

Removal Of Lead Ions From Aqueous Solution Using (Sodium Alginate / Itaconic Acid) Hydrogel Prepared By Gamma Radiation

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Abstract: In the present investigation a sodium alginate, extracted from the brown marine alga *Turbinaria decurrens* -based hydrogel, grafted polymerized with poly(itaconic acid), NaAlg/IA, was employed in studies on the adsorption kinetic of Pb⁺² in aqueous solution. The prepared polymer was characterized by FTIR and TGA analysis. The maximum capacity for the adsorption of Pb⁺² was found to be 1.23 mmol/L. Isotherm models of Langmuir, Freundlich and Temkin suggest that there may be variation in the physicochemical phenomena involving metal adsorption. These isotherms reveal that , there are multilayer coverage of Pb⁺² onto the hydrogel. Also Freundlich parameter (n=1.84) indicated that the adsorption intensity was favorable at high concentration but much less at lower concentration.

Key words: *Turbinaria decurrence*, hydrogel, adsorption isotherm, wastewater.

INTRODUCTION

Most of the heavy metals such as Pb (II), Cu(II) and Cd (II) that are toxic and carcinogenic even at very low concentrations usually cause a serious threat to the environment and to the public health (Liu C., *et al.*, 2008; Janga S.H., *et al.*, 2008; Zhou L., *et al.*, 2009; Zhuang Y. *et al.*, 2009). It is well known that heavy metals ions such as Pb (II) may cause severe health problems in animals and human because it can specifically bind to proteins, nucleic acid and small metabolites in living organisms inhibiting their functions. Heavy metals are detected in industrial waste water originating from metal plating, mining activities, smelting, battery manufacture (Xiong and Yao 2009). Petroleum refining (Rao M.M., *et al.*, 2009) printing and photographic industries.

Different types of methods have been proposed for the treatment of water and industrial waste water containing heavy metals (Chadlia A., *et al.*, 2009) such as biological treatments, procedures using a filtration membrane, advanced oxidation processes, electrochemical methods and adsorption processes have proven to be more viable alternative due to low cost of processing and instrumentation, ease of operation and no need for large facilities (Tang Q., *et al.*, 2009).

Hydrogels have a wide range of applications as controlled drug delivery vehicles (Sahera F. M., *et al.*, 2012), in tissue regeneration, as artificial organs in biotechnology, sensors, in separation and purification processes, and the recognition of certain molecules, bio-molecules and proteins (Sahiner and Singh 2007; Ozay O., *et al.* 2009). Several polysaccharides-based hydrogels have been employed to adsorb chemicals in waste water treatment processes and have attracted particular interest (Zhao and Mitomo 2008).

Hydrogels, are water-swollen crosslinked networks of hydrophilic polymers due to the hydrophilic groups (OH- COOH- NH₂-CONH₂ and SO₃H) in their backbones. The hydrophilic groups give them the ability to remove toxic metal-ions and they can absorb large amounts of water and swell (Ozay O., *et al.*, 2009; Satarkar and Hilt 2008). Furthermore, hydrogels can be modified with new functional groups or prepared as composites to increase their metal absorption capacity and their versatility for practical usage (Ozay O., *et al.*, 2009; Pekel N., *et al.*, 2001).

Alginate is a high molecular weight polysaccharide extracted from various species of brown algae. It is a linear, anionic block copolymer heteropolysaccharide consisting of 1, 4 linked β-D- mannuronic acid (M) and α-L-guluronic acid (G), Figure (1). The relative amount and sequential distribution of homogeneous M-M segments (M blocks), homogeneous G-G segments (G- blocks) and alternative M-G segments (MG-blocks), which represent the primary structure of alginate, depending on the producing species, and for marine sources, on seasonal and geographical variations.

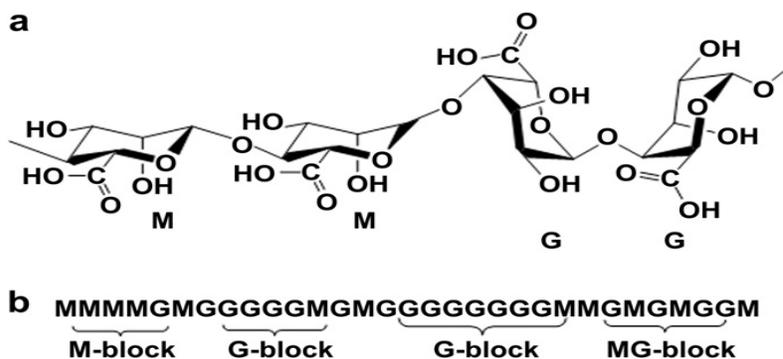


Fig. 1: Representative alginate structure: (a) chain conformation and (b) block distribution.

