenium and Antimony and 0.0015 mg/L for Iron and 0.002 mg/L for Arsenic. The cadmium and Copper ion metals are present in traces that were not detected by AAS. This elemental composition could not affect the removal behavior of lead from the waste effluents.

The column trials were achieved with the chelating resin Amberlite 748 as a stationary phase by packing a known amount of the adsorbent beads (5 g) in polyacrylic column (1.14 × 13 cm) in the sodium form. The removal process of lead in packed bed was conducted by loading the column by 10 mL of waste sample from top to bottom under a pump flow rate of 1 ml min^{-1}. during 30 and 60 min of reaction. The effluent fractions at the end of removal procedure were collected and the ion metal content was determined by using atomic absorption spectrophotometer. This operation is repeated further time until the level of lead in collected fractions reaches to the limits of international requirements. In order to evaluate the ability of reusability of the chelating adsorbent, desorption trial was achieved on column by dynamic regeneration by passing through a packed bed charged by lead metal effluents a 1 M HCl solution at the same controlled flow rate. Lead eluted fractions were collected and analyzed by AAS until the metal content recovery stretch out to zero.

Results and Discussion

FT-IR characterization

The complexation of metal ion on iminodiacetic acid ligand of the chelating resin Amberlite IRC 748 inducts slight changes in the absorption bands spectra. The spectrum of the native resin and its complexes with lead and cadmium presented in (Fig. 1) shows number of broad and sharp band at 3430 cm^{-1} was assigned to the stretching and bending vibrations of O–H of carboxylic groups, which confers the resin its relative hydrophilic property[20,22]. The band which appears at 2930 cm^{-1} is attributed to the stretching vibrations of CH, CH_2 groups of the polystyrene matrix of the chelating resin. The absorbance bands at 1730 and 1630 cm^{-1} correspond to stretching vibrations of carbonyl groups (C=O) of the carboxylic groups (COOH) which reflect that some of these

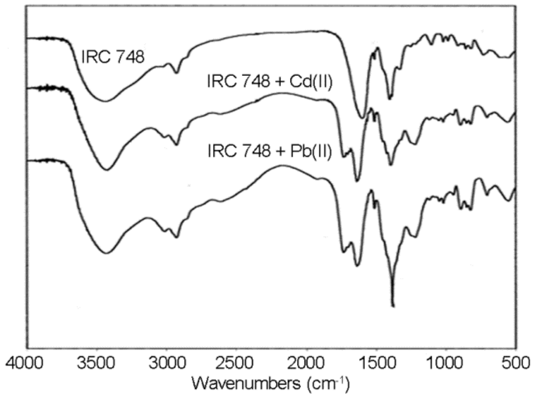

Fig. 1 — FTIR spectrum of native IRC 748 chelating resin and its metal complexes with Pb(II) and Cd(II).

groups remained in the nonionized form at the used *p*H in native and metal complexes state (Refs 20, 28). Moreover, the protonated carboxylic groups are identified by a characteristic absorption band which observed near 1390 cm^{-1} (Refs 20, 22, 29). Finally, absorption bands at 665 and 570 cm^{-1} reveal the coordination metal complexes to oxygen and nitrogen stretching vibrations as reported in the literature[20,30].

Adsorption isotherms

In the first approach, the chelating resin Amberlite IRC 748 was investigated in adsorption of Pb(II) and Cd(II) in non competitive or single system by varying the contact time at *p*H of 5.10 and ambient temperature using a constant content of resin. The effect of the contact time reported in Figs 2a and 2b demonstrate that the content or concentration of the adsorbed ion metal on the chelating resin increased with increase in the time of equilibration with an adsorption capacity (Qe) of 137.40 mg/g for lead and 90.40 mg/g for cadmium with in 360 min at which the saturation plateau value occurred as it has been established elsewhere in many research works[21,23,28]. A further increase in the contact time had a slight effect in the sorption process and the capacity increased slowly for both metals until the equilibrium state was reached. Thus, the contact time of 360 min was used thereafter in the experiments of establishing the equilibrium of uptake of these metals at interface.

