Optimizing the Adsorption Conditions of Lead from Aqueous Solutions onto Chitosan Nano Particles

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ABSTRACT

Biosorbents have become increasingly important for removal of heavy metal from water and wastewater due to their and biodegradability low costs. Chitosan is a hydrophilic and cationic polymer product of chitin deacetylation and used as an absorbent for removal of heavy metals. Chitosan is a Hydrophilic polymer and cationic which is gained from chitin acetyl groups removal in basic environments. And recently has been widely used as an absorbent for remove the heavy metals. In this research we studied the adsorption of lead metal ions from aqueous solutions by chitosan nano particles. Nano particles were synthesized by maleic acid from chitosan crosslinking and the particle size was identified by laser light scattering (DLS). The average size of the particles measured by DLS was in the range 70-350 nm. The experiments were performed in batch system, at room temperature (20 ± 0.5 °C), on analyzing the effects of the following variables: initial solution pH, absorbent dosage and initial lead (II) concentration. Under these conditions, the optimal values of initial pH solution, concentration of metal ions and adsorbent dose were found at 6, 55 mg/l and 4 g/l respectively. The maximum adsorption of 28.5 mg/g based on optimal values was achieved. The adsorption data fairly fitted to Langmuir and Freundlich isotherms. The maximum adsorption rate of 27.35 mg/g based on Langmuir isotherm was obtained.

KEYWORDS: Nano particles, Chitosan, Adsorption, Lead, Aqueous Solutions.

1. INTRODUCTION

Water pollution by heavy metals is an environmental issue that is increased across the globe through activities such as, mins' utilization and operation, industrial and urbanization activities[1]. The heavy metals ions have the ability to bioaccumulation in the environment and also during the food chain have Biomagnification. Therefore, their toxicity effect in higher levels animal of food chain will have more appearance and growth[2].

The lead has high toxic effect, and is one of the most dangerous metals due to cause damages to the brain, nervous system, kidney and gastrointestinal tract especially in children[3]. That's why the disposal of heavy metals in the environment is considered a very real threat to human health and ecosystems[4]. Membrane separation, Ion Exchange, Sorption and bio-sorption, Reverse Osmosis, Deposition and Extract are of the conventional and common methods of lead removal from chemicals. However, most of them have disadvantages such as high cost, incomplete removal, high sludge production and high energy consumption[5] .

Adsorption is considered of the effective and economical method for removing the pollutants from wastewater. Metal adsorption via nanoparticles is an environmentally friendly technology which has been investigated as an effective factor to remove organic pollution and heavy metal ions from water and wastewater in recent years[6]. In this method of separation, different absorbents were used such as biological absorbents like yeast, algae, Fungi, and bacteria, silica gel, activated carbon (charcoal) and zeolite[7,8].

The biopolymer production has been recently considered by many researchers as a tool for absorb the heavy elements due to reasons like lack of toxicity in the environment, availability and low cost[9]. Both cellulose and chitin are polysaccharides that play a protective role for flora and fauna (plants and animals), respectively.

So that the plants produce the cellulose in their cell wall and the insects and crustaceans produce the chitin in their shell. Cellulose and chitin are very similar to each other in structure.

In cellulose the hydroxyl groups are replaced with acetamide group at C-2 position. And about chitin the amino groups are replaced with the cellulose hydroxyl groups[16].

Chitosan is a Hydrophilic polymer and cationic which is obtained by removing chitin acetyl groups from basic environments. Chitin is the most abundant biopolymer in nature after cellulose. Chitosan is able to combine with metal ions by ion-exchange absorption. Therefore, it is used widely to absorb the heavy metal ions[10].

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Chitosan is modified by chemical and physical processes in order to prepare chitosan derivatives or change situation (membrane preparation, nano particles, powder and fiber)[11]. These processes are used to control the polymer reactivity or enhance the absorption synthetic. In order to design the absorption process it is good to control the polymer situation. Uranium ions, nickel, vanadium, chromium, cadmium absorption with chitosan have been studied so far[12,13]. The absorption of metal ions was also investigated with chitosan derivatives such as Chitosan with crosslinking, polyamide porous chitosan, Peptide chitosan, Chitosan composites and new derivatives of chitosan[14,15].

The researches indicated that we can use chitosan as absorbent due to the presence of hydroxyl and amino groups; and as ligand sites in removal of heavy metals. Optimization and modeling of lead adsorption from aqueous solutions onto chitosan nano particles are studied in this paper. The effects of PH, initial concentration of metal ions and amount of absorbent on lead absorption process parameters are also studied.