Alginate salts are used in a wide range of food, leather, pharmaceutical and industrial applications. They are important hydrocolloids that are capable of both thickening and gelling water (Liu Y., *et al.*, 2005).

However, they are prone to enzymatic degradation and suffer from limitations in fabrication, which limits its application in some fields, for example, in controlled-release technology. To overcome this problem, efforts have been made to develop chemically modified matrices by grafting. Grafting is a well-established and powerful method for the development of natural-synthetic polymer hybrid materials.

Itaconic acid (IA) is one of the monomers, which is readily available at low cost. It is obtained from renewable resources by fermentation with *Aspergillus terreus* using carbohydrate materials as molasses and hydrolyzed starch (Kalagasidis K., *et al.*, 2004; Mahdavian A., *et al.*, 2006). Poly itaconic acid (PIA) is interesting as a polyelectrolyte having two ionizable groups, with different pKa values, which can form H-bonds. These groups bring additional capability of chelate formation under certain cases. The grafting of IA onto polypropylene (Pesetskii S., *et al.*, 2002), low density polyethylene (Krivoguz Y., *et al.*, 2003) and chitin (Mostafa T., *et al.*, 2005) have been studied. It was therefore decided to graft IA onto sodium alginate (NaAlg).

Nuran *et al.*, (2010) are the first who reported the optimum condition for Graft copolymerization of IA onto NaAlg by using benzoyl peroxide. The optimum grafting conditions for maximum graft yield were obtained with reaction time of 1 h, reaction temperature of 85°C, IA concentration of 1.38 M, BPO concentration of 1.82 x10⁻² M and percentage of NaAlg 1.5 g/dL.

The objective of the present work was to investigate a pH-sensitive hydrogel based on (NaAlg), (IA) as a sorbent for removal of Pb⁺² ions from aqueous solution. The novelty of this work is to identify applicability of NaAlg/ IA hydrogel and also to identify various important parameters on the removal of Pb metal ions from its aqueous solution. Kinetic and isotherm models were used for the quantitative description and prediction of the metal uptake behavior of this hydrogel. The hydrogel was characterized with and without lead by using Fourier transformed infrared spectroscopy (FTIR) and field emission-scanning electron microscopy (FE-SEM) in order to determine possible metal binding mechanism. Also determination of atomic percentages and mapping of lead inside the gel were done by using Electron dispersive X-Ray (EDX).

MATERIALS AND METHODS

Materials:

Marine brown seaweed *Turbinaria decurrens*, collected in summer season, from Jazan coast-KSA, was used for extraction of alginate. Dried seaweed crushed and silted (10-20 mesh). Reagent grade IA purity 99% (Merck) was used as received. All other chemicals used, lead nitrate, the components of the citrate and phosphate buffers purchased from El-Nasr Co, Egypt.

Extraction of NaAlg from marine brown seaweed:

A crushed sample (100 g) of dry seaweed, *Turbinaria decurrens*, was moistened by addition of distilled water; 4000 ml and 0.1N aqueous solution of HCl were added under high stirring in order to have a pH 4 following a similar extraction method reported before (Cesar G., *et al.*, 2009). This mixture was stirred during 15 min at room temperature and then the supernatant was eliminated. This pre-treatment was repeated three times with every sample-using each time 400, 250 and 200 ml of HCl solution respectively. Then, the moistened seaweed was placed in a beaker with 2500 ml of a 1N Na₂CO₃ solution (pH, 11.5) and mechanically stirred at 60 °C for two h. The extracted sodium alginate from the initial material was subjected to purification.

Preparation of copolymer:

The NaAlg/IA hydrogel were synthesized by the free radical polymerization. An aqueous solution of 20% IA (v/v) was mixed with 10wt% NaAlg. Then they were irradiated at radiation dose 20 kGy, at room temperature, with a ⁶⁰Co source at a dose rate of 3.065 kGy/h at the National Center for Radiation Research and Technology, Cairo, Egypt. The hydrogel was purified by washing in excess water so that unreacted chemicals were leached out then air dried at room temperature.

Adsorption experiments:

The biosorption experiments were carried out with mono metallic solutions prepared from stock solutions of 0.5 M of pb²⁺ from chemical reagent of analytical grade. Pb(NO₃)₂ Lead nitrate was used to avoid metal precipitation, though the effect of the anion is negligible. Initial pH value of the solutions (5), optimized from previous tests, and was adjusted with acetate buffer as recommended before, (Sahera F.M., *et al.*, 2011). Known weight of hydrogel were placed in contact with the metal ion solution-100 ml containing 5% buffer v/v- of different concentrations in the rang 0.5- 4 mM in glass 250 ml Erlenmeyer's flasks. The flasks were put in a shaker at 150 rpm at 32°C and were left shaking overnight for complete equilibration. Initial and final metal concentrations were measured by Flame atomic absorption spectrometer (Varian model spectra A.A 220). In all experiments, triplicates were used. Biosorption of metal ions (q) in the sorption system was calculated using the mass balance.

$$q_e = \frac{V(C_i - C_e)}{W} \quad (1)$$

Where V is the solution volume (Ll), W is the weight of hydrogel pieces (g), and C_i and C_e are the initial and final (or equilibrium) metal ion concentrations (mmol of metal ion / l) respectively.

