RADIATION SYNTHESIS OF FUNCTIONALIZED POLYPROPYLENE FIBERS AND THEIR APPLICATION IN THE TREATMENT OF THE GROUNDWATER IN EL DAKHLA OASIS, WESTERN DESERT OF EGYPT.

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Functionalized polypropylene (PP) fibers were prepared by radiation induced graft copolymerization of acrylamide (AAm) and 4-vinyl pyridine (4-VP) binary system onto the (PP) fibers. Preparation conditions such as type of solvent used, comonomer composition and total concentration were investigated to obtain a suitable grafting degree for the proposed application as a metal recovery polymer. The effect of pH on the adsorption of individual metal ions was investigated to estimate the optimum pH value for each metal at which maximum adsorption takes place. It was found that the sorption capacity of the functionalized fiber was 247.3, 221.3, 202.1, 161.5, 135.4, 128.89, 122.06 and 104.1 (mg/g) for Pb, Cd, Zn, Cu, Fe, Mn, Sr and Al respectively. Dynamic metal uptake behavior and the thermodynamics parameters of the metal adsorption process were studied. The results illustrate the values of the adsorption rate for each metal ion and that the metal chelation by functionalized PP fibers is an exothermic process. Re-generation test shows that the prepared fibers kept their capacity unchanged up to, at least, 10 cycles. The prepared functionalized PP fibers were used to treat some groundwater samples containing high concentrations of iron and manganese collected from El Dakhla Oasis which is located at the Western Desert of Egypt. The obtained results show that the prepared fibers acquire a promising potential in improving the quality of water resources.

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Due to the urgent need for water in the development of the huge desert areas in Egypt, the contamination of some water resources by heavy metals has become a serious issue (Fenoglio *et al.,* 2005). Heavy metals, especially iron and manganese are naturally found in water resources as a result of the nature of water bearing formation and surrounding environment. Groundwater in the Nubian sandstone aquifer of the Western Desert of Egypt contains high concentrations of iron and manganese (Razowska, 2001; Houben, 2003). The concentrations of these two metal ions in an aerobic groundwater can reach as high as several mg/l and is therefore unsuitable for different uses without appropriate treatment process. The determination of trace toxic metal ions and their removal with functionalized polymers have gained great importance in environmental applications because of their high degree of selectivity, high loading capacity, versatility, durability, and enhanced hydrophilicity (El-Hag Ali *et al.,* 2003; Shawky *et al.,* 2006; Hardin *et al.,* 2005; Salih *et al.,* 2001). The necessity of reducing the concentration of heavy metals to acceptable levels in water resources and the need for more highly specific metal recovery processes in both hydrometallurgical and environmental applications have led to increasing interest in polymer- based adsorbents. The specific and rapid complexation of the metals and the reusability of the chelating polymeric ligands are important criteria for the selection and design of chelating polymers with substantial stability for the selective removal of heavy metal ions. Chelating ion-exchanger with specific chelating groups attached to polymer substrate has found extensive use in the separation and pre-concentration of metal ions. Researches on fibrous reactive agents have shown many advantages over their resin counterparts. The high specific surface area of fibrous supported materials improves the accessibilities of functional groups resulting in higher reaction rate than the resin type agents (Hegazy *et al.,* 2000; Buchenska, 2002 Dong and Liu, 2004). Moreover, importantly, the fibrous agents perform a superior handling properties and a wide range of architectures, which not only simplify the process but also diversify applications. Poly propylene (PP) fiber has attracted the attention as adsorption polymer substrate for various reasons; it is a highly useful thermoplastic, broadly used as a molding in many extruded forms and it is to graft with most kinds of monomers.

In this research, the direct radiation grafting technique was used to graft (4-VP/AAm) binary comonomer onto poly-propylene (PP) fiber substrate. The optimum preparation conditions at which the grafting process proceeds extensively and homogeneously were determined. The characterization of some selected properties of the prepared chelating polymer was studied. The possible use of the prepared functionalized fibers in water treatment was investigated.

