RESEARCH ARTICLE

PREPARATION OF CROSSLINKED POLYACRYLAMIDE HYDROGELS AND THEIR APPLICATION TO THE REMOVAL OF MANGANESE (II) IONS FROM AQUEOUS SOLUTION

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ABSTRACT

Modified crosslinked polyacrylamide hydrogels having different functional groups were prepared by transamidation reaction using thiosemicarbazide (TSC) and benzene-1,4-diamine (BEN) as amine compounds while N,N'-methylene-bis-acrylamide was used as crosslinking agent. Viscosimetric measurements showed that the resins obtained namely Poly[N-(thiosemicarbazid)-acrylamide] (PAM_{TSC}) and Poly[N-(4-aminobenzyl)-acrylamide](PAM_{BEN}) have average molecular masses of 463818, and 511887 $g.mol^{-1}$, respectively. Then they were used as adsorbent for the removal of Manganese (II) from aqueous solutions under varying conditions of contact time, adsorbent mass, pH and initial concentration. The both chelating resins showed a high speed of adsorption less than 5 minutes attributed to their porous nature. The application of the kinetics models of pseudo-first order, pseudo-second order, and the intraparticle diffusion model on experimental data showed that the adsorption of Mn^{2+} is best fitted the pseudo-order model for the two chelating resins. The study of Freundlich and Langmuir isotherms models showed that the latter model describe well experimental data both for (PAM_{TSC}) and (PAM_{BEN}). The mono layer adsorbed amount of Mn^{2+}calculated from Langmuir model were 37.04 $mg.g^{-1}$ and 12.82 $mg.g^{-1}$ for the PAM_{TSC} and the $PAM_{BEN,}$ respectively.The results suggested that polyacrylamide produced could be used as potential adsorbent for removal of heavy metals ions from aqueous solution.

Key words: Adsorption, Crosslinked polyacrylamide, Isotherms models, Kinetic models, Langmuir model, Polyacrylamide.

INTRODUCTION

Water pollution by heavy metal remains a great matter of concern for wastewater treatment strategy according to the growth of industrial activities. These pollutants are mainly discharged by electroplating wastewater, metallurgical industries, metallurgical industries and mining industries (Taffarel and Rubio, 2010; Chen*et al.,* 2013). Heavy metals are considered to be the following elements: Copper, Silver, Zinc, Cadmium, Gold, Mercury, Lead, Chromium, Iron, Nickel, Arsenic, Selenium, Molybdenum, Cobalt, and Manganese. These compounds are highly soluble in water and cannot be affected by chemically or biologically degradation leading to their persistence in the environment. Some heavy metals produce serious human health problems once they enter the food chain. Hazardous effect such as poisoning principally results in neurological and renal disturbances, and can also cause mental retardation and semi-permanent brain damage (Btatkeu*et al.,* 2014).As water is well known as the main carrier of pollutants trough environment, there is a need for efficient treatment options which can effectively reduce the

heavy metal contained in the wastewater before their discharging in the receiving area.Various techniques such as chemical precipitation (González-Munõz *et al.,* 2006), adsorption (Omri and M. Benzina, 2012; Domga *et al.,* 2015; Domga *et al.,* 2016), membrane filtration , biological treatment (Bessbousse *et al.,* 20058) and electrochemical oxidation processes (Chen *et al.,* 2013) have been employed for the treatment of wastewaters. Among these techniques, adsorption on activated carbon has proved to be one of the most efficient and effective technique for separation and removal of organic pollutants from wastewater (Omri and Benzina, 2012).However, commercial activated carbons manufactured to produce precise surface properties are expensive and require elaborate reactivation and regeneration processes (Gupta*et al.,* 2011). Nowadays, the development of new low cost adsorbents having good properties such as high adsorption capacity and fast adsorption rate has gained great interests for wastewater treatment (Omri and Benzina, 2012; Rahchamani *et al.,* 2011). In this point of view, modified polymers with different functional groups appear as a promising solution due to their high adsorption capacities, especially regeneration abilities and reuse for continuous processes (Senkal and Yavuz, 2006). Similarly functionalized polymers are also favoured adsorbents for heavy metals due to their good mechanical strength, large