Biosorbent characterization:

FTIR analysis:

FTIR analysis was performed on KBr discs with 2% finely ground sample analyzed on an FT/IR300e (Jasco) spectrophotometer within the range 400–4,000 cm⁻¹ using a KBr window. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectra. All spectra were plotted using the same scale on the transmittance axis.

SEM and EDX analysis:

Examination of the hydrogel surface, coated with a thin layer of gold, was made by using a scanning electron microscope (JEOL-JX-840). To analyze the cross section of metal loaded hydrogel coated with a thin layer of graphite, an electron probe X-ray microanalyzer in EDX mode (JEOLJX- 840) was used.

RESULTS AND DISCUSSION

Biosorption equilibria:

Two important physicochemical aspects for the evaluation of the sorption process as a unit operation are the equilibria of sorption and the kinetics. Sorption equilibrium is established when the concentration of metal in a bulk solution is in dynamic balance with that of the interface.

The kinetic experiment Adsorption of Pb(II) ions:

The results of kinetic experiment are presented in Fig (2). The amount Pb²⁺ (mmol) adsorbed per gram of NaAlg/ IA (q_t), versus contact time at initial meta ion concentration 5 mM and temperature 37 °C is shown. The increase of contact time leads to an increase in the amount of metal ion adsorbed and the equilibrium is reached within 6 h.

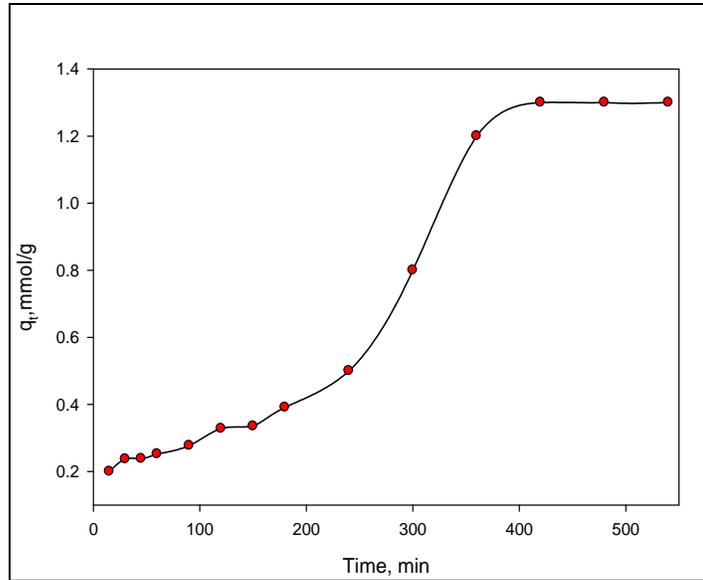


Fig. 2: Effect of contact time on adsorption of Pb^{2+} by NaAlg/IA at pH5 and initial concentration 5 mmol/l .

In order to investigate the rate constant , adsorption process was analyzed using the most widely applied kinetic models in sorption processes, pseudo-first model proposed by Lagergren,(1898) (eq. 2) pseudo-second order proposed by Ho and McKay (1999) (eq. 3) and intra-particle diffusion by Weber and Morris (1963) (eq. 4)

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

$$q_t = k_{id} t^{0.5} + C \quad (4)$$

where q_e and q_t are the amounts of Pb^{2+} adsorbed (mmol/g) at equilibrium and time t , respectively, k_1 (min^{-1}) is the pseudo-first-order rate constant and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the pseudo-second-order rate constant and k_{id} ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the intra-particle diffusion rate constant. The k_1 was calculated by plotting $\log (q_e - q_t)$ vs. t (Fig.3). The k_2 was calculated by plotting t/q_t vs. t (Fig.4) and k_{id} can be obtained from the slope of the plot q_t vs. $t^{0.5}$ (Fig.5).