2. MATERIALS AND METHODS

The low molecular weight chitosan with a purity of 99% and 75% removal of acetyl was purchased from Sigma-Aldrich Company. Malic acid(C4H4O4), lead nitrate (Pb(No3)2), hydrochloric acid (HCL), sodium hydroxide(NaOH) and Potassium persulfate(K2S2O8) all have high purity and are manufactured by Merck, the German company.

2.1. Synthesis method of Chitosan nano particles

In this research, the Hydrophilic chitosan nano particles was Synthesized based on Maleic acid polymerization in chitosan solution. An amount of 0/003 m of maleic acid was dissolved in 100 mL of deionized water. Then the amount of 0/006 m of chitosan (with low molecular weight) was added to it. The sample was mixed for 3 h using a magnetic stirrer[17].

The pH solution is measured by pH meter, Inotube model, made in Germany. And by use of hydrochloric solutions 0/1 m acid and 0/1 m sodium hydroxide was brought to 4. The Sample was placed for 8 hours in anaerobic jars that were completely sealed and its oxygen was taken by oxygen absorbent at 25 ° C. (to avoid the premature termination of the polymerization process due to the presence of oxygen prevention molecules). Then 0/054 g of potassium persulfate was added in order to provide context for nanoparticles be placed on it and facilitate the separation during the action of centrifuge. And for 2 h was placed in the same oxygen less conditions under the same stirring temperature. The resulting mixture was cooled in an ice bath with the appearance of the Suspended particles and the obtained nano particles were separated in 30 minutes 16000 rpm with high speed centrifuge, sykma (sigma) model, made in Germany. The obtained nano particles were dried by freeze dryer, ALPHA model, made in Germany and were used for absorption tests[18].

2.2. Determine the dynamic diameter and analysis of nano particles

The ultrasonic bath, t-ih-20 model, made in Germany is used to initial preparation of the sample to determine the diameter of size synthesized nano particles. The nano particles size measuring device, Vasco model, made in France is used to analyze and measure the hydrodynamic diameter of nano particles. The produced nano particles are solubilized in deionized water and then are placed in ultrasonic bath for an hour in order to nano particles to be uniformly dispersed in solution and to avoid agglomeration. Then the solution is placed in a glass cell of nano particles measuring device in 250 ° C and a laser beam with a wavelength of 657 nm with a power of 50% of the time 1/5 minutes is irradiated. Then the scattering (diffraction) of the laser beam is detected by a detector and in analyzed through nano-Q software. (Agglomeration of nano particles happens due to delayed separation of nano particles from solution or during high-speed centrifugation).

Nano particle size is calculated according to the Stokes- Einstein equation.

$$D_z = \frac{K_B T}{3\pi\mu Q_n} \tag{1}$$

where: K_B is a Boltzmann constant; T is a temperature; μ is a solvent Viscosity; Q_n is a particle hydrodynamic diameter; D_z is a Effective coefficient of laser scattering (diffraction) which is calculated due to the wavelength of the laser beam.

2.3. Batch Adsorption Experiments

The design of tests was done using Design expert Ver.8 statistical software, with RSM method, and central cube model in order to perform the lead metal ions experiments.

The effect of three factors was examined such as PH (in three levels of 3, 4/5 and 6), concentration of lead pollutant (in three levels of 10, 55 and 100 Mg /L) and absorbent dosage (in three levels of 1, 4/25 and 7/5g /L) on absorption amount.

Table1. Factors and levels introduction

Level 3	Level 2	Level 1	levels Factors
6	4/5	3	pH
100	55	10	Initial Concentration of lead(mg/L)
7/5	4/25	1	Absorbent dosage(g/L)

A stock solution of lead (II) ions, containing 100 cc lead metal ions solution (II) with concentration (10, 55 and 100 mg/L) in PH (5, 4/5 and 6). The amounts of chitosan nano particles were added to them. The samples were placed for 2 h in 25 °c environment temperature under 120 rpm stirring speed. Chitosan nano particles were separated from the samples by centrifugation with 16000 rpm round for 15 minutes after the absorption process and the remaining solutions were passed from the membrane filter with a pore size of 0/45 micrometers. The concentration of remaining lead ions in the solution was measured by flame atomic absorption device, Shimazo model, made in Japan. The solution samples are sprayed in form of smog into a flame of acetylene gas. Lead metal ions are changed to atom as an effect of flame temperature. Irradiations with visible and ultraviolet wavelength are flashed and emitted to the atomic ions in flame by Sources of radiation. The amount of absorbed radiation is measured by an optical detector at a wavelength related to lead ion. Measured absorption intensity at each wavelength is dependent on the concentration of lead ions in solution.

