



Adsorption Studies of Zn (II) onto Nano Biomaterials from Aqueous Media

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Hydroxyapatite and β -tricalcium phosphate as porous composites were prepared by a sol-gel process. We got a solid powder form composites as small particles. Mixed powder by ultrasonically dispersed throughout the aqueous solution containing an optimum amount of Ring-opening- polymerization for solid-phase extraction of metal ions from aqueous medium. The zinc ions adsorption with poly(lactic-co-glycolic) acid (PLGA) as original technique for scaffolds where, the cations adsorption zinc(II) and Co(II) with PLGA-polymer opening ring is considered eco-friendly alternative technology for water treatment. However, the application of PLGA to zinc (II) adsorption is limited, due to its lower surface area and porosity. Then, the prepared a PLGA scaffold with a huge structure was used as an alternative absorbent material to remove zinc ion and cobalt from nitrate solutions. Characterization of structure and analysis of spectral of the most important features of PLGA scaffold and carried out. The PLGA scaffold offered pore sizes from 100-200 μ m. Porosity up to 95.4% and the specific surface area of PLGA $81 \pm 2.4 \text{ m}^2 \text{ g}^{-1}$ (SEM); moreover, the adsorption of isotherm was applied by the models Langmuir and Freundlich, the adsorption of metal ions can explain the effect of composites recycle on the adsorption of two models, fitting of zinc and cobalt ions adsorption of correlation coefficient the Langmuir model is the best than Freundlich model.

Keywords: Hydroxyapatite; β - TCP; PLGA scaffolds; $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; Adsorption; Langmuir and Freundlich models

Introduction

Hydroxyapatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ and beta-Tricalcium phosphate $[\text{Ca}_3(\text{PO}_4)_2]$ ceramics are bio-compatible materials that offer a chemical environment and a surface conducive to new bone formation. Now day's unique techniques have been evolved to comprehend hydroxyapatite/Poly caprolactone composites by means of bodily blending [1].

Sol-gel methods have attracted a whole lot attention [2]. Because of the well-recognized inherent benefits of technique to generate glass, glass-ceramic and ceramics powders; these consist of: homogeneous molecular mixing, low processing temperature, the potential to generate nano-sized debris, bulk amorphous and skinny

films. Natural-inorganic hybrid composite materials put together through the sol-gel process are very promising materials [3].

The sol-gel strategies studied up to now but have some shortcomings, most drastically, the use of both expensive alkoxide-based precursors or the want for numerous complex steps to make certain whole dissolution of precursors to generate phase pure HAP.

Nanoparticles (Nano powders, nanocrystals, or nano structured particles) are microscopic particles with at least one dimension in the nanometer scale (usually, 100 nm or less). In general, nanoparticles offer improved properties compared with conventional-sized materials because of their large surface-to-volume ratio (specific surface area)

[4,5]. To control the properties of HAP nanoparticles, it is important to control the particle morphology, which can be achieved by adjusting their synthesis methods. Modification of HAP is also important for the regulation of its physiochemical properties. ROP of cyclic dimers has been examined to get high molecular mass and having specific micro structured polymers for biomedical applications using various metal initiators, organo metal complexes and metal free initiator systems. Heavy metal catalysts (Co, Zn, Pb, Zr, Bi and Y) are not recommended for biomedical applications. zinc (II) is frequently found in effluents discharged from industries, such as electroplating, pigments, battery manufacturing units, mining, metallurgy and municipal wastewater treatment plants. zinc (II) is a well-known toxic metal ion [6, 7]. The removal of zinc (II) ions from wastewater includes precipitation, coagulation, ion exchange, membrane filtration, and electrolysis [8–16].

In this work, the Sorption experiments of Co (II) and Zn (II) ions in nitrate medium on nano-apatite with addition of poly (d, l-lactide-co-glycolide Acid (PLGA) as matrix composites to constitute polymer composites scaffold as surface modified materials. The effect of adsorption isotherm for applying Langmuir and Freundlich models was studied.