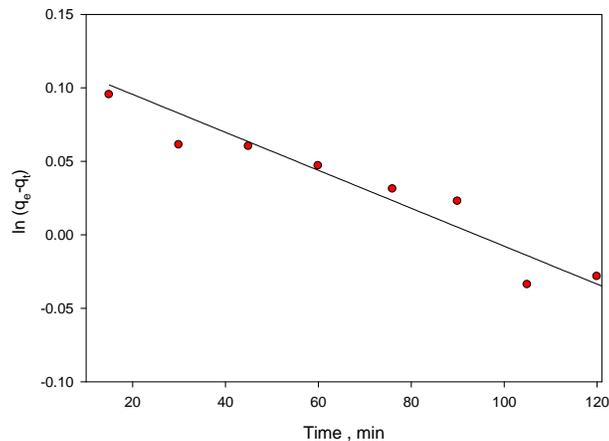


Fig. 3:The kinetic plots for adsorption of Pb^{2+} ions onto NaAlg/IA by pseudo-first-order model.

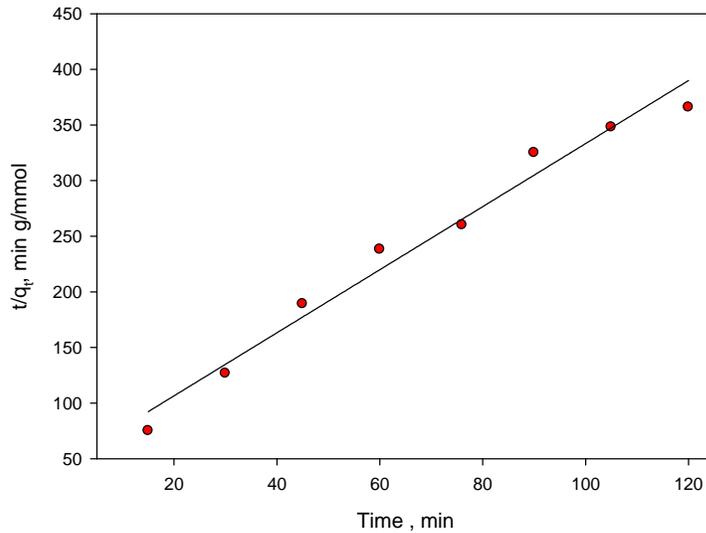


Fig. 4: The kinetic plots for adsorption of Pb^{2+} ions onto IA/ NaAlg by pseudo-second-order model.

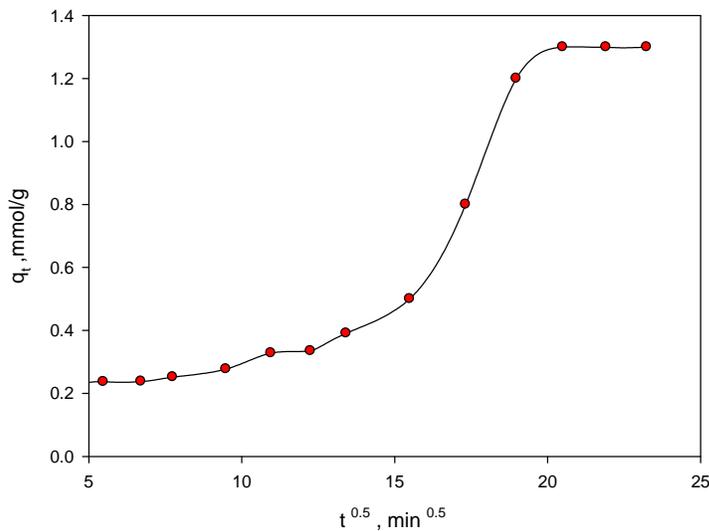


Fig. 5: The kinetic plots for adsorption of Pb^{2+} ions onto NaAlg/ IA by intra-particle diffusion model.

The characteristic parameters of the studied kinetic models and their corresponding correlation coefficients are presented in Table 1. Judging from the correlation coefficients, R^2 , the pseudo-second-order model have higher correlation coefficients ($R^2 \approx 0.97$) compared to the correlation coefficient for both pseudo-first-order ($R^2 \approx 0.95$) and intra-particle diffusion model ($R^2 \approx 0.86$). Obviously, the adsorption of Pb^{2+} ions on NaAlg/ IA can be well described by the pseudo-second-order adsorption mechanism and adsorption rates of Pb^{2+} onto NaAlg/ IA hydrogel were probably controlled by the chemical process.