It is clearly admitted that the chelating ion exchange resin involves coordinate bonding between metal ion and carboxylic groups of IDA ligand in addition of ion exchange process depending on *p*H of the medium which had a strong effect in adsorption capacity of lead and cadmium metal. Effectively, the adsorption capacity increased with the *p*H value until it attained the optimum point in the range of *p*H between 5.0 and 5.5 (Refs 21-23, 26, 35). At low *p*H value, the carboxylic groups of IDA immobilized on the resin are slightly or weakly dissociated and the hydrogen ion compete with metal ions for the binding/adsorption sites on the surface inducing a significant decreases in the adsorption capacities of Pb(II) and Cd(II). At high *p*H values, the resin adsorption is capacity is also affected by the presence of OH^- ions which form an insoluble hydroxide metal ions complexes. In the *p*H range (5.10) where our experiments are achieved, this adsorbent exists in an amphoteric form with protonated nitrogen and at least one deprotonated carboxylic groups[25,27,31]. Therefore, the adsorption phenomenon capacity occurred at interface is high and it is due to metal ion oxygen and nitrogen bonding as observed in the FT-IR spectrum and as established elsewhere[20,32].

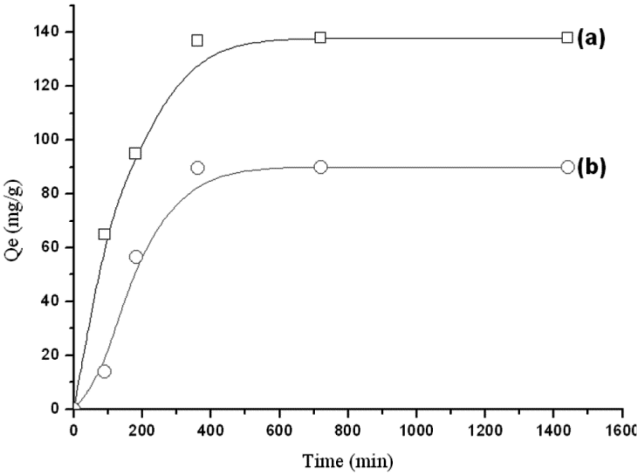

Fig. 2 — Effect of the contact time on the adsorption of Pb(II) (a) and Cd(II) (b) on the Na-form chelating resin at *p*H=5,10 and ambient temperature (each point represents a mean of two tests).

The adsorption isotherms of lead and cadmium ion metals onto the sodium form chelating resin was obtained by plotting the initial content of metal (mg/L) and the metal ion adsorbed per gram of adsorbent (mg/g) at equilibrium state (Figs 3a and 4a). The profile isotherms of Pb(II) (Fig. 3a) and Cd(II) (Fig. 4a) in single non competitive mode reflect a gradual increased sorption of these metals at interface as their initial concentrations in medium increased until they attained or reached 6 × 10^{-3} mole/L for both metals. This value represents the plateau of saturation of IDA functional accessible groups on the resin versus the metals of interest at interface. In fact, the maximum adsorption capacity of metals per gram of resin was 137,40 mg for lead (Fig. 3a) and 90, 40 mg

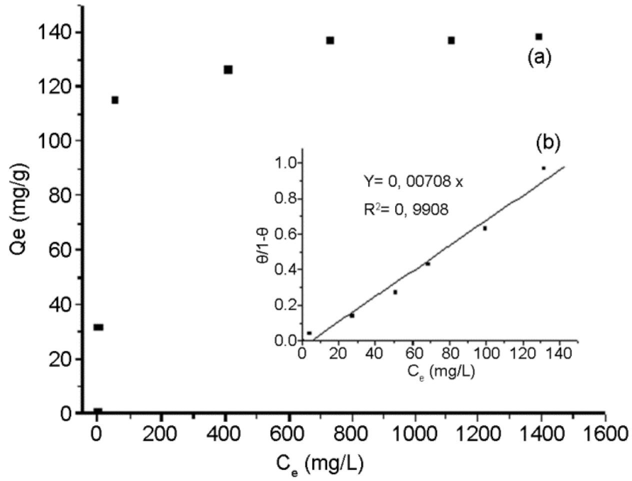

Fig. 3 — Adsorption of Pb(II) on chelating resin (0.025 g) at *p*H=5,10 and ambient temperature (each point represents a mean of two tests) (a) and its Langmuir isotherm profile (b). The ratio of θ/1- θ versus Pb(II) content in solution represents the affinity constant.