The absorption operation and performance and the absorbent ability for absorbing the lead ions (II) from aqueous solution were evaluated by Langmuir and Freundlich models[19,20].
The Langmuir isotherm equation may be formulated as

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$
(2)

where: q_e (mg/g) is the amount of equilibrium absorbed metal ions; q_m (mg/g) is the maximum adsorption ratio upon complete saturation of the chitosan surface; C_e (mg/L) is lead (II) concentration at equilibrium; K_L is the Langmuir constant
The Freundlich isotherm is an exponential equation that may be written as

$$q_e = K C_e^{1/n}$$
(3)

Where: q_e (mg/g) is the amount of equilibrium absorbed metal ions; C_e (mg/L) is lead (II) concentration at equilibrium; K is the Freundlich constant, indicating the adsorption capacity; n is a constant characterizing the affinity of the metal ion towards chitosan,

The equilibrium absorption capacity of absorbent was calculated using the Eq. 4;

$$q_e = \frac{(C_0 - C_e)V}{m}$$
(4)

Where C_0 and C_e (mg/L) are the initial and equilibrium lead (II) concentrations in solution; V (L) is the volume of solution and W (g) is the weight of adsorbent.
And the absorption percentage was calculated using the Eq.5;

$$Adsorption \% = \frac{(C_0 - C_e)}{C_0} \times 100$$
(5)

Where C_0 and C_e (mg/L) are the initial and equilibrium lead (II) concentrations in solution

3. RESULTS AND DISCUSSION

3.1. The results of the analysis of the diameter of the chitosan polymer and chitosan nano particles

The particle size was identified by laser light scattering (DLS). Figures (1 to 4) shows the distribution of nano particles size and polymer particles of chitosan. The nano particles size is often in the range of 70-300 nm. As a