Table 1: Constants of different kinetic models for Pb(II) ions adsorbed onto NaAlg/IA adsorbents

Rate constants	Parameters	Value
Pseudo-first order	k_1 (min^{-1})	2.97×10^{-3}
	$q_{e,cal}$ (mmol/ g)	1.32
	R^2	0.95
Pseudo-second order	k_2 (g/ mmol min)	0.16
	$q_{e,cal}$ (mmol/ g)	0.35
	R^2	0.97
intraparticle diffusion model	k_{id} (mmol /g $\text{min}^{1/2}$)	0.06
	C (mmol/ g)	-0.20
	R^2	0.86

Adsorption isotherm:

The equilibrium isotherm is fundamental in describing the interactive behavior between solutes and adsorbent. The adsorption of Pb^{2+} was investigated in batch experiments at 37 °C and pH 5.0. The initial concentration of the Pb^{2+} varied between 0.5 and 5 mM, and treated with definite weight of NaAlg/IA hydrogel polymer. Sorption was carried out for 24 h to ensure equilibrium. After the adsorption, the supernatant was separated and concentration of Pb ions was measured. In all experiments, triplicates were used. Standard deviation did not exceed $\pm 12\%$ and the results were presented in Fig. 6. The adsorption capacity of Pb^{2+} ions nearly linearly increased with the increase in the initial concentrations of Pb^{2+} ions, then reached surface saturation at concentrations around 1.23 mmol/l. This indicated that at lower initial concentrations, the adsorption sites on the hydrogel were sufficient, increase in Pb^{2+} concentration can accelerate the diffusion of Pb^{2+} ion into the polymeric networks as a result of an increase in the driving force of concentration gradient. However, at higher initial concentrations, the adsorption sites on the surfaces of the hydrogel reached saturation, and the adsorption of Pb^{2+} achieved equilibrium.

The equilibrium adsorption data were subjected to the three widely used isotherms, Langmuir and Freundlich as two parameter isotherm and Temkin isotherm models.

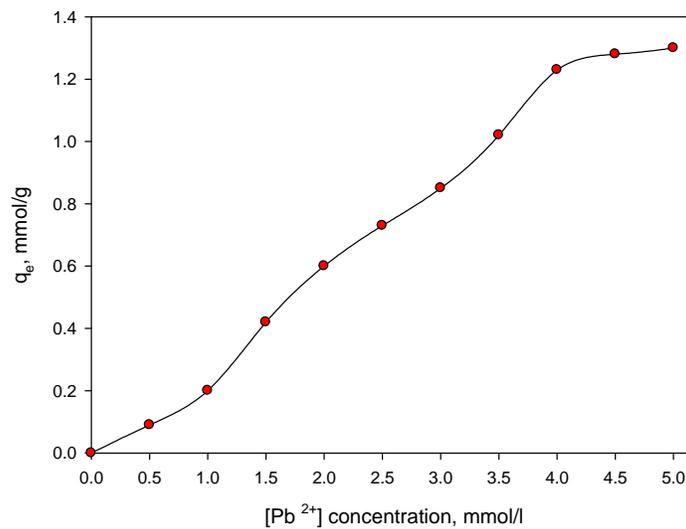


Fig. 6: The Langmuir Adsorption isotherm of Pb^{2+} onto NaAlg/ IA hydrogel at pH5.

The Langmuir sorption isotherm (Langmuir I., 1918), was used to fit the experimental biosorption data, It is represented as follows

$$q_e = \frac{q_{max} \cdot b \cdot C_e}{1 + C_e} \tag{5}$$

Where q_e is the metalion uptake at equilibrium (mmol of metal ion /g of biomass), q_{max} is the maximum Langmuir uptake (mmol of metal/g of biomass), C_e is the final metalions concentration at equilibrium (mmol of metal/l), b is the Langmuir affinity constant (l/mmol of metal) which indicates the affinity between the biomass and certain metalions. These sorption parameters obtained from the slope and the intercept of the linear line of C_e/q_e versus C_e , respectively (Fig.7).

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b \cdot q_{max}} \tag{6}$$

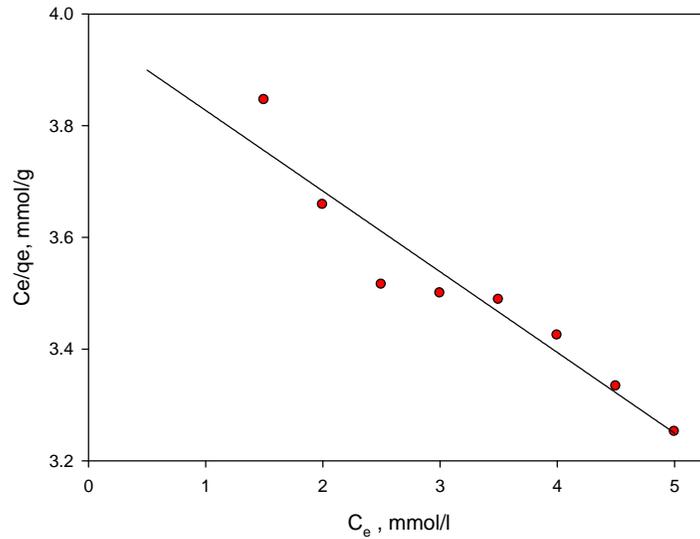


Fig. 7: Langmuir isotherm plot for adsorption of Pb^{2+} ions onto NaAlg/IA hydrogel

The Freundlich model (Freundlich H.M.F., 1906) is applied to describe a heterogeneous system characterized by a heterogeneity factor of $1/n$. This model describes reversible adsorption and is not restricted to the formation of the monolayer. The Freundlich model is expressed as follows

$$\log q_e = \log K_F + 1/n \log C_e \tag{7}$$

where K is the Freundlich isotherm constant, and $1/n$ (dimensionless) is the heterogeneity factor.