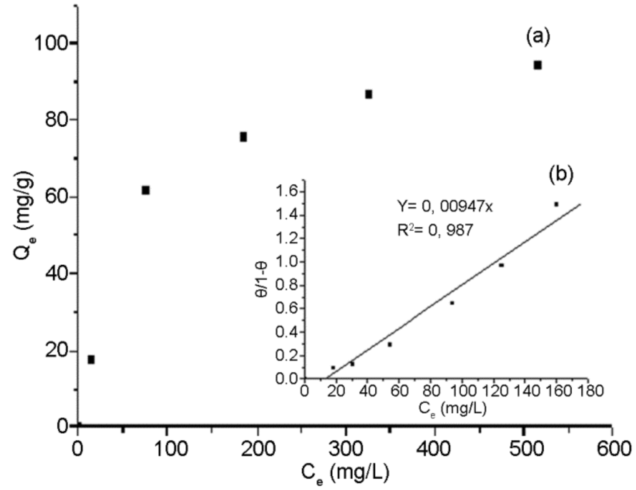

Fig. 4 — Adsorption of Cd(II) on to chelating resin (0.025 g) at *p*H=5,10 and ambient temperature (each point represents a mean of two tests) (a) and its Langmuir isotherm profile (b). The ratio of θ/1- θ versus Cd(II) content in solution represents the affinity constant.

for cadmium (Fig. 4a) with a recovery of 96, 25 and 76, 20% for both metals respectively. This result demonstrates the high capacity sorption of lead than cadmium on the chelating resin. Effectively, different studies have established that the capacity of adsorption of the two metals on various support bearing iminodiacetic acid functional groups at *p*H= 4-5,5 and room temperature vary between 84, 96 and 244,5 mg/g of resin for lead metal and between 44,96 and 87,7 mg/g for cadmium ion metal[22-24,26,28,33].

In term of adsorption isotherm which describes the comportment of a given exchanged metal ions on to the surface chelating functional groups, the Langmuir equation model is the most commonly adopted or used because the interactions between the two entities at interface is predominantly a kind of chemical reaction. The applicability or validity of this model is conditioned by different parameters or criteria such as (i) the surface of adsorbent is characterized by an uniform distribution of the adsorption sites, (ii) the adsorption equilibrium of the solute molecules depends on the saturation level of a monolayer adsorbent surface, (iii) the adsorbed molecule on the surface site has the same affinity[34]. On the basis of this concept, the obtained adsorption isotherm graphics of lead and cadmium were fitted by the Langmuir equation 3 previously mentioned in order to determine their affinity constants (K_a). It is clear that the Langmuir isotherm provide an excellent fit to the equilibrium adsorption data, giving good correlation coefficients (R^2) of 0.991 and 0.987 for Pb(II and Cd(II) respectively (Figs 3b and 4b). The affinity constants evaluated from the slope and x and y axis intercept of the linear representation were in the order of 0.00708 $L.mg^{-1}$(1.471 $L.mmol^{-1}$) for lead (Fig. 3b) and 0.0058 $L.mg^{-1}$ (0.652 $L.mmol^{-1}$) for cadmium ion metals (Fig. 4b). These values confirmed our previous findings and are in the same order of the obtained adsorption abilities mentioned above with similar magnitude and reflect the high effectiveness of the iminodiacetic acid functional groups grafted on the polystyrene back bone in the chemisorptions process of lead and cadmium metal ions.

Removal of lead by packed bed

The removing trials of lead from industrial effluents aim to ascertain which volume of waste water might be treated in dynamic conditions in correlation with the real adsorption capacity of the chelating resin while generating effluents whose concentration in lead allow it to be discharged into a watercourse or public sewage system in respect of the limits established by law. The recovery and regeneration, another purposes approach, consist in to establish the reusability of the adsorbent support.