Experimental

Reagents and Instruments

Hydroxyapatite as a natural bone from animals, β -Tricalcium phosphate as prepared from natural bone underwent a calcination process at different temperatures. Then, they were washed from ethanol and water deionized, dried in the microwave at 50°C, and a white powder from nano- $[\text{PO}_4]^{3-}$ was obtained. The structure of PLGA (polymer) was purchased from Sigma-Aldrich, n-Dodecane (Merck with a purity of over 99%). Concentrations of polymer and nano-biomaterials were determined using Atomic Absorption spectrophotometer. Model 210 VGP, USA, pH measured by CG-820 Schott Gerate pH-meter. The heavy metal cations such as Co (II) and Zn (II) were obtained from Merck-as analytical grade, prepared stock solution in HNO_3 , yield $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ has been put in deionized water and adjusted pH –meter by diluted sodium hydroxide and 0.1M HCl.

Preparation of nHAP- β -TCP and nHAP/PLGA- β -TCP

One g/L Hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ which has a solubility constant at $2.34.4 \times 10^{-59} \text{ mol dm}^{-3}$ powder for calcium phosphate was dissolved in 100 cm^3 of H_2O . Then it was mixed with the nHAP solution, and the mixture was stirred for 20 min at 60-80°C. Then, nHAP-n- β -TCP was obtained by co-precipitation of the mixture of the nano-composites and the zinc ions compounds in the presence in nitrate medium solution and the final pH of the solution was 10.06 ± 0.03 after co-precipitation. In Addition, the prepared nano sphere composites were suspended in aqueous solution for crosslinking, and left standing for 4-4.5 h at 25°C under continuous stirring. The ultimate, product was washed by distilled water for several times until pH reached to stable state, and stored for further applications. nHAP/PLGA- β -TCP was synthesized approximately by the same method as nHAP- β -TCP. Except for the addition of PLGA. In the mixture of nano-composites and the zinc, cobalt salts, 0.5 g PLGA powder was added under strong stirring Fig. (1a). The PLGA blended nano sphere composites were obtained by the same co-precipitation technique. Subsequently, the nano sphere composites were crosslinked as usual. Thereafter, the finished products were washed and stored for further applications.

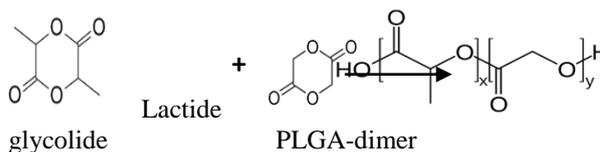


Fig. (1a): Preparation of Poly Lactic-co-Glycolic Acid (dimer)

Preparation of β -Tri calcium phosphate by Sol-gel technique

Synthesized calcium phosphate powders by ethanol Based sol-gel method, phosphorus pentoxide (P_2O_5 , MERCK Co.) and $(\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O})$, Sigma-Aldrich MERCK Co) were utilized, as chemical progenitors, for Ca/P, respectively. Aqueous solutions of both phosphorus pentoxide 0.5 M and calcium nitrate 1.5 M in pure ethanol 99% were prepared separately. Then, the P_2O_5 solution was slowly poured into the solution containing $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ which was stirred vigorously with mechanical stirrer (1200-1450 rpm). As a result of sol stirring for 15-20 min. the gel was obtained, through the

process of longevity, the resulted transparent sol was kept in a closed container for 36 h at 25°C. After drying in furnace with 100 -120°C, the resulted powders were calcined at 900 °C for 8h [17].

Characterization of nHAP-β-TCP and nHAP/PLGA-β-TCP

Poly (Lactic-co-glycolic) acid was coated by β-tricalcium phosphate as scaffold. of The morphology and structure of the scaffold were studied using scanning electron microscope (JEOL (JSM-5500 LV) in the Regional Center of Mycology, Al-Azhar University, Cairo, Egypt. Determination of pore size of β-TCP, HAP and PLGA scaffolds before and after coating by β-TCP and HAP was carried out using *Quantachrome* Nova 1000 E, USA. The pore sizes of β-TCP 2.86μm strengths reached 0.4 MPa, PLGA 6.80 ± 1.34μm and pore size of nHAP was 80μm respectively [17].

The FTIR spectra of nHAP, β-HAP and PLGA/ n-Dodecane, were recorded using a Fourier transform infrared spectrometer (Spectrum BX 11, Perkin Elmer Model). Total samples were prepared as the range of the scanning wave numbers was 400–4000 cm⁻¹.