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surface area, and fast adsorption (Kasgöz *et al.,* 2003; Xu *et al.,* 2014; Atta *et al.,* 2016). Indeed, increasing the porosity of the resin or crosslinking can help improve the kinetics by increasing the accessibility of the polymer-supported ligands to the metal ions. It has been determined that crosslinked polymeric materials having amine as functional groups could be used as good complexing agents for the removal of metal ions from aqueous solutions (Hicks and Updike, 1966). The aim of this study was to test the application of modified crosslinked polyacrylamide for the treatment of water contaminated by Mn^{2+} ions. Manganese (II) has been chosen as heavy metal model in this study due to its widely availability and hazardous effect on human health. The effect of contact time, pH, and adsorbent mass and metal initial concentration were reviewed. Kinetics adsorption models and isotherms models were applied to the experimental data.

MATERIALS AND METHODS

Material and chemical reagent

Chemicals reagent (Potassium permanganate, dibenzoyle peroxide) and solvents (N,N-dimethylformamide (DMF), dimethylsufoxide (DMSO), acetone, toluene, methanol) used in the present work were purchased from Fluka and Merck, respectively and were used without further purification. N, N'-methylene-bis-acrylamide, acrylamide, thiosemicarbazide and benzene-1,4-diaminewere purchased from Sigma-Aldrich.

preparation of modified crosslinking agent

The microspheres of modified crosslinked polyacrylamide were obtained by the technique of radicalizing polymerization in dispersion as indicated by Hicks and Updike (Hicks and Updike, 1966). Redox initiator was obtained by dissolving dibenzoyle peroxide (1.22 g) in distilled water (96.94 mL). The mixture of monomer acrylamide (0.62 g) and crosslinking agent N,N'-methylene-bis-acrylamide (1.22 g) was added to the initiator solution progressively under magnetic stirring (400 rpm) at 70-75°C for 5 hours. Toluene (0.5 ml) was previously added to the solution to put out oxygen. The precipitated polymer (PAMc) obtained was filtered, washed with distilled water, recrystallized in acetone, and dried at 60°C until obtaining a constant mass**.**

Functionalization of modified crosslinked polyacrylamide

Functionalization With Benzene-1,4-Diamine: A solution of 1M benzene-1,4-diamine (0,5 mL) was added to a 1M solution of Chlorhydricacid (0,5 mL) and was left (30 mn) in Erlenmeyer at ambient temperature. The preceding mixture is then added to the PAMc (5 g) in distilled water (94 mL) under magnetic stirring (400 rpm) and heated (100°C) for 24h. A NaOH (1M) was added to the preceding mixture to regenerate protected amino group. The modified polymer (PAM_{BEN}) was then recovered by filtration and washed successively with hot and cold water till the polymer is free from amine as determined by colour reaction with ninhydrin which detects amino group up to 0.1 µmol.g[1]. Finally the modified polymer has been washed with methanol and dried at 50°C until obtaining a constant mass.

Functionalization With Thiosemicarbazide: A mixture constituted of excess of thiosemicarbazide (9 g), 5g of PAMc were dissolved in distilled water (86 mL). The mixture was stirred (400 rpm) for 24 h at 100°C.The modified polymer (PAM_{TSC}) is recovered and treated under the same conditions as the previous procedure.

Characterization of cross linked polyacrylamide

The characterization of modified cross linked produced was made by measuring the viscosity with capillary Viscometer (Ostwald, Fried Electric). Measurements of intrinsic viscosities $[\eta]_{int}$of polymers in organic solvents above were carried out in a water bath thermostat at 29°C for 24h (Amira, 2010) and it expressed as given by equation (1)

$$\eta = \lim_{C \to 0} \frac{\eta - \eta_0}{\eta_0 . C} \quad\text{.. (1)}$$

Where: η is absolute viscosity of dissolved polymer solution, η_0 absolute viscosity of pure solvent, C concentration of polymer solution.