In the light of the obtained results, it seems clearly that the chelating adsorbent functionalized by iminodiacetate groups possess a high adsorption capacity toward this metal ion. Effectively, the content of lead in recovered fractions after three cycles of sorption during neither for 30 or 60 min of contact is in the order of 0.014 mg/L. This value is at least three time less low to the discharge limit of national environment regulations of Algeria which requires a level of 0.5 mg/L of lead in the industrial liquid effluents[36] and slightly high to the regulation of the world health organization (WHO) and food and agriculture organization (FAO) that need a level of 0, 01mg/L of lead in water beverage. On the other hands, the ion exchange removal process of lead from the actual liquid effluents by chelating resin is more effective than the flocculation procedure used by the ENPEC unit that the discharged level of lead in effluents is six time higher to the limit lawful (3 mg/L).

The regeneration study of the chelating resin IRC 748 after three adsorption cycles of lead using identical and actual effluent solutions from ENPEC factory carried out using 1M HCl solution is presented in the Fig. 5. It was found that the recovery elutes is apparently effective for the desorption process of lead adsorbat at interface. In effect, the totality of the complexed lead on to the chelating adsorbent was desorbed by passing through the column bed, at least 10 volumes of eluent under a flow rate of 60 mL h^{-1} at room temperature and atmospheric pressure. At same conditions, cadmium presents in traces in the initial industrial effluents was entirely absent in the same eluted fractions. On the basis of these results, it is claimed or asserted that the chelating adsorbent can be used efficiently at least during three times or cycles for extraction of Pb(II) from actual effluents with a complete recovery.

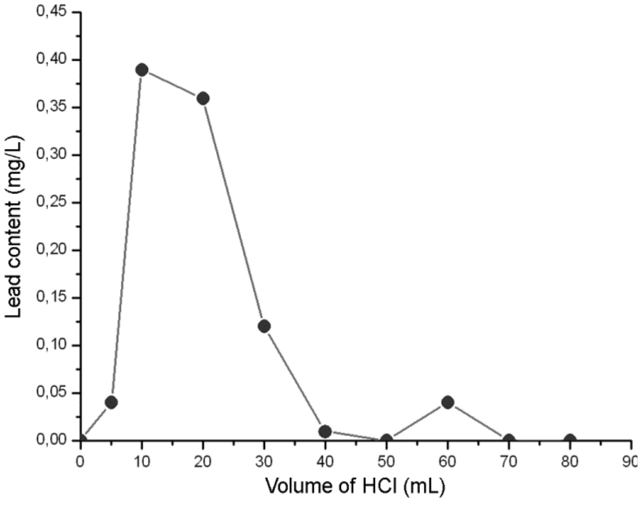

Fig. 5 — Recovery of adsorbed Pb(II) from chelating resin by 1M HCl solution.

Conclusion

The work presented here focus on the investigation of the sorption of lead and cadmium metal ions from artificial solutions and actual effluents of battery factory unit by using a chelating polystyrene adsorbent functionalized by iminodiacetic acid groups in sodium form (Amberlite IRC 748). The results demonstrate that the chelating resin can efficiently extract the Pb (II) and Cd(II) in 6 h from single aqueous solutions of initial metal ions concentrations in the range of 0.5×10^{-3} to 10^{-2} M at room temperature and *p*H of 5.10. This *p*H value found in battery industry is more appropriate in the sorption of these metals at interface as explained formerly.

The experimental obtained data for adsorption of Pb (II) and Cd(II) onto the chelating sorbent follow well the Langmuir model isotherm which gave a good representation of the equilibrium with correlation coefficients of 0.991 and 0.987 respectively. The monolayer adsorption capacities of these metals ion at interface obtained from their respective isotherm profiles are 137.40 and 90.40 mg/g of resin. The affinity constants of the two metals, under non competitive conditions, are high in the same order of their adsorption capacities. In the packed bed adsorption procedure, the content of Pb (II) from the actual or real effluent is sequestered entirely during the two first cycles, at the third cycle a tiny unbounded fraction is detected that responds to the environmental requirements. In addition, the recovery of the adsorbed Pb(II) is achieved with 10 bed /volumes of the regenerating solution (1M HCl) where no traces of Pb(II) in eluate is detected. These results demonstrate the effectiveness of the adsorbent in the extraction and recovery of lead from wastewaters. In future investigations, our search will be focused on using a green competitive ligand as a regenerant instead of the aggressive one.

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