EXPERIMENTAL MATERIALS

Polypropylene fiber, produced by oriental waver, Egypt, 4-Vinyl pyridine (4-VP) (Acros Organics,) of purity 99% and Acrylamide (AAm) of purity 99.9% (Aldrich, Germany) were used as received. The other chemicals, such as solvents, inorganic salts, organic compounds, and other reagents were reagent grade and used without further purification

METHODS AND INSTRUMENTS

Functionalization of polypropylene PP fibers (0.2 gm) were washed with acetone, dried at 50°C in oven until constant weight and then immersed in fixed weight of comonomer-solvent mixture (20 gm) in glass tubes. The direct radiation induced grafting was used as a technique in nitrogen atmosphere. The glass tubes containing the monomer solution and the fiber substrates were subjected to 60Co-gamma irradiation at dose rate of 10.28 kGy/h. The grafted polymers were removed and washed thoroughly with H2O/methanol mixture in order to remove homopolymer that may be formed, and then soaked overnight in the solvent to extract the residual monomer and homopolymer, which may be included in the grafted polymer followed by several times washing with H2O/methanol mixture. These grafted polymers were then dried in oven at 40°C for 24 h and weighed. The degree of grafting was calculated by using the following equation:

$$\text{Degree of grafting (\%)} = \frac{\left(W_g - W_o\right)}{W_o} \times 100$$

Where W_o and W_g represent the weights of blank and grafted fiber, respectively.

Adsorption experiments

Batch adsorption experiments

Batch adsorption experiments were carried out by shaking the dried grafted fibers (0.5 g) with 100 ml aqueous metal ion solutions of various concentrations, pH values, and time intervals. The concentration of metal ions was detected by Plasma Optical Emission-Mass Spectrometer (POEMS III); Thermo Jarrell Ash, USA. The amount of metal ions adsorbed was calculated through the difference in the concentration of metal ions in solution before and after adsorption.

Groundwater sample collection and analysis

Groundwater samples were collected from different water points in the area under investigation and the position of such points (longitude & latitude) were detected using GPS model Magellan, Nava 5000 pro. Two kinds of samples were collected:-

Al sample was collected in a clean, washed polyethylene bottle and subjected to the measurements of physical and chemical properties of water samples. The physical properties of water samples were determined by measuring the specific electrical conductance (EC) by EC meter Model LF

538, WTW, USA and expressed in micromhos per centimeter (μS/cm) at 25° C, and pH value was measured using 3320 pH meter (Jenway, UK). The Chemical properties were determined by measuring total dissolved salts (TDS), Ca^{2+}, Mg^{2+}, Na^+, K^+, CO_3^-, HCO_3^-, SO_4^- and Cl^- ions concentration.

The other sample was collected in 100 ml acid washed polyethylene bottle, followed by in-situ acidification by nitric acid, brought to the laboratory in iceboxes and stored at 4° C until analysis for heavy metal content. Samples were analyzed for Al^{3+}, B^{3+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sr^{2+}, V^{2+} and Zn^{2+} using POEMS III. 1000 ppm multi-element certified standard solution, Merck, Germany was used as stock solution for instrument calibration.

All the analyses were carried out according to the methods adopted by American Society for Testing and Materials (ASTM 2002) and the obtained chemical data was expressed as parts per million (ppm).

Water treatment process

A 100 ml of the collected contaminated samples were equilibrated with 0.5 gm of the prepared hydrogel for 24 h at room temperature (25°C), and then the remaining solution was re-analyzed.

RESULTS AND DISCUSSION

The graft copolymerization of 4VP/AAm binary comonomer system onto PP fibers was carried out by direct irradiation of PP fibers immersed in excess diluted comonomer solution. Radiation-initiated graft copolymerization involves two simultaneous processes in which active sites are formed on PP fibers by irradiation followed by the polymerization of the monomers on these sites.

Several factors would contribute to obtain considerable grafting yield of homogeneous distribution.

Effect of solvent composition and concentration

The use of suitable solvent would enhance the efficiency and uniformity of the grafting process by promoting the accessibility of the monomers to the active site located within the polymeric substrate. It was reported that water and methanol are the proper solvents for the grafting of 4-VP and AAm respectively, onto several polymeric substrates (Martin and Garnett, 1976; Bhattacharyya and Maldas, 1982). Consequently, it was expected that a mixture of water and methanol may be the suitable solvent for such grafting process.

To determine the suitable co-solvent composition able to achieve a reasonable grafting degree, different H_2O/MeOH mixtures of various compositions were used. As shown in figure (1), the degree of grafting increases by increasing the ratio of H_2O content in the co-solvent to reach its maximum value at co-solvent composition of 50/50 wt% then it tends to

decrease once more when any further increment change in the H_2O content. These results could be explained in the light of solvent/monomer interaction. In case of methanol rich co-solvent mixtures, the obtained low degree of grafting could be attributed to the various chain transfer and hydrogen abstraction reactions due to the presence of methanol (Ivanova and Boudevska, 1982); whereas, in case of H_2O rich co-solvent mixtures, the degree of grafting is higher than that in methanol-rich ones due to the presence of water which has zero chain transfer constant and as a result minimum chain transfer reactions taking place. On the other hand, even H_2O rich co-solvent mixtures achieve higher grafting degree relative to that in MeOH rich co-solvent mixtures; it is still lower than that in co-solvent of composition 50/50 wt%. Such lowering may be attributed to the increase in the viscosity of water-rich medium; so that the presence of excess water could facilitate branching and crosslinking of the copolymer in the reaction medium, and prevent the diffusion of the comonomer into PP fibers.
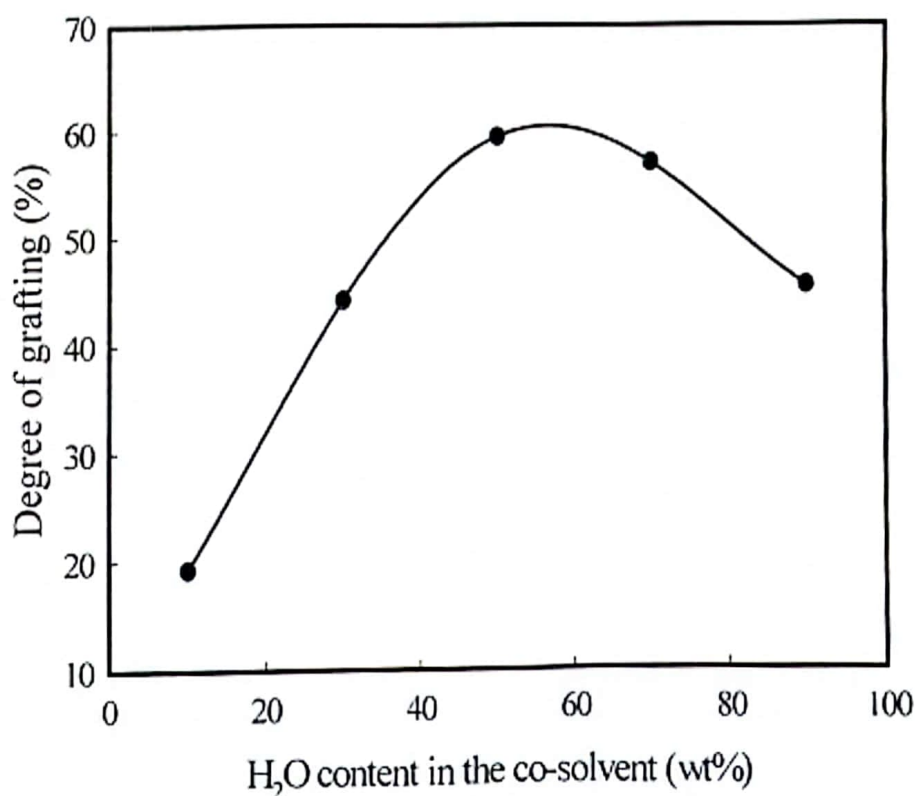

Fig. (1). Effect of H_2O/MeOH co-solvent composition on the grafting degree of 4-VP and AAm onto PP fibers.

From the abovementioned results, it could be concluded that the H_2O/MeOH mixture of composition 50/50wt% is the most suitable for

obtaining the highest grafting degree of (4-VP/AAm) binary comonomer onto PP fibers.

Solvents, which facilitate the diffusion of the monomers into the polymeric substrate, would reduce the propagation rate in case it is more than enough. Also, depending on the solvent type and amount, gel effect, which is directly proportional to the degree of homopolymerization of the monomer in the reaction medium, may be either enhanced or reduced. Figure (2) shows the effect of (4-VP/AAm) binary comonomer concentrations on their grafting yield onto PP fibers. The figure illustrates that the increase in the comonomer overall concentration results an increase in the grafting yield. Such increase may be attributed to the increase in the number of monomer molecules available to react with the free radical formed in the polymer backbone i.e. the degree of grafting is directly proportional to the comonomer concentration, which facilitates the selection of suitable concentration to obtain a reasonable grafting degree for the suitable conditions of the proposed practical application.