The average molecular mass (Mm) was obtained by using equation:

$$M = \left(\frac{[\eta]_{int}}{k} \right)^{\frac{1}{\alpha}} \quad\text{... (2)}$$

Where K and α are constants for a polymer-solvent couple given at a specified given temperature (Moreira *et al.,* 2004).

Batch adsorption experiments

Stock solution of Mn^{2+} ions was prepared by dissolving 1g of $KMnO_4$ in distilled water (1 L). Working solutions were then prepared by dilution of the stock solution for desired concentrations. Adsorption experiments were carried out under batch mode at (25 ± 1° C) in an Erlenmeyer flask. The pH of solution was measure by pH-Meter (CG 820, SCHOTT GERATE), and the desired value for working solutions was adjusted with 0.1 M H_2SO_4 or 0.1 M NaOH. Known amount of polyacrylamide (PAM_{TSC} and PAM_{BEN}) was added to 50 mL solution of Mn^{2+} and then stirs at 160 rpm. After the equilibrium, the mixture was filtered and the supernatants were analysed by spectrophotometer at maximum wavelength (λ = 525 nm). Distilled water has been used as blank.The mechanisms of Mn^{2+}uptake by PAM_{BEN} and PMA_{TSC} chelating resins can be illustrated by Equation (3) and (4), respectively.
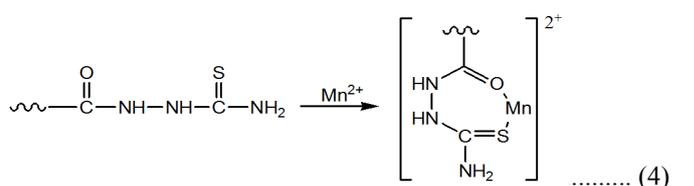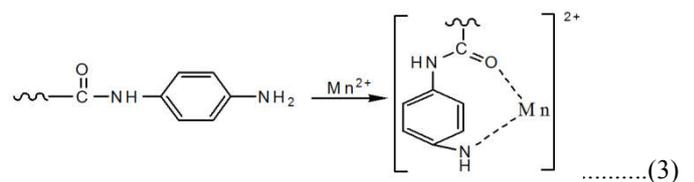
The adsorption kinetics was carried out by varying the pH, the initial concentration of Mn^{2+}, contact time and the mass of polyacrylamide.

Mn^{2+} uptake at equilibrium time, Qe (mg/g) was calculated using the following equation (5):

$$Qe = \frac{C_0 - Ce}{m} \times V \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (5)$$

Where C_0 and C_t are initial and equilibrium concentrations (mg/L) of Mn(II), respectively; m is mass of resin used(g) and V is the volume of the solution (L).

Kinetic tests

For evaluation the kinetic parameters the most commonly known kinetic expressions that is the pseudo first order kinetic and the pseudo second order kinetic models were used according to the equation (6) and (7):

$$\log(q_1 - q_t) = \log(q_1)\frac{k_1}{2.303}t\dots\dots\dots\dots\dots\dots\dots (6)$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2}t \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (7)$$

Where q_t is the amount of metal absorbed at time *t* [mg/g], q_1, q_2 are the amounts of metal complexes sorbed at equilibrium for the pseudo first order kinetic and the pseudo second order kinetic models [mg/g], respectively, k_1 is the pseudo first order rate constant [1/min] and k_2 is the rate constant of the pseudo second order adsorption [g/(mg.min)].Based on the plots of $\log(q_e - q_t)$ vs. *t* and t/q_t vs. *t* the kinetic parameters (q_1, k_1, q_2, k_2, h) were calculated.