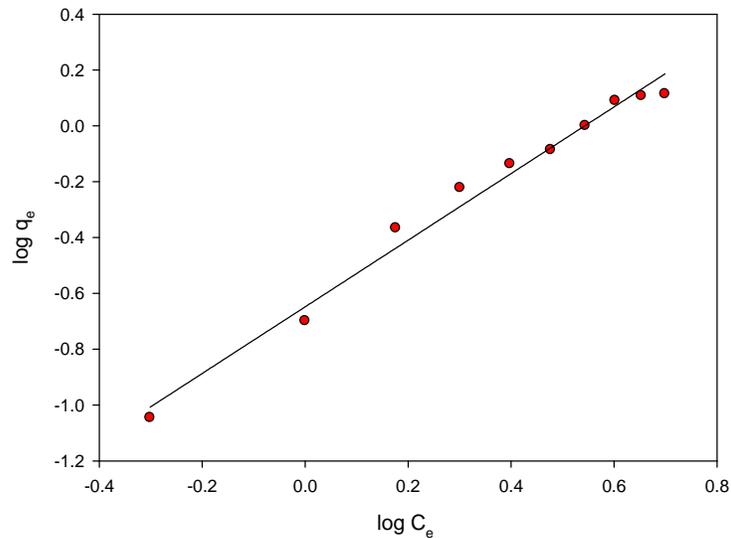


Fig. 8: Freundlich isotherm plot for adsorption of Pb^{2+} ions onto NaAlg/IA hydrogel

The Temkin isotherm (Temkin and Pyzhev, 1940) has generally been applied in the form given by Eq. (8)

$$q_e = B \ln A + B \ln C_e \tag{8}$$

where A is the Temkin isotherm constant (L/g), B is the Temkin constant related to heat of sorption (J/mol), $B = RT/b$, R the gas constant (8.314 J/mol K), b is Temkin isotherm constant and T is the absolute temperature (K).

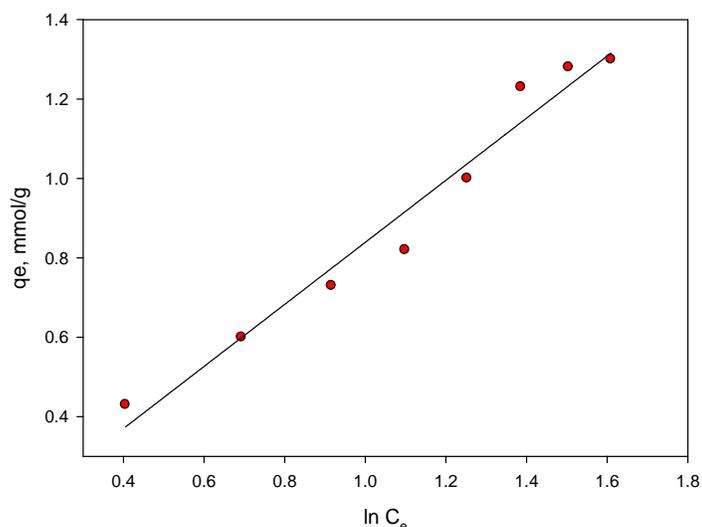


Fig. 9: Temkin isotherm plot for adsorption of Pb²⁺ ions onto NaAlg/IA hydrogel

The constant parameters and correlation coefficients were calculated from the Langmuir (Fig.7), Freundlich (Fig.8) and Temkin equations (8) (Fig.9) mentioned above, as summarized in Table 2. It can be seen that the values of correlation coefficients of Freundlich equation were higher than the other two isotherm values, which indicated the Freundlich isotherm correctly fitted the equilibrium data, confirming the multilayer coverage of Pb²⁺ onto the hydrogel. In addition, Freundlich parameter, n indicated the favorability of the adsorption. If n was less than one, it indicated that adsorption intensity was good (or favorable) over the entire range of concentration studied, but in this study the n value was more than one, (n=1.84) it meant that adsorption intensity was good (or favorable) at high concentration but much less at lower concentration (Dai J., *et al* 2010).