Adsorption methods

Adsorption of 0.14 ppm from Zn (II) and Co (II) in 50 ml agitation for 30 minutes after removal of Zn (II) from HNO₃ aqueous solution, the concentration of heavy metals can be determination by ICP-MS. The equalization of adsorption, q (mg g⁻¹), was calculated according to the following equation (1):

$$q = \frac{C_0 - C_e}{w} \cdot xV \quad (1)$$

Where C₀ and C_e (mg dm⁻³) are the initial and final Zn(II) ,Co(II) concentrations, V is the volume of the Zn(II) and Co(II) ions solution(dm³), and m is the weight of the PLGA (g) in the dried adsorbents.

Study of batch uptake%

The ion exchange PLGA-composites of Zn (II) and Co (II) ions on polymeric ring opening as modified was accomplished using the batch process [18-22]. The batch adsorption experiments were proceed using 100 mg of adsorbent of desired concentrations at room temperature, shaken of the bottles in a sieve for 2h, the solutions containing

zinc and cobalt ions were separated after precipitation ratio (K_d) calculated by equation (2) and equal the distribution ratios of zinc ions=199.7 ml/g and cobalt ions=168 ml/g respectively and show the figure.4.

$$D = K_d(1 + K_a)/[H^+] \quad (2)$$

Recycling and desorption procedures

Recycling techniques (R & D)

Utilizing of the nano-composites nHAP-βTCP/PLGA is advantageous when repeating adsorption-desorption procedure. After the first batch reaction of nano-calcium phosphate/polymer (dimer),it was washed using deionized water to remove the raffinat acid and was dried by oven vacuum at 60°C, in the preparation for next adsorption of zinc ions and the capacities of adsorption-desorption of the resin for Zn (II) ions which were determined by ICP-MS. The recovery of nHAPTCP/PLGA scaffold was used three-seven recycles of adsorption-desorption process and the results indicated that the weight losses in the activity of the nano-composites, for the first seven recycles the composition will be negligible.

Results and Discussion

Characterization of Poly Lactic-co-Glycolic Acid/ β-Tri Calcium Phosphate

Study the FT-IR spectrum of β-TCP/PLGA before and after 37°C incubation was carried out. The absorption bands at maximum values were 1094, 1034,603 and 564 cm⁻¹, from phosphate group [23], β-TCP. The approximately band at 3420 cm⁻¹ as the result of OH⁻group and H⁺ bonds at 1420 and 631 Cm⁻¹ as the result of OH was attributed to the bending vibrations of OH-group. The approximately band at 1600 Cm⁻¹ was observed for H-O-H, for characterization absorption bands at 1750 to 2926 Cm⁻¹., stretching vibrations of the C=O and C-H group of PLGA, respectively absorption[23] at 1457 Cm⁻¹. CH₂-group as originates from the bending vibrations 875-860 Cm⁻¹., alternative OH-group in C-P group [24-26]. Fig. (1b) shows (as supplementary material) FT-IR spectrum spectroscopy of β-TCP/PLGA before and after 37°C incubation.

Scanning electron microscope analysis

The SEM micrographs of the synthesized HAp Nano powder from animal scale and β-TCP sources (β-Ca₃(PO₄)₂) is a synthetic, completely inorganic compound, this was shownfrom Figures 2a and 2b (supplementary materials).