RESULTS AND DISCUSSION

Characterization of cross linked polyacrylamide

The suspension of polymerization procedure provided here crosslinked polyacrylamide. It obtained by the technique of ridicalizing polymerization in dispersion as indicated by Hicks and Updike (Hicks and Updike, 1966). The characterization of modified crosslinked produced was made by measuring the viscosity with capillary Viscometer (Ostwald, Fried Electric). Measurements of intrinsic viscosities $[\eta]_{int}$ of polymers in organic solvents above were carried out in a water bath thermostat at 29°C for 24h (Amira, 2010) and it expressed as given by equation (1).We carried out the tests of solubility of different polymers in some organic solvents at 25 °C. The results enabled us to make the following observations: the PAM is soluble in DMF, dichloromethane and acetone. The PAM_{TSC} is soluble in DMF while the PAM_{BEN} is solubilized better in DMSO. The experimental parameters of the characterization of crosslinked polyacrylamide are presented in table 1.The Table 1 shows that the average molar masses differ from/to each other depending on whether one modified polyacrylamide is modified or not by the introduction of a functional group. The high crosslinking of polyacrylamide and solvents used explains its high mass. Average molar masses of functionalized polyacryl amide PAM_{TSC} and PAM_{BEN} higher than not modified polyacrylamide PAMc are due to the incorporation of thiosemicarbazide (91,14 g/mol) and benzene-1,4-diamine (108,14 g/mol) molecules. The values of the HUGGINS constants K and α obtained vary in opposite directions to one another (Moreira *et al.,* 2004).

Table 1. The intrinsic viscosities[η]$_{int}$,α, k, and M constants of polymers

Polymer	Solvent at 29°C	$[\eta]_{int}$(ml/g)	Log k	α	Molecular massM (g/mol)
PAM	DMF	71.4	0.85	0.71	436346
PAM_{TSC}	DMF	78.6	0.36	0.78	463818
PAM_{BEN}	DMSO	80.5	0.34	0.80	511887

Effect of contact time

The adsorption of metal ions from aqueous solution is controlled by the rate of reaction which determines the equilibrium time. It is one of the important characteristics defining the efficiency of an adsorbent (Krishnan*et al.,* 2003). The effect of contact time on adsorption of Mn^{2+} by PAM_{TSC} and PAM_{BEN} is shown in Fig. 1. The operating conditions were: PAM_{TSC} (0.02 g) and PAM_{BEN} (0.05 g), C_0= 25 mg.L^{-1}, pH= 6, Temperature =25°C.The Fig. 1 shows the time taken to attain equilibrium for Mn^{2+} at pH= 6, temperature of 25°C using PAM_{TSC} (0.02 g) and PAM_{BEN} (0.05 g). It was observed that the remaining amounts of Mn^{2+} in solution increase during first minutes. The time of equilibrium is established at 2 minutes for the PAM_{TSC} and 4 minutes for the PAM_{BEN}. The necessary contact time to reach the equilibrium depends on the initial metal ion concentration (Eruola, 2012). Thus, the metals adsorption in solution on modified polyacrylamide polymers by amino groups are done in the first 5 minutes. Others authors also reported the same effect (Kasgöz *et al.,* 2003; Latha*et al.,* 1991; Shaw and R. P. Haddad, 2004; Kiefer *et al.,* 2004). In order to find the possible mechanisms brought into play during the adsorption of the Mn^{2+}ions by two adsorbent polymers, we compared our experimental results of adsorption kinetics according to models of pseudo-first order, pseudo-second order, and intra-particular diffusion.
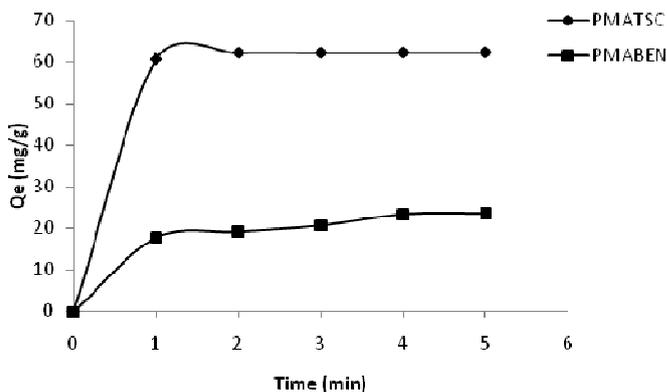
Figure 1. Effect of contact time on adsorption of Mn^{2+} by PAM_{TSC} and PAM_{BEN}