result, 70% of nano particles have the diameter in range of 70-300 nm and 30% of them have the diameter more than 300 nm due to the adherence of nano particles. It was observed that the dispersion index (PDI) in nano particles is 0/239. It means that the scattering of the nano particles diameter is acceptable. But the dispersion index (PDI) in chitosan polymer particles is 2/8510 that the scattering of the chitosan polymer particles diameter is including wide range of measures and sizes.
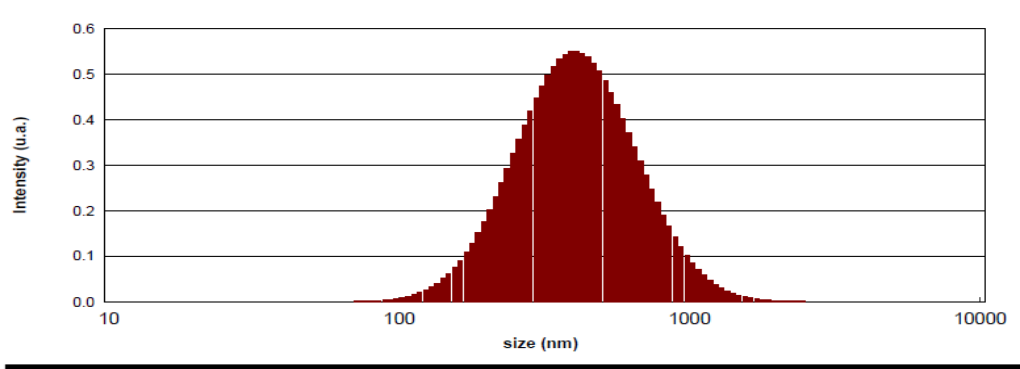
Figure1. Scattering of the produced nano particles at laser beam diffraction intensity.
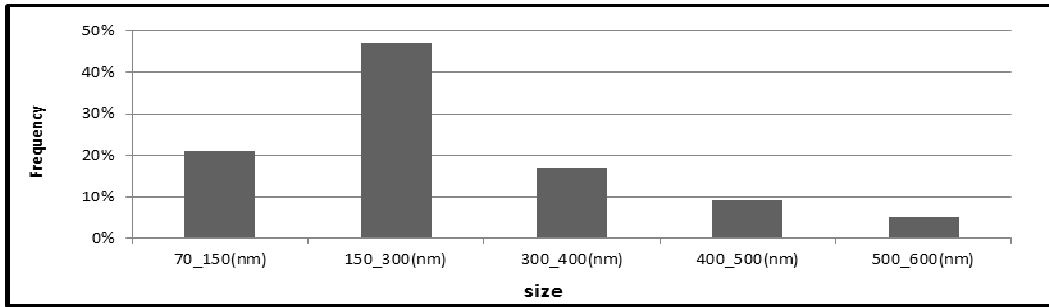
Figure2. Distribution the size of produced nano particles.
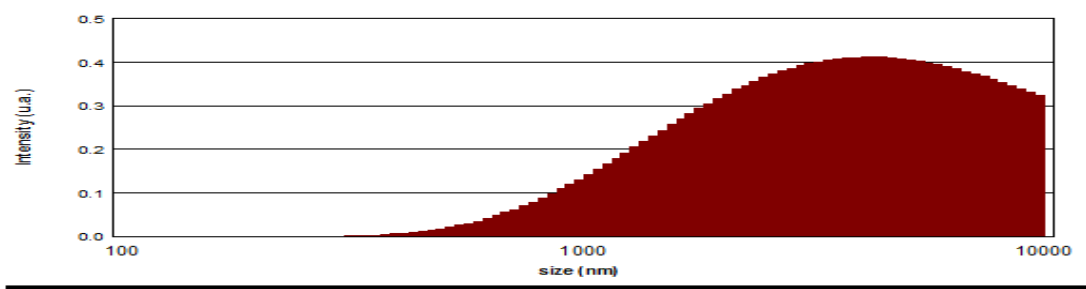
Figure3. Scattering the size of chitosan polymer particles at laser beam diffraction intensity.
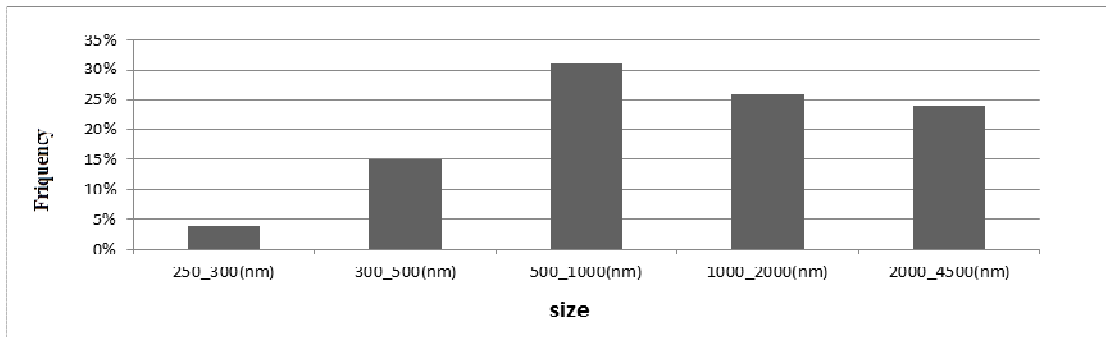
Figure4. Distribution the size of chitosan polymer particles.

3.2. The results of Adsorption Experiments
    The amount of optimal absorption in initial concentration of metal ions is 55 mg/L, PH is 6 and the absorbent amount is obtained 4 gr/L with 92/9 of Desirability factor. The effect of PH, initial concentration of metal ions and absorbent doses on lead absorption ratio and lead absorption capacity from aqueous solution were studied through chitosan nano particles at each step of the experiments by keeping all parameters consonant and changing one parameter.

