LEAD (II) ADSORPTION FROM AQUEOUS SOLUTION BY CHITIN TREATED WITH NON-THEMAL PLASMA (COLD PLASMA)

HẤP PHỤ Pb(II) TỪ DUNG DỊCH NƯỚC BẰNG CHITIN ĐƯỢC XỬ LÝ VỚI PLASMA KHÔNG NHIỆT (PLASMA LẠNH)

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ABSTRACT

Chitin ($C_8H_{13}O_5N)_n$, a long-chain polymer of N-acetylglucosamine, is a derivative of glucose. It is a primary component of cell walls in fungi, the exoskeletons of arthropods , such as crustaceans (e.g., shrimps and crabs) and insects, the radulae of molluscs, cephalopod beaks, and the scales of fishes...In this study, chitin prepared from shell of shrimp that was treated with the non-thermal plasma (T-Ch) and used for study of the lead (II) adsorption from aqueous solution. The optimum conditions for the adsorption of lead (II) ions were found to be pH 6.0, and 100 min of contact time. It was also found that the experimental data of lead (II) ion adsorption onto T-Ch were in reliable consistence with the pseudo-second-order kinetic model and the adsorption rate of lead (II) ions was controlled by intraparticle and boundary layer diffusion. For adsorption isotherm study, the Freundlich isotherm model was found to be best model for description of the adsorption process. From results obtained, it could be concluded that the cold plasma technology can be used for modification of the chitin surface to effectively increase the Pb(II) adsorption from aqueous solution.

Keywords: *Chitin; Pb (II); Cold plasma; Adsorption kinetics; Adsorption equilibrium.*

TÓM TẮT

Chitin ($C_8H_{13}O_5N)_n$, một polymer mạch dài của N-acetylglucosamine, là một dẫn xuất của glucose. Chitin là thành phần chính của thành tế bào trong nấm, bộ xương bên ngoài của động vật giáp xác (ví dụ, tôm, cua) và côn trùng, dải răng của các loại động vật nhuyễn thể, mỏ của động vật thân mềm và vảy cá… Trong nghiên cứu này, chitin điều chế từ vỏ tôm được xử lý bề mặt bằng plasma lạnh (T-Ch) sử dụng để nghiên cứu hấp phụ ion Pb(II) từ dung dịch nước. Các điều kiện tối ưu để hấp phụ ion Pb(II) đã tìm được bao gồm pH 5.0, thời gian tiếp xúc: 100 phút. Kết quả thu được cho thấy số liệu thực nghiệm của sự hấp phụ Pb(II) lên T-Ch phù hợp với mô hình động học giả định bậc hai và tốc của quá trình độ hấp phụ được kiểm soát bởi tốc độ khuếch tán màng và khuếch tán nội hạt. Trong nghiên cứu hấp phụ đẳng nhiệt, mô hình đẳng nhiệt Freundlich được xác nhận là mộ hình thích hợp để mô tả quá trình hấp phụ. Từ kết quả nghiên cứu, có thể khẳng định công nghệ plasma lạnh có thể sử dụng để biến tính bề mặt chitin để nâng cao hiệu quả hấp phụ Pb(II) từ dung dịch nước.

Từ khóa: *Chitin; Pb(II); Plasma lạnh; Hấp phụ; Động học hấp phụ; Cân bằng hấp phụ.*

1. INTRODUCTION

Lead (II) pollution in the natural water systems attracts much attention due to its high toxicity to human health. The accumulation of lead in human body above certain levels can cause variety of problems, ranging from increasing in blood pressure and causing kidney problems to delaying in physical and mental development [1,2]. Major sources of lead pollution are wastewater from industries such as battery manufacturing, chemical production, and mining [3-5]. In order to remove lead from wastewater and contaminated waters, a number of technologies have been used such as membrane, ion exchanger, precipitation, etc. [6]. However, these technologies are still expensive and less common used in developing countries like Vietnam. Currently, adsorption technology is considered a possible solution for this problem. The adsorption technology is proved to have many advantages over other technologies, because the process of adsorption method is simple and easy to control and sludge waste reducing. Recently, the study of the adsorption materials derived from nature have been extensively conduced. Because of diversity and availability in nature, these materials can be considered a replacement for other costly material used in the adsorption technology.