Table 2: Coefficients of different isotherms models for Pb(II) ions adsorbed onto NaAlg/IA hydrogel

Model	Parameters	Value
Langmuir	q _m (mmol/g)	6.9
	k _s (L/mmol)	0.04
	R ²	0.93
Freundlich	K _F (mmol/g(L/g) ^{1/n})	4.45
	1/n	0.54
	n	1.84
	R ²	0.98
Temkin	A (L/g)	1.07
	B (J/mol)	0.87
	R ²	0.97

Biosorbent characterization:

The FTIR spectra of NaAlg and NaAlg/IA hydrogel are shown in Fig. 10. For NaAlg, the strong absorption peak at 3345 cm⁻¹ is attributed to O–H stretching. Peaks at 1618 and 1481 cm⁻¹ are attributed to COO- (asymmetric) and COO- (symmetric), respectively. The characteristic peak of sodium alginate appeared at 840 cm⁻¹ (Na-O). In the case of NaAlg/IA hydrogel, a new sharp band appears at 1713 cm⁻¹ corresponding to C=O stretching for carboxylic group, the vibration absorption peak at 3345 cm⁻¹ has weakened or disappeared which imply the interaction between poly(itaconic acid) and sodium alginate.

The hydrogel material was subjected to thermogravimetric analysis to study its stability. Fig 11 shows the primary thermogram (TG) for the hydrogel copolymer. The polymeric material exhibited three steps thermogram, respectively. A slight weight loss is observed in the first stage at 110 °C probably due to moisture evaporation. A rapid decomposition occurs in following stages at 200 °C with a major weight loss of 70 %. The maximum temperature of decomposition occurs at 480 °C.

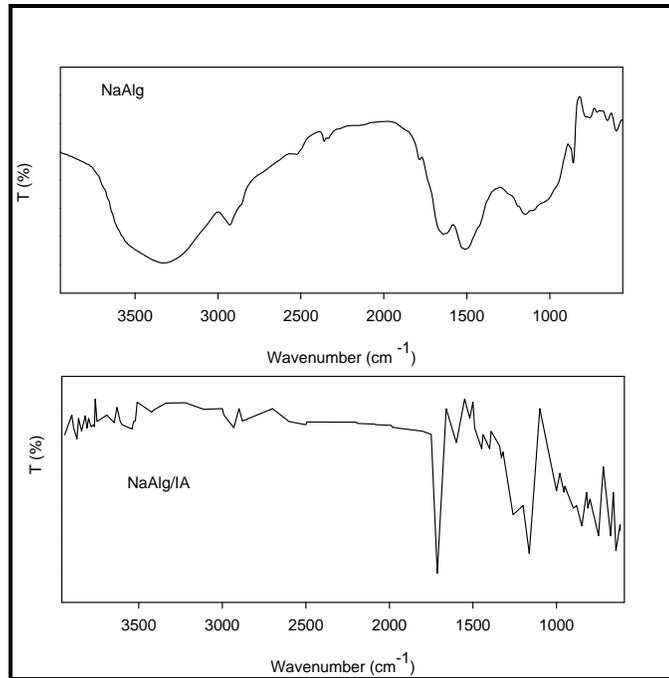


Fig. 10: FTIR spectra of NaAlg and NaAlg/IA hydrogel

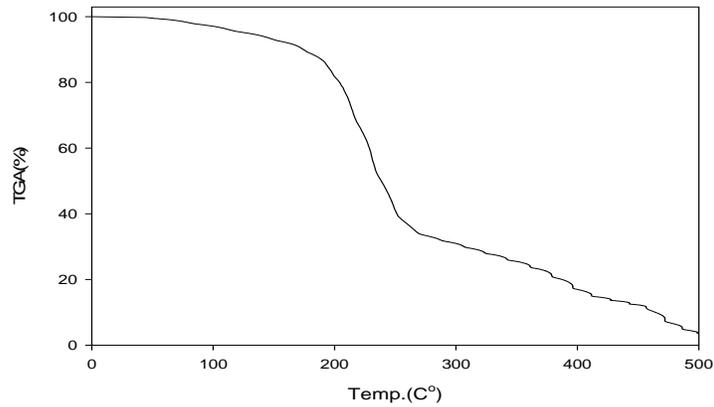
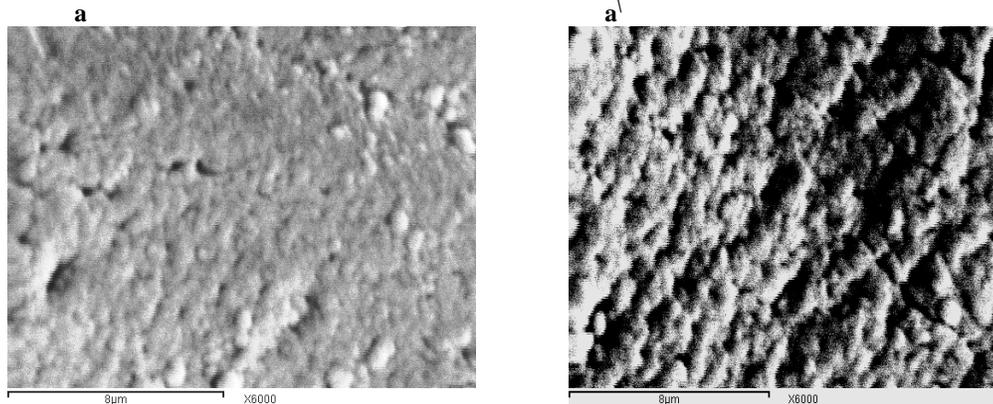