The effect of initial solution PH
    In this study we have investigated the PH effect in the range of 3 to 6 on lead metal ions absorption amount. The chitosan particles are solved in the PH less than 3 Nano, and in PH more than 6, the metal ions sediments and deposits are occurred in the form of metal hydroxide. Because lowering the solution PH, the available amino groups in combination of chitosan nano particles are protonated with different degrees. Consequently, the amount of available sites for complexion the lead ions are decreased, and causes to metal cations (kations) be removed electrostatically[23] .
    Based on the (Fig. 5 and Fig. 6) the absorption ratio of metal ions was increased in 55 mg/l initial concentration and 4 gr absorbent by PH increase. So that by increasing PH from 3 to 6, the absorption ratio is increasing from 66/43 to 82/65 and the absorption capacity is increasing from 7/76 to 13/83 mg/g .
    Vaskansouls et al.(2008) have obtained the maximum adsorption ratio for copper ions II through extension chitosan in 5/5 PH. Capplo et al. (2008) have determined the PH optimum amount for absorption of Cr(III), Cr(II) and cd(II) ions, 7,4 an7, respectively [24].
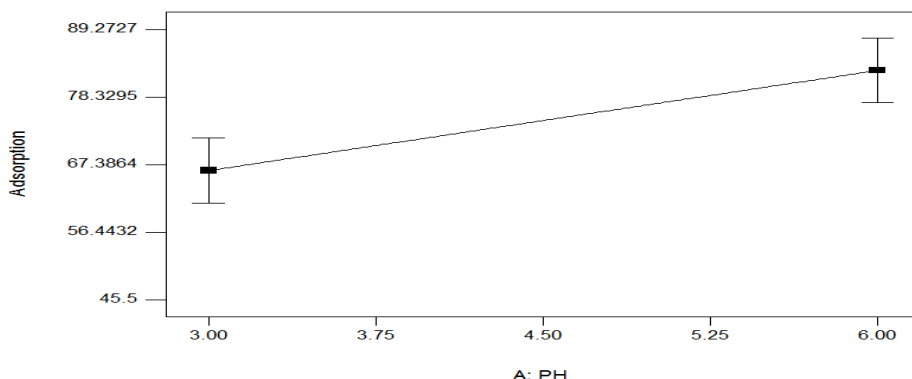

Figure5. Adsorption ratio of Lead onto chitosan nano particles as a function of initial solution pH.
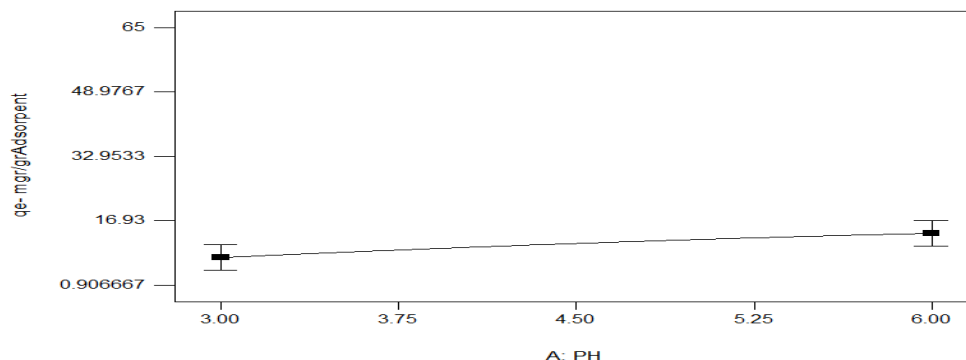

Figure6. Adsorption capacity of Lead onto chitosan nano particles as a function of initial solution pH.

The effect of absorbent dose
    The experiments were performed at a constant initial lead (II) concentration of 55 mg/L and pH = 6.0. Based on the (Fig. 7 and Fig. 8) the absorption ratio of metal ions increases from 74/59 to 92/08 and the absorption capacity decreases from 34/99 to 5/84 mg/g, respectively, by increasing the absorbent amount from 1 to 7/5 gr/l. The number of available absorption sites increase with the increase of absorbent amount which leads to increase the amount of absorbed metal amount. Decreasing the absorption capacity by increasing the absorbent amount is mainly

due to absorption sites saturations during absorption process and due to accumulation of particles in large amount of absorbent which leads to a reduction in its surface area[25,26] .

The obtained results in this regard are consistent with the results of Nadavala et al. (2009) about Nickel and chromium absorption from aqueous solutions by chitosan which is coated with perlite particles[27].
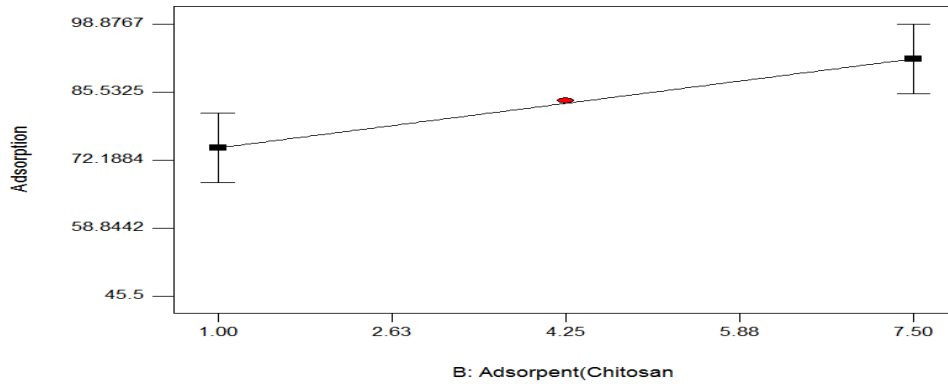