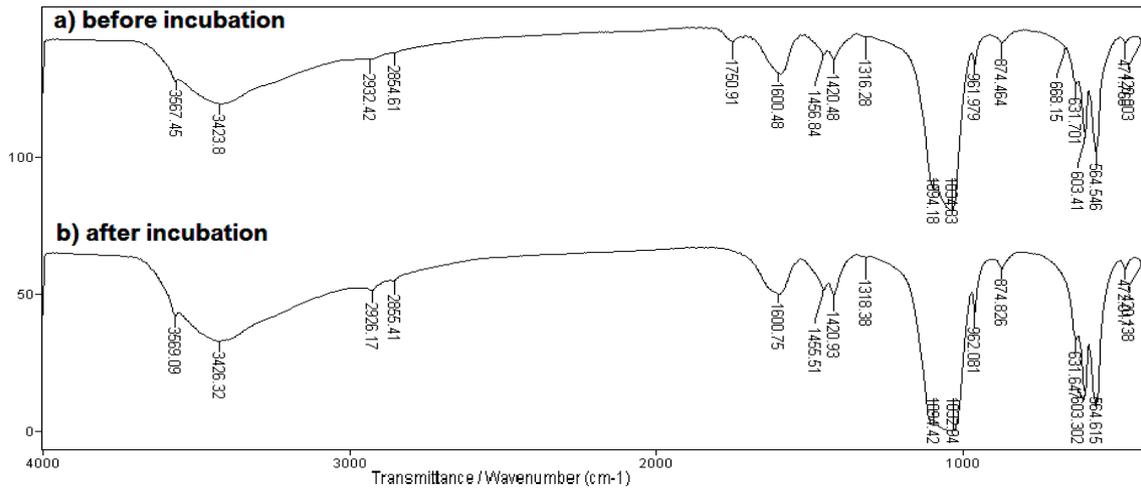


Fig. (1b): FT-IR spectrum spectroscopy of β -TCP/PLGA before and after 37^oC .

SEM investigation was conducted for the nano-composites/polymer before and after removal of zinc ions. Scanning electron microscope analysis of nano-composites before and after addition of PLGA are shown in Figs. (2a, 2b) where the small particles from HAP/ β -TCP are revealed in Fig. (2a) which shows the diffused resin without regularity and therefore it is difficult to determine of crystalline composite [27] Fig. (2b) shows the combination of product 2a, with a numerous pores and relatively decreased size which leads to an increase in the contact areas and activated pores for PLGA.

Study of Adsorption process

The amount of metal ions absorbed from aqueous solution onto PLGA-composites in contact after an appropriate connection reached the balance. The adsorption of Zn(II) and Co(II) ions by Poly Lactic-co-Glycolic Acid (PLGA) was found at a period of 90 min as sufficient to the composites resin saturated with metal ions using different data from uptake experiment and calculating the distribution ratios of the adsorption in Fig. (3): This Figure shows the adsorption of different metal ions as a function of initial concentration and the adsorption of metal ions such as zinc and cobalt by the modification PLGA as a function of their concentrations under room temperature .The percentage of adsorption of metal ions decreased with increasing of metal ions concentration in aqueous solutions. These results indicated that an increase of metal ions concentrations occur due to lower energetic sites *c* in aqueous solutions. The maximum percentage of Zn was 78% and Co (II)

was 65%, these values are satisfactory for artificial bones and low cost as the uptake metal ions that depend on diffusion ions in aqueous solution mechanism of exchanger surface.

The distribution ratio as a function of metal ion concentrations is shown in Fig. (4). It was noticed that the distribution coefficient values (*K_d*) increase with decreasing metal ions concentrations as a result of the fact that the energetic sites became of a lower contribution with the metal concentration increasing in nitric acid solution.

Modeling of adsorption isotherms

Equilibrium of adsorption isotherms plays a substantial role in the adsorption systems between solid-liquid phases with increasing concentration reaching equilibrium phase. Figure (5) shows the adsorption isotherms plotted between amount of adsorbed versus the amount of metal ions in equilibrium *C₀* as initial concentration of metal ions such as zinc and cobalt where the amount of Zinc ions sorbed is greater than the Co(II) and sorbent ions at 0.82 mmol/g for zinc, 0.3 mmol/g for cobalt respectively as a result of various sorption capacity .The differential sorption between two ions is attributed to the ionic radii for Zn(II) > Co(II). Generally: adsorption experimental measurements and Langmuir and Freundlich models isotherm, can be applied for contaminant sorbent investigations.

Figs. (6,7). reveal the sorption data of correlation linear from Langmuir isotherm according to equation (3):