Fig. 11: Thermogravimetric analysis of (IA-NaAlg) hydrogel

The drying process resulted in hydrogel of high porosity with channels and open pores throughout the structure. Hence, the ions interacted with the functional groups on the external surface of the hydrogel. Figure 12a shows SEM micrographs of hydrogel surfaces before lead uptake, whereas Fig. 12 a¹ shows micrographs after binding of lead with the functional groups of the external surfaces of the hydrogel.



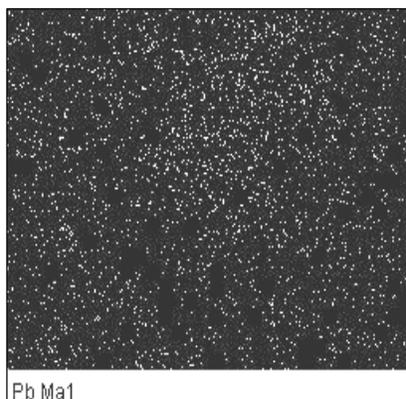


Fig. 12: SEM micrograph of the hydrogel surface before (a) and after lead uptake (a)

After lead uptake the presence and mapping of lead distribution inside the hydrogel were determined using EPMA–EDX (electron probe X-ray microanalysis in EDX mode) micrographs. Figures 13 b show the EDX micrographs of the cross section of the hydrogel after lead uptake at pH5. The distribution pattern of lead was measured on a unit surface area of 20 μm of the gel. X ray of hydrogel after lead uptake (Fig. 13 b¹) shows that the functional groups are homogeneously distributed in the hydrogel structure. This homogeneous distribution indicated that Pb^{2+} ions are capable of penetrating into the hydrogel and reacting with functional groups. Therefore, the hydrogel can be considered as porous ion exchangers having high permeability.

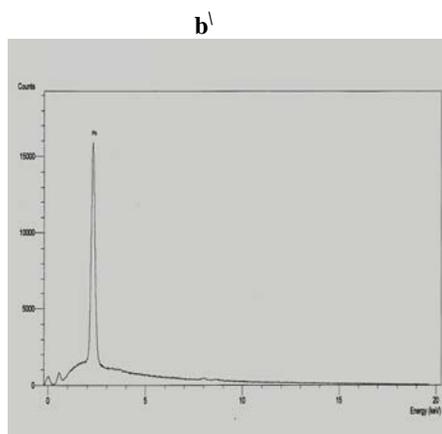


Fig. 13: EDX monograph of hydrogel after lead uptake, the sum spectrum for quantities of ions (b) inside the hydrogel and the x ray of hydrogel after lead uptake (b¹)

Conclusions:

The results of the present study demonstrated that the NaAlg/IA hydrogel may be an extremely viable adsorption for application in the treatment of water and industrial waste water contaminated with Pb^{+2} . The adsorption capacity of Pb^{2+} ions nearly linearly increased with the increase in the initial concentrations of Pb^{2+} ions, then reached surface saturation at concentrations around 1.23 mmol/l. This indicated that at lower initial concentrations, the adsorption sites on the hydrogel were sufficient, increase in Pb^{2+} concentration can accelerate the diffusion of Pb^{2+} ion into the polymeric networks as a result of an increase in the driving force of concentration gradient. However, at higher initial concentrations, the adsorption sites on the surfaces of the hydrogel reached saturation, and the adsorption of Pb^{2+} achieved equilibrium. Judging from the correlation coefficients, R^2 , the pseudo-second-order model have higher correlation coefficients ($R^2 \approx 0.97$) compared to the correlation coefficient for both pseudo-first-order ($R^2 \approx 0.95$) and intra-particle diffusion model ($R^2 \approx 0.86$). Obviously, the adsorption of Pb^{2+} ions on NaAlg/ IA can be well described by the pseudo-second-order adsorption mechanism. The values of correlation coefficients of Freundlich equation were higher than the other two isotherm values, which indicated the Freundlich isotherm correctly fitted the equilibrium data, confirming the multilayer coverage of Pb^{2+} onto the hydrogel. In addition, Freundlich parameter, ($n=1.84$) meant that adsorption intensity was favorable at high concentration but much less at lower concentration

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