Chitin is a well-known nature polymer that has been employed in many applications [7]. The –NHCO- group of chitin's glucose ring allow the formation of complexion forms with transition and post-transition metals; thus, chitin has been shown to be an effective absorbent in removing heavy metals from wastewater and contaminated waters. However, the use of natural chitin in this process is practically limited due to its low adsorption capacity and low selectivity, particularly in conditions containing high concentrations of other metals which may affect the activities of other metals in solution as well as the chitin surface charge. In order to improve the adsorption capacity of chitin, several authors have reported that the surface of chitin can be modified with chemical compounds containing functional groups that have high affinity with metals.

Recently, cold plasma technology has been used to modify polymer surface [8]. Advantages of this technology such as the reactions involved in plasma interaction are contamination free and dry, and only the surfaces of materials are modified, make cold plasma process an attractive environmental friendly alternative to chemical one. Jama and Delobel (2007) [9] investigated interaction of nitrogen cold plasma and a polymeric surface, leading to an important surface functionalization and consequently to a surface having a Lewis character. Their results showed that the polymer surface becomes hydrophilic and nitrogen and oxygen functional groups are formed immediately after plasma treatment. These authors also studied the effect of argon plasma on the wettability, surface chemistry and surface morphology of polypropylene; as results of argon plasma treatment, increase in surface energy and surface roughness of polypropylene were observed. Obviously, if the treatment conditions by cold plasma were appropriately selected, it could create the desired effect on the material surface for different purposes. However, cold plasma technology is still less attention in the modification of adsorbent surface for use in the adsorption technology.

The objective of this research is to investigate lead (II) adsorption characteristics of the modified chitin by cold atmospheric plasma with a view to enhance its adsorption capacity for lead ions. Experiments were also conducted to assess the effectiveness of this modified chin in removing lead (II) from aqueous solution.

2. MATERIALS AND METHOD

2.1. Preparation of chitin from shrimp shell

Chitin was extracted from shrimp shells following previous published method [10]. Firstly, dried shrimp shells were cleaned protein by dissolving in 2.0 % NaOH solution at a temperature of 60°C for 6 hr. Secondly, the cleaned shells were washed with distilled water until pH was at 6-7, then digested in 1.0 M hydrochloric acid solution for 24 hr at room temperature in order to de-mineralize Ca and Mg. The chitin product was washed with distilled water and dried at 80°C. It was crushed and sieved. The 0.25 mm fraction was collected for experiments.

2.2. Atmosphere cold plasma treatment of chitin surface

Atmosphere non-equilibrium plasma (cold plasma) was used to activate the chitin surface. The home-made cold plasma system at HCMUTE consists of a power supply and a plasma reactor, a thin wire anode is covered with a cylindrical dielectric to prevent arcing that was connected to a power supply (20 kV, 2 A, and 45 kHz) and a carrier aluminium plate is driven through the reactor by a step motor and connected to the ground. Samples were placed on the metal plate and manually adjusted to control the discharge gap. In this study, the chitin samples were exposed to the air atmosphere cold plasma at power of 140 watts for 5 min. The modified chitin (T-Ch) was stored in glass bottles and ready for use.

2.3. Adsorption experiment

Batch adsorption experiments were conducted at 30 ± 1^{0}C K by agitating 0.3 g of modified chitin with 50 mL of lead (II) solution in flasks at 250 rpm. The effect of pH on the absorption process was studied by conducting experiment at pH from 1 to 7. Adsorption kinetics were studied at pH 5 by varying lead (II) initial concentrations at 15, 50, and 100 mg/L. Samples of the adsorption solution were collected, filtered to analyze lead (II) content in the liquid phase in regular interval to monitor the lead (II) concentrations using voltammetry method [6].

3. RESULTS AND DISCUSSION

3.1. Charatristics of adsorbent

The FTIR spectra of chitin and modified chitin are presented in Fig. 1a and Fig. 1b, respectively. The FTIR of chitin (Fig. 1a) exhibited a characteristic band at 3448 cm^{-1} is attributed to -NH and -OH groups stretching vibration and the band 2885 cm^{-1} were an aliphatic C-H stretching bands that converges to OH stretching with N-H. The characteristic carbonyl C = O stretching of chitin at 1647 cm^{-1} are attributed to the vibrations of the amide I band. The sharp band at 1427 cm^{-1} corresponds to a symmetrical deformation of the CH_3 group and at 1558 cm^{-1} corresponds to the N-H deformation of amide II. The vibrations bands at 1072 cm^{-1} showed C-O-C vibration inside chitin ring and produced many peaks caused by the presence of hydroxide from chitin which contains a single bond C = O. There are somewhat difference between FTIR spectra of chitin and modified chitin with cold plasma. The band at 3435 cm^{-1} was spited into two peeks including peak at 3442 cm^{-1} and 3268 cm^{-1}. This may be contributed by NH_2 groups which formed in cold plasma treatment.