$$\frac{C_f}{C_{ads}} = \frac{1}{Q_b} + \frac{C_f}{Q} \quad (3)$$

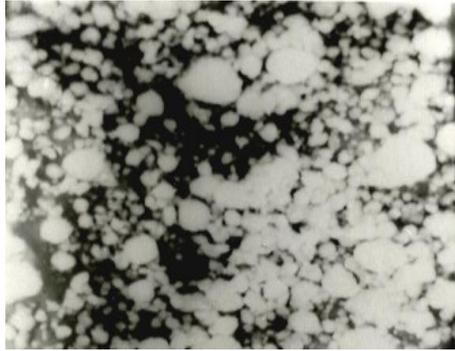


Fig. (2a): SEM for HAP/β-TCP-composites without polymer Before PLGA

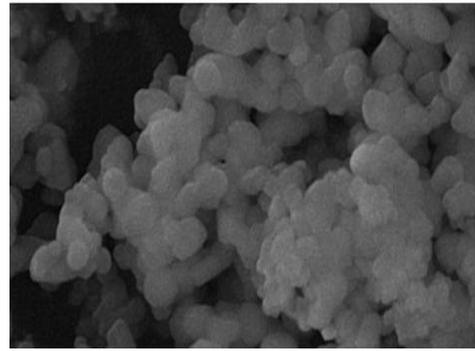


Fig. (2b): SEM for HAP/β-TCP after added PLGA

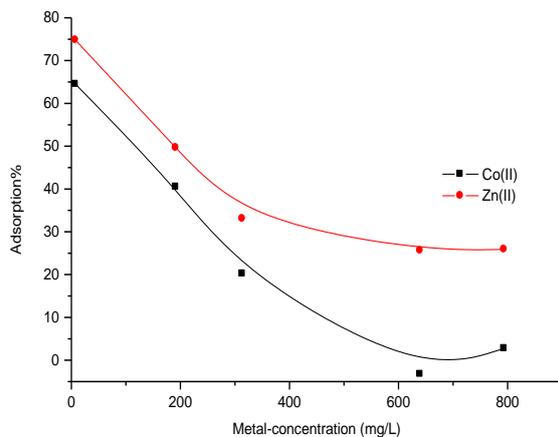


Fig. (3): Effect of the Adsorption on the metal ion concentrations

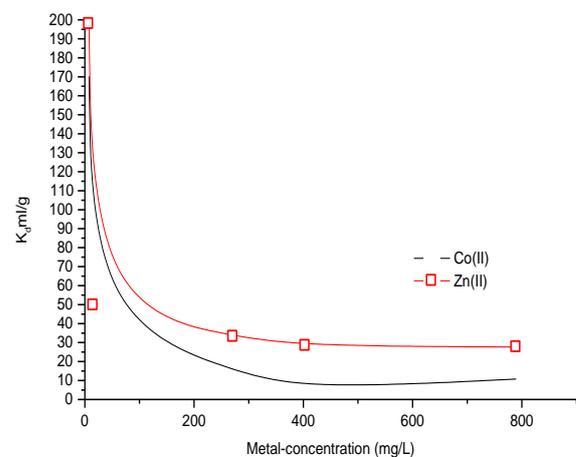


Fig. (4): Effect of K_d of Zn (II)/ Co (II) concentrations

C_f is equilibrium concentration of Zn(II) and Co(II) in aqueous solution, C_{ads} is number of metal adsorbed onto PLGA-composites, Q and b as Langmuir constants are related to capacity and energy sorption respectively. The maximum sorption capacity Q is a monolayer a perfusion of PLGA-composites-metal ions Zn (II) & Co (II) or sorbate-sorbent and b enthalpy of sorption at various temperature, from Freundlich isotherm linearized

$$\log C_{ads} = \log K + \frac{1}{n} \log C_e \quad (4).$$

C_e is equilibrium, concentration in mg/l for metal ions, Q and b are Langmuir isotherm constants, K and n are Freundlich isotherm constants; R is correlation coefficient for linear regression on the results and represented in Table (1). Freundlich's isotherm equation for zinc and cobalt metals is the constant K depending on the temperature and n is a distinguishing constant for the adsorption system

under conditions. n value (> 1) shows the best adsorption and the comparison of correlation coefficients for two models. The experimental data correlated the Langmuir model is the better than Freundlich isotherm (28,29).

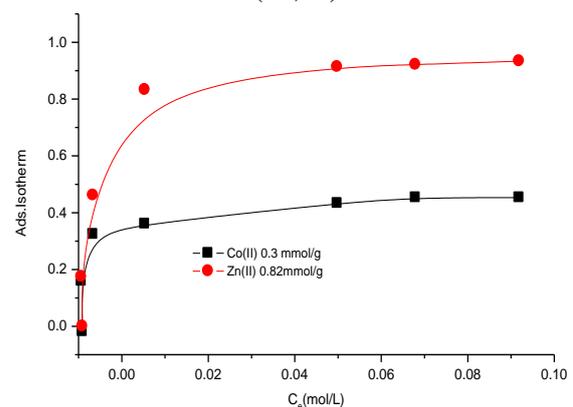


Fig. (5): Isotherm constants for adsorbents at different initial concentrations for Co (II) and Zn (II) metal ions