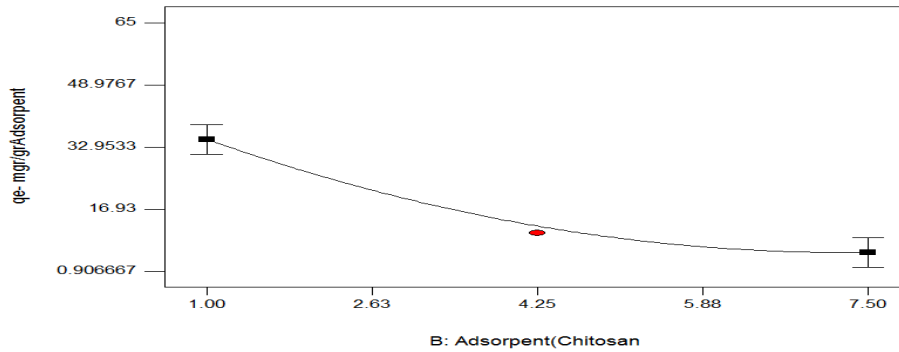**Figure7. Adsorption ratio of lead (II) onto chitosan nano particles as a function of chitosan dosage.**

Figure8. Adsorption capacity of Lead onto chitosan nano particles as a function of chitosan dosage.

The effect of Lead initial concentration

The absorption ratio of metal ions by chitosan nano particles was studied under the effect of metal ions initial concentration in the range of 10 to 100 mg/l and 6 PH and 4 gr/l absorbent amount. Based on the (Fig. 9 and Fig. 10) the absorption ratio is decreased from 85/76 to 79/56 by increasing metal ions initial concentration from 10 to 100 mg/l. The absorption capacity from 7/89 to 31/76 mg/g is also increasing. Increasing the metal ions initial concentration leads to increase in concentration gradient driving force and absorption capacity. In low concentrations all of the metal ions with active sites are reacted but yet there are still free absorption sites in the absorbent surface. So the absorption capacity is increased with more occupancy of absorption sites. The obtained results are consistent with Kantamatia et al. (2013) in this regard. They reported that the optimum amount of copper and Co(II) Ions at a constant initial concentration of 50 mg/ l[28].
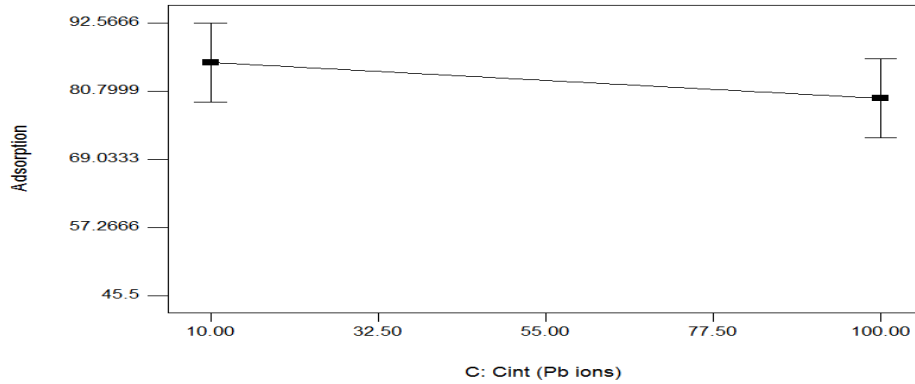
Figure9. Adsorption ratio of lead (II) onto chitosan nano particles as a function of initial concentration in lead (II) solution.
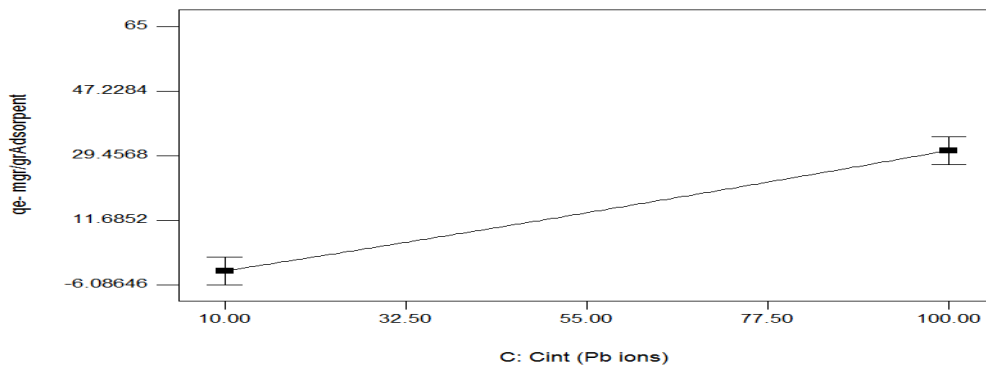

Figure10. Adsorption capacity of lead (II) onto chitosan nano particles as a function of initial concentration in lead (II) solution.