Effect of pH

The pH solution is an important factor in any adsorption study, because it may influence both the structure of adsorbent and adsorbate, and the mechanism of adsorption (Domga *et al.,* 2015; Domga *et al.,* 2016). It affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate (El-Sayed *et al.,* 2011). To study the effect of pH on the adsorption Mn(II) onto the PAM_{TSC} and PAM_{BEN}, the pH was varied from 2 to 12. The operating conditions were: C_0= 25 mg.L^{-1}, pH= 6, Temperature =25°C. The initial pH of solution

was adjusted using sodium hydroxide NaOH (0.1 M) or sulphuric acid (0.1 M). The evolution of the Mn^{2+}ion quantities adsorbed according to the pH is given by the Fig. 2.
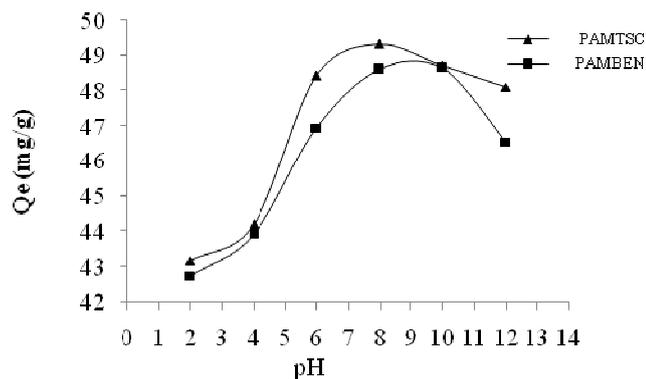
Figure 2. Effect of pH on adsorption of Mn^{2+} on PAM_{TSC} (0.05 g) and PAM_{BEN} (0.05 g)

As can be seen from the Fig. 2, the curve of Mn^{2+} uptake according to pH followed the same trend whatever the polymer used. The amount adsorbed of metal ions by PAM_{TSC} and PAM_{BEN} increased with increase in pH up to a certain value and then decreased with further increase in pH.The lesser amounts adsorbed obtained in acid media (pH = 2), were 43.16 $mg.g^{-1}$ and 42.73 $mg.g^{-1}$ for PAM_{TSC} and $PAM_{BEN,}$ respectively. This result could be due to a competition between Mn^{2+} ions and hydroniums ions (H_3O^+) for the sites of adsorption or by an electrostatic repulsion between ions having same signs charge. The excess of H_3O^+ ion surrounding the blinding sites making sorption unfavorable (Eruola, 2012).Then, the adsorbed quantities increase with the pH and reached the maximum adsorption (49.31 $mg.g^{-1}$ and 48.63 $mg.g^{-1}$) of Mn^{2+} atslightly alkaline (pH=8). Several authors have reported the same findings for the adsorption of metal ions in aqueous solution by adsorbent polymers containing amine functional groups (Sharma*et al.,* 2009).The decreasing of amounts adsorbed for pH values high than 8 may be explained by the competitive reaction of Mn^{2+}ions with hydroxide ions to form manganese hydroxides ($Mn(OH)_2$) (Mengistie*et al.,* 2012; Nkwaju*et al.,* 2015).