Study of the recycling and recovery adsorbent

It has been proven from Research and Development (R&D) in the field of engineering techniques to recycle some compounds that these compounds need high temperature to break resin sufficiently and get the metal that can be used again. For example, zinc has been processed for recycling to improve surface quality conditions and recoverable organic product value while providing a significant portion of energy and chemical reagents and cost -effective strategies. The recycling and recovery of the nHAP/ β TCP/PLGA composites scaffold would decrease the processing costs and recovery may

occur after Zn (II) ions extraction from aqueous solutions. There is an ability to reuse the composites scaffold. The application of recycling nanoparticles plays an influential role in the reuse of scaffold resins tested through seven absorption / capacity absorption cycles. Table (2): shows the influence of the recycles number of zinc ions solution. The nano-composites could be recycled above 6 times for recycle of zinc , and the adsorption capacity from 1st -7st 30.78 and 18.67 from adsorption- desorption respectively(Table 2)Therefore, the results, indicated that the nano-composites can be used as adsorbent.

Table (1): Linear forms of the Langmuir and Freundlich isotherm models

Langmuir		Freundlich				
Metals	b	Q	R ²	K _f (mg/g)	1/n	R ²
Zn(II)	1034.46	0.286	0.9913	1.31298	0.678	0.890
Co(II)	963.09	0.247	0.97815	0.569	0.455	0.654

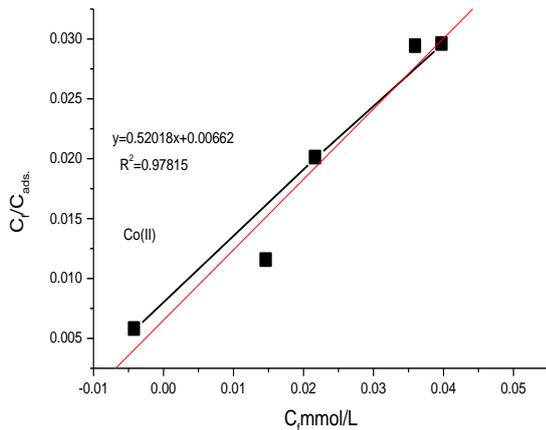


Fig. (7): Non-linear fitting of Langmuir, isotherm model for the adsorbents of Co (II) ion

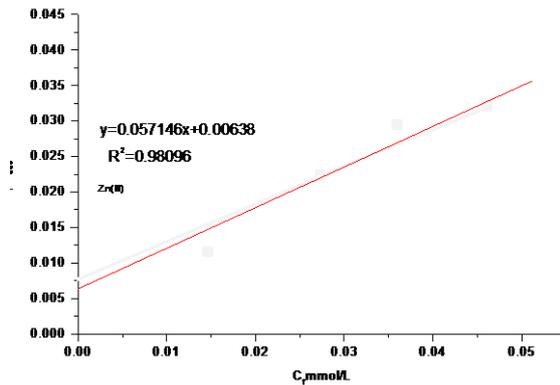


Fig. (6): Non-linear fitting of Langmuir, isotherm model for the adsorbents of Zn (II) ion.

Table (2): Recovery and Reuse Adsorbent

	Ads. Capacity	1st	2st	3st	4st	5st	6st	7st
Final Adsorption Capacity	568.792	233.045	133.67	74.002	45.783	22.132	10.798	2.339
Initial Adsorption Capacity	48.832	29.65	18.62	11.78	8.986	4.675	2.879	0.000

Conclusions

This study proved the possibility of the use of polymerization opening ring (POR) for the treatment of metal ions such as zinc and cobalt ions from aqueous medium. Poly Lactic-co-Glycolic Acid (PLGA) carboxylic groups as a functional to polymer chains, represents the degree of Carboxylic acid and cation exchanges capacity was 0.63 meq/100 g of hydroxyapatite with β -Tricalcium phosphate. Studying the adsorption isotherms of PLGA-composites resin with artificial, wastewater containing zinc and cobalt ions specified, cation exchanges capacity of PLGA were 30 and 83 meq/100g for cobalt and zinc ions respectively. For the two different metal ions removal percentage larger than 85%, the adsorption % as a result was obtained at different concentrations which depicts the pattern of adsorption for Langmuir isotherms. Modification with PLGA show that the cycle's number of adsorptions ranging from 3-6 do not exceed at 7 cycles. Studying the influence of adsorption isotherm for two models and the fitting of cations occur at the Langmuir model shows that it is better than Freundlich model.

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