Adsorption isotherm – Langmuir and Freundlich mathematical models

The values of the correlation coefficients (R^2) indicate that lead (II) adsorption onto chitosan nanoparticles is very well described by the Langmuir isotherm model ($R^2 = 1.0$), although a good correlation coefficient ($R^2 = 0.9729$) may be also provided by the Freundlich isotherm model. These results permit the supposition that a monolayer adsorption of lead (II) on chitosan occurs, with the observation that the adsorption sites from the chitosan surface are heterogeneous. This means that, when lead (II) is adsorbed on the surface, different sorption sites had different affinity for lead (II) ions and different adsorption energy.
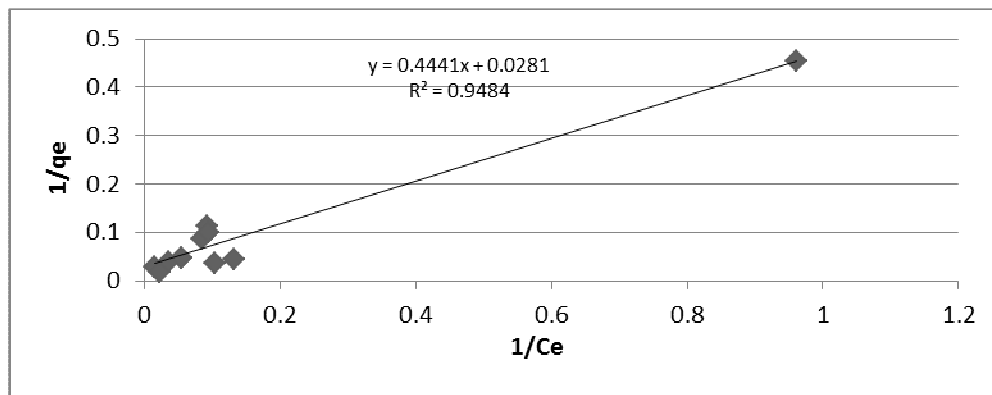

Figure11. Linear model of Langmuir isotherm for lead (II) adsorption onto chitosan nano particles.
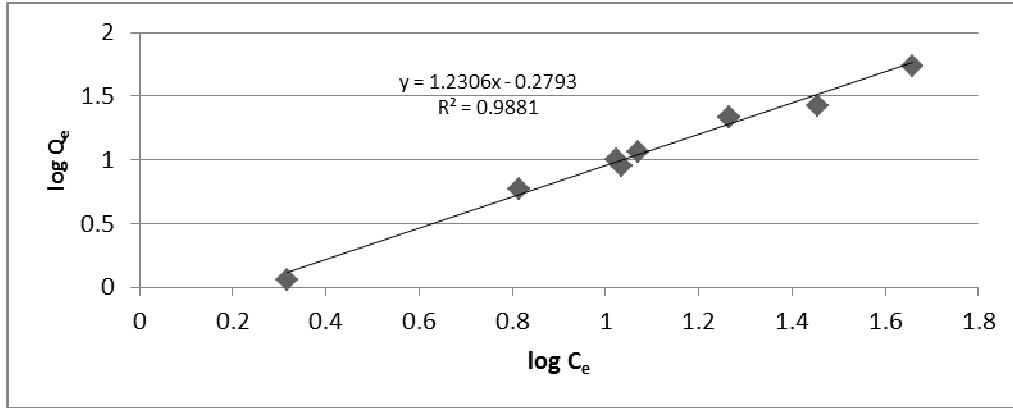
Figure12. Linear model of Freundlich isotherm for lead (II) adsorption onto chitosan nano particles.
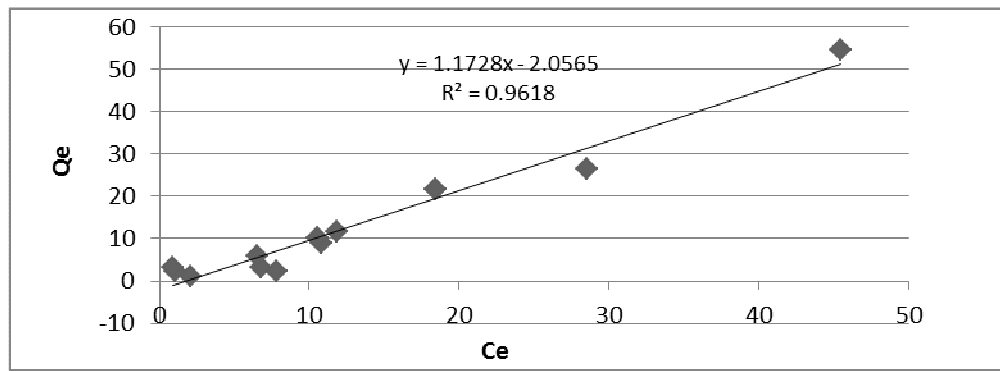