Effect of adsorbent mass

The effect of mass adsorbent on the adsorption of Mn(II) ions is shown in Fig.3. Dilutions to hundredth and to tenth were carried out for PAM_{TSC} and PAM_{BEN} respectively.The Fig. 3 shows firstly that the amounts adsorbed increase at the equilibrium (22.92to 31.36 $mg.g^{-1}$) according to PAM_{TSC} resin mass (0.04 to 0.1 g). This is explained by the increase in the number of adsorption sites involve as the amount of adsorbent resin increase. On the contrary, the amounts adsorbed at equilibrium decrease (96.73 to 23.45 $mg.g^{-1}$) when the amounts of PAM_{BEN} resin increase (0.05-0.2 g).This can be due to congestion of adsorption sites by other polymer particles in excess in the solution or channels and porous shrinkage by the creation of chelating resin aggregates and consequently a reduction of the intercellular distances; this produced a screen affect leading to protection of the sites of connection of the adsorbate (Domga *et al.,* 2015; Nkwaju *et al.,* 2015; Shukla *et al.,* 2002; Saifuddin and Raziah, 2007). So, the less saturated the medium, the more Mn^{2+} ions diffuse easily towards the adsorbent sites.
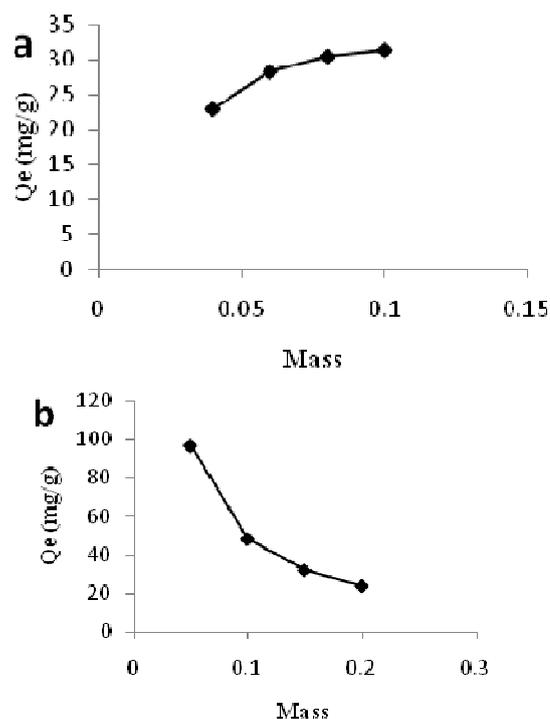
Figure 3.Effect of mass adsorbent on adsorption of Mn^{2+} a) PAM_{TSC} $[Mn(II)]_0$ = 25 mg.l^{-1}; t=5 mn; pH=7; Temperature=25°C; V= 0.05L and b) PAM_{BEN}: $[Mn(II)]_0$ = 25 mg.L^{-1}; t=5 mn ; pH=7; Temperature=25°C; V= 0.05L.
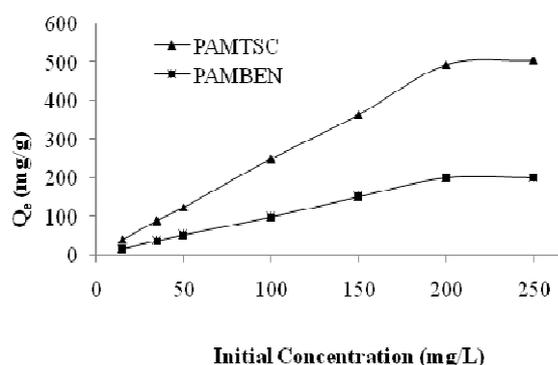
Figure 4. Effect of initial metal concentration Mn(II) on the adsorption of PAM_{TSC} (0.02g)and PAM_{BEN} (0.05g) adsorbent, pH=6

Effect of initial metal ion concentration

The adsorption of metal ions by an adsorbent is particularly dependent on the initial heavy metal concentration in solution. It provides a driving force to overcome all mass transfer resistances on the metals ion in the aqueous and solid phase. The effect of initial metal ion concentration on the adsorption at equilibrium conditions is shown in Fig. 4. As seen from Fig. 4, the amount of ion sorbed per unit of PAM_{TSC} (0.02g) and PAM_{BEN} (0.05g) adsorbent at pH=6 was increased with the increase of the initial concentration of metal ion Mn(II). This indicates that at higher concentration of metal ion (200 mg/L), the active sites of PAM_{TSC} and PAM_{BEN} adsorbents were surrounded by much more metal ions and the process of adsorption continues, leading to an increased uptake of metal ions from the solution. Similar results have been reported in literature (Domga *et al.,* 2016; Emmanuel and Veerabhadra Rao, 2009; Makeswari *et al.,* 2016).

Table 2.Comparison of the correlation coefficients of kinetic parameters for adsorption of Mn(II) ions onto PAM$_{TSC}$ and PAM$_{BEN}$ adsorbents

	Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
	q_{cal}	K_1	R^2	q_{cal}	K_2	R^2	K_{int}	C	R^2
PAM$_{TSC}$	0.14	0.09	0.67	62.5	0.01	0.99	0.04	62.22	0.49
PAM$_{BEN}$	21.84	0.85	0.87	25	0.1	0.99	2.13	16.93	0.68

Kinetic adsorption study of Mn(II)

In order to find the possible mechanisms brought into play during the adsorption of the Mn(II) ions by two adsorbent polymers, we compared our experimental results of adsorption kinetics with theory models of pseudo-first order, pseudo-second order, and intra-particular diffusion. The linearized 1st order rate equation (Ho, 2004) for adsorption in the solid systems is of the form:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \qquad (9)$$

Where Q_t and Q_e are adsorbed amount at time t and at equilibrium per unit of mass respectively, the pseudo-first order speed constant is K_1 (in min^{-1}). By plotting $\log(Q_e - Q_t) = f(t)$ we obtain a straight line where $-K_1$ is the gradient and $\ln Q_e$, the origin. The rate constant of the pseudo-first order model on the PAM$_{TSC}$ ($K_1 = 0.097$ min^{-1}) is low compared to that on the PAM$_{BEN}$ ($K_1 = 0.856$ min^{-1}). This first order mechanism suffers for a significant limitation compared to the amounts adsorbed values at equilibrium Q_e(Ho, 2002).So, the second order adsorption mechanism was (Ho, 1999):

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \qquad (10)$$

While plotting $t/Q_t = f(t)$, we obtain a straight line where $1/Q_e$ is the slope and $1/K_2 Q_e^2$ the origin. The amount adsorbed of Mn^{2+} $Q_e$at the equilibrium and the rate constant K_2 (g.mg^{-1}.min^{-1}) are determined from the slope and the origin. The rate constant of the second order K_2 (0.1 g.mg^{-1} .min^{-1}) on PAM$_{BEN}$ being higher than that of PAM$_{TSC}$ K_2 (0.01 g.mg^{-1} min^{-1}) showing that PAM$_{BEN}$ has a greater affinity for the Mn(II) ions than PAM$_{TSC}$.When there is a diffusion possibility of the ionic species inside the adsorbent porous, the rate constant of intraparticular diffusion (K_i) can be obtained using equation (11):

$$Q_t = K_{int}\sqrt{t} + C \qquad (11)$$

The intraparticle diffusion model has a significant role in the control of adsorption kinetics process of (Bhattacharyya and Gupta, 2008).If the plotting of Qt=f(t) is a line passing through the origin, the slope gives the rate constant K_i. In this case, the correlation coefficients are respectively $R^2=0.49$ and $R^2=0.68$ on the PAM$_{TSC}$($K_{int}=0.037$ mg.g^{-1}.min$^{-1/2}$) and PAM$_{BEN}$ ($K_{int}=2.13$ mg.g^{-1}.min$^{-1/2}$).The lines have as origin 62.22 for PAM$_{TSC}$ and 16.93 for PAM$_{BEN}$, indicating then that, the intraparticlediffusion does not determine probably the low rate at this stage (Bhattacharyya and Gupta, 2008). The value of the directing coefficient of the right-hand side of the intraparticle diffusion model of PAM$_{TSC}$ is low (0.26 when the initial concentration is 25 mg/L). This coefficient which is not close to the unit shows that the diffusion of the Mn(II) ions inside the porous is limited and very slow.

According to coefficient values from Table 2, it can be conclude that the pseudo-second order model better describes the experimental data and suggests that adsorption is carried out in two stages. Firstly a diffusion of Mn(II) ions towards the polymers area and Secondly an interaction of Mn(II) ions on the polymers area. Moreover, this result also suggests that the adsorption process of Mn(II) on both chelating resins may be controlled by chemical adsorption involving valence forces through sharing or exchange electrons between sorbent and (Taffarel and J. Rubio, 2010; Xu *et al.,* 2014).

Adsorption isotherms modeling

Adsorption isotherm is a fundamental tool elucidating the relationship between adsorbate molecules and the adsorbent surface. In this study, two common isotherm models were established: the Langmuir and Freundlich model. The linearized form of Langmuir and Freundlich models is given by the equation (12) and (13), respectively.

$$\frac{C_e}{Q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (12)$$

Where C_e is the concentration of Mn^{2+} at equilibrium in the solution (mg.L^{-1}), Q_e the Mn^{2+} amounts adsorbed at equilibrium (mg.g^{-1}), q_m is the monolayer amount of metal ion adsorbed (mg.g^{-1}), and K_L (L.mg^{-1}) is the equilibrium Langmuir constant.

$$\ln q_e = \ln K_f + \frac{1}{n}\ln(C_e) \qquad (13)$$

Where $\ln K_f$is the origin and $1/n$ the slope of the line $\ln q_e = f(\ln(C_e))$ calculated by using the experimental data. Table 3 shows the various Freundlich constants obtained for the two resins.

Where: K_F (mg/g) (L/mg) and $1/n$ are the Freundlich adsorption constant, and a measure of the adsorption intensity.

The Table 3 shows that the experimental data are in conformity with the model of Langmuir for the adsorption of Mn(II) ions on PAM$_{TSC}$ and PAM$_{BEN}$ with an correlation coefficients R^2 higher than 0.90 (0.99 for both adsorbents).The table 4 reveals that the adsorption capacities of PAM$_{TSC}$ and PAM$_{BEN}$ resins are 37.04 mg.g^{-1} and 12.82 mg.g^{-1} respectively which indicates that PAM$_{TSC}$ has a higher mono-layer adsorbent capacity than PAM$_{BEN}$. The model of Langmuir shows that there is homogeneous distribution of adsorption sites on the chelating resins surface. On the other hand, the Freundlich model values of $1/n$ smaller than 1 during the Mn(II) ions adsorption on PAM$_{TSC}$, indicating that adsorption is higher for low values of Mn(II) ions initial concentrations in aqueous solution.

Table 3. Isotherm parameters obtained for the adsorption of Mn²⁺ onto PAM_BEN and PAM_TSC

	Langmuir parameters			Freundlich parameters		
	Q_0	K_L	R^2	K_F	n	R^2
PAM$_{TSC}$	37.04	0.09	0.99	286.86	1.74	0.67
PAM$_{BEN}$	12.82	0.35	0.99	1391.30	0.42	0.88

Conclusion

This work constituted a new insight for preparation of adsorbent as chelating resins and their application to remove heavy metals from aqueous solutions. The chelating resins obtained namely Poly[N-(thiosemicarbazid)-acrylamide] (PAM$_{TSC}$) and Poly[N-(4-aminobenzyl)-acrylamide] (PAM$_{BEN}$)showed that their molecular mass values are related to the functional group used during the preparation. The PAM$_{TSC}$ is soluble in dimethylformamide while the PAM$_{BEN}$ is solubilized better in Dimethylsulfoxide. Adsorption studies show that removal is dependent upon process parameters like contact time, pH, adsorbent mass and metal ion concentration. PAM$_{TSC}$ was found to adsorbed more than the PAM$_{BEN}$ for the removal of Mn(II) ions from aqueous solution as confirmed by their adsorption capacities. The experimental data were best described by the pseudo-second order kinetic model while Langmuir isotherm indicates that interactions are mainly of chemical nature. The higher rate adsorption of Mn(II) ions adsorption in the first five minutes on two modified polymers exhibited their highest degree of porosity and flexibility as well as the hydrophobicity of the amino ligands. These adsorption properties can be valorising for wastewater treatment.

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