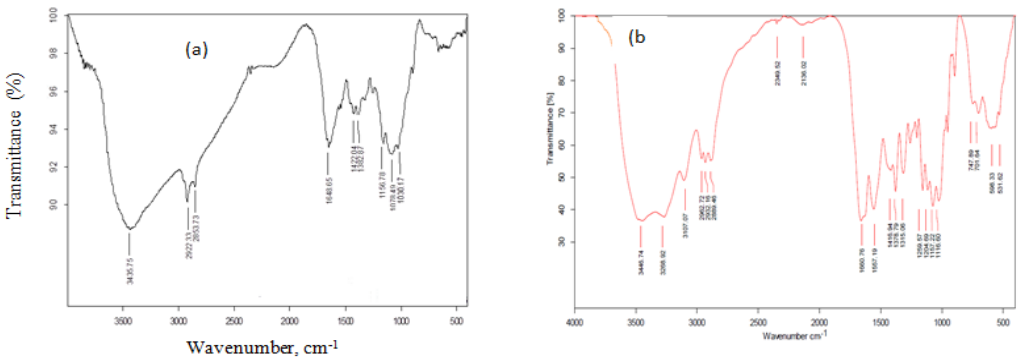

Fig.1. *FTIR spectra of (a) modified chitin and (b) chitin*

Table 1*. Calculated kinetic model parameters for lead (II) adsorption*

Initial lead (II) concentration (mg/L)	Lagergren pseudo-first order model		Pseudo-second order model		Inter-particale diffusion model		
	k_1 (L/min)	R^2	k_2 (g/mg.min)	R^2	k_i (mg/g.min)	C	R^2
15	0.018	0.967	0.312	1.00	0.009	7.24	0.961
50	0.024	0.848	0.009	0.999	0.326	19.4	0873
100	0.037	0.917	0.002	0.998	1.432	27.8	0.892

3.2. Adsorption kinetics

Figure 2 presents the change in lead (II) concentration changes versus reaction time. Results obtained indicate that the adsorption rate for all initial lead (II) concentrations in range of 15 – 100 mg/L increases with increasing reaction time. After 120 min it is observed a plateau was reached after 98.5 % of lead (II) based on its initial concentrations were adsorbed, indicating the absorption reactions reached equilibrium. For adsorption kinetic study of lead (II) on the modified chitin, the experimental data were fitted to Lagergren pseudo-first order model, pseudo-second order model, and intraparticle diffusion model [11].

The fitting parameters of these two models are given in Table 1. It can be seen in the plot of pseudo-first order model, there are a small deviation between experimental and calculation using the model with fitting parameters. The correlation coefficients (R^2) for different lead concentration range of 15, 50 and 100 mg/l were found to be 0.967, 0.848, and 0.917, respectively. On the contrary, the experimental data are well fitted with the pseudo-second order model; the calculated correlation coefficients are greater than 0.999 for all concentrations.

Figure 3 shows the plots of the intra-particle model for the adsorption of lead (II) on modified chitin at initial lead (II) concentrations of 15, 50, and 100 mg/L. It can be seen in plots, the relationship between q_t and $t^{0.5}$ was relatively non-linear, especially at large initial concentrations of lead (II). This probably is because the adsorption process of lead (II) may occur on several distinctive steps. The steeper portions of these plots indicate the external surface adsorption, while the more plat portions of these plats indicate intra-particle diffusion process. The last portions of these plots show that the adsorption process is at equilibrium which normally has a very low concentration of lead (II) in the liquid phase.

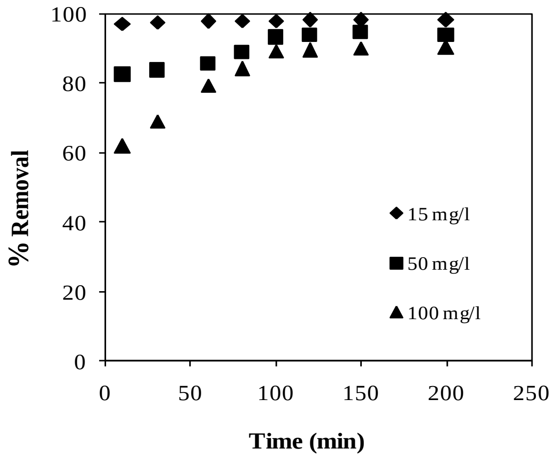

Fig.2. *Effect of reaction time on the adsorption of lead (II) onto modified chitin*

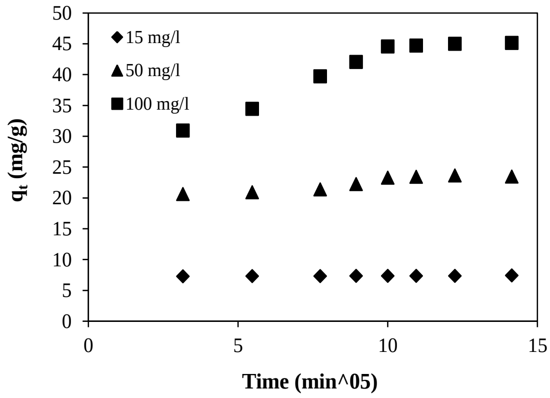

Fig.3. *Plots of inter-particle diffusion model of lead (II) adsorption process*

3.3. Effect of pH

Typical lead adsorption by the modified chitin as a function of pH is presented in Figure 4. Results show that the adsorption of lead ions significantly increase with increasing pH values of the adsorption solution. The maximum adsorption percentage achieved are greater than 98.0, 97.2, and 93.0 % at pH 5 for initial lead (II) concentrations of 15, 50, and 100 mg/L, respectively. This effect is probably because the changes in surface charges of the modified chitin and the presence of lead ion species at different pH values. Thus, at low pH (< 5.8), Pb^{2+} and $Pb_2(OH)^+$ strongly compete against H^+ ions for adsorption sites. However, the adsorption rate of lead (II) increased even at very low pH was observed.

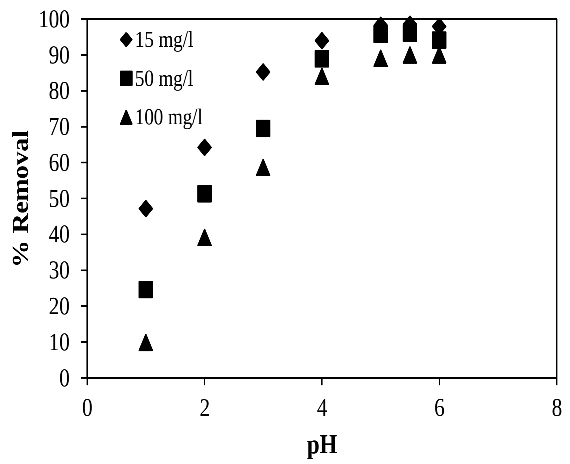

***Fig.4**. Effect of pH on the adsorption of lead (II) on the modified chitin absorbent.*

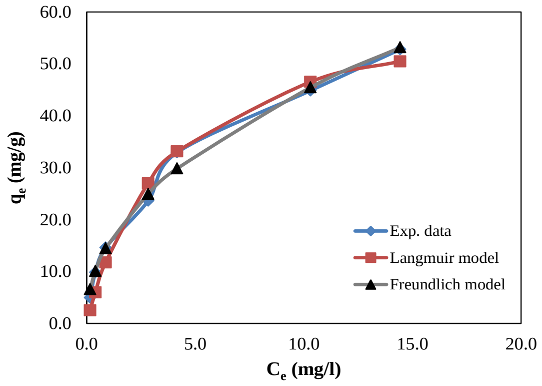

***Fig.5.** Non-linear models for the adsorption process of lead (II) onto the modified chitinat 303K, pH 5, and adsorbent dose of 4 g/L.*

3.4. Adsorption isotherm

The Langmuir and Freundlich isotherm models [6] were used to fit the experimental data obtained at equilibrium time to obtain information of lead (II) ion partition between liquid and solid phase.

The plots of the non-linear Langmuir and Freundlich linear models at temperatures of 303K and are presented in Figure 5. The calculated residual root mean square errors (RMSE) are used to evaluate these fitting equations. In general, the smaller the RMSE value is, the better the curve fitting is. The calculated results of parameters of the two models are presented in Tables 2. It was observed that, experimental data are better fitted with the Freundlich model, indicating by smaller values of RMSE, than with the Langmuir model. This suggests that the modified chitin surface is more heterogeneous, probably resulting from the rearrangement of the adsorption sites on chitin surface after cold plasma treatment. Maximum adsorption capacities (Q_{max}) of the modified chitin for lead (II) were found to be 59.6 mg/g. For untreated chitin, in the same experimental conditions (investigations of untreated chitin not shown here), the maximum capacity for lead (II) was only 20.3 mg/g at 303K. Obviously, adsorption of lead (II) from aqueous solution by modified chitin after treating atmosphere cold plasma treatment is feasible.

3.5. Effect of competitive ions

Ca^{2+}, Na^{+} and SO_4^{2-} ions are major composition in wastewater from industries relating to lead metal. They may affect the activities of lead (II) ions in solution as well as affecting surface charge of chitin [12]. The Effect of calcium, sodium and sulfate ions on the removal parentage of lead (II) by modified chitin presents in Figure 6 and 7, respectively. It was observed that sodium and sulfate ions only slightly affect the adsorption of lead while calcium ions strongly compete against with lead ions for adsorption sites on the surface of modified chitin. Calcium has been found to adsorb tightly on chitin with the aid of acetamide as well as hydroxyl groups in chitin molecule. These results suggest that, in pH adjustment step for adsorption of lead by modified chitin, the use of sodium hydroxide is suitable for the adsorption process.

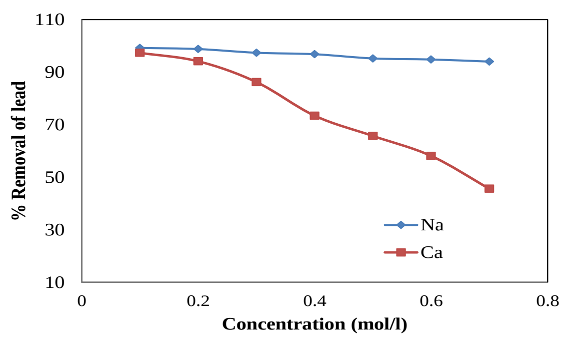

***Fig.6.** Effect of calcium and sodium on the adsorption of lead (II) by the modified chitin absorbent at pH 5, temperature 303K, and adsorbent dose of 4 g/L.*

Table 2. *Calculated parameters of Langmuir and Freundlic isotherm models for the adsorption process of lead (II) onto the modified chitin absorbent*

Temp-erature	Langmuir model			Freundlich model		
	K_L	q_m	RSME	K_F	n	RSME
303 K	0.257	64.1	2.83	15.3	2.15	1.56

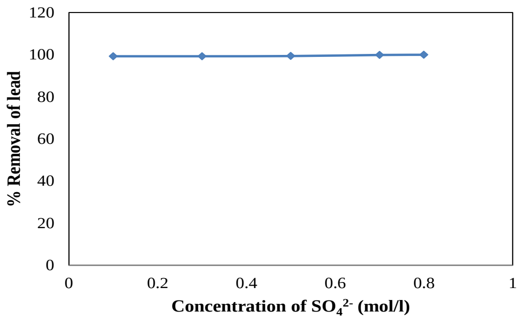

Fig.7. *Effect of SO_4^{2-} ions on the adsorption of lead (II) by the modified chitin absorbent at pH 5, temperature 303K, and adsorbent dose of 4 g/L.*

4. CONCLUSIONS

This study demonstrates that chitin was treated by atmosphere cold plasma can enhance adsorption capacity for lead (II) ions. The kinetics of lead (II) adsorption process was studied, showing this process was well fitted the pseudo-second order model and the adsorption rate was controlled by intra-particle and boundary layer diffusion processes. Isothermal adsorption data are also well fitted with the Freundlich model. The effects of Na^+, Ca^{2+} and SO_4^{2-} ions on the adsorption process were studied, it was observed that sodium and sulfate ions only slightly affect the adsorption of lead while calcium ions strongly compete against with lead ions for adsorption sites on the surface of modified chitin.

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