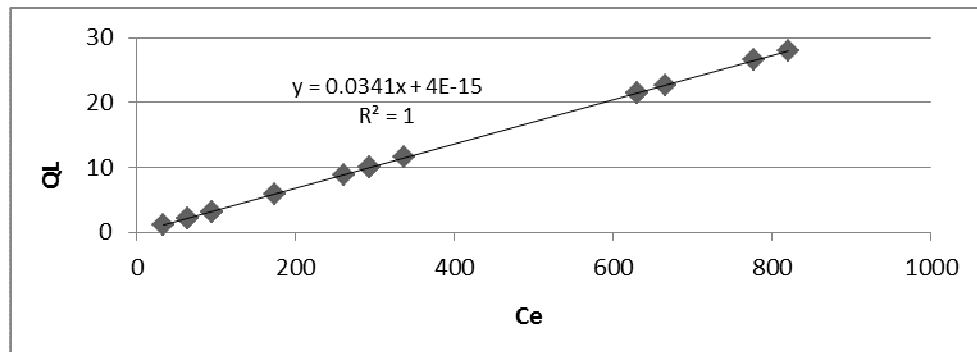**Figure13. Adsorption isotherm of lead (II) on chitosan nano particles.**

Figure14. Langmuir plot for lead (II) adsorption on chitosan nano particles.
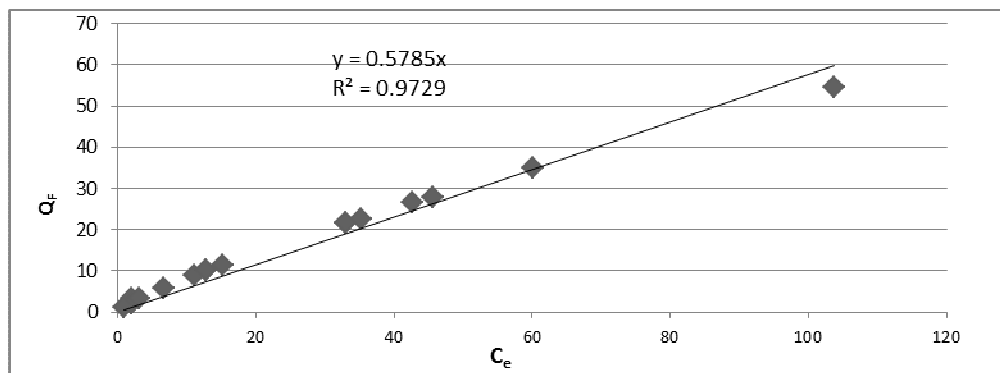
Figure15. Freundlich plot for the adsorption of lead (II) on chitosan nano particles.

Table2. Isotherm parameters of adsorption of lead (II) ions onto chitosan nano particles

	Freundlich		Langmuir				
lead(II)	$q_{e \ (mg/g)}$	$q_{m \ (mg/g)}$	K_L	R^2	K_f	n	R^2
	28/5	27/35	0/44	1	0/756	0/81	0/976

4. CONCLUSION

The adsorption of lead (II) from aqueous solutions onto chitosan nano particles was investigated. Comparison the analysis of nano particles with chitosan polimer particles represents an increase in the effective surface of nano particles which increase the efficiency of absorption process, partly and decreases the costs and the duration of the process, greatly. The maximum adsorption of 28.5 mg/g based on optimized conditions was achieved. The adsorption data are consistent with Langmuir and Freundlich isotherm models. The maximum adsorption rate– of 27/35 mg/g – occurring under the optimized conditions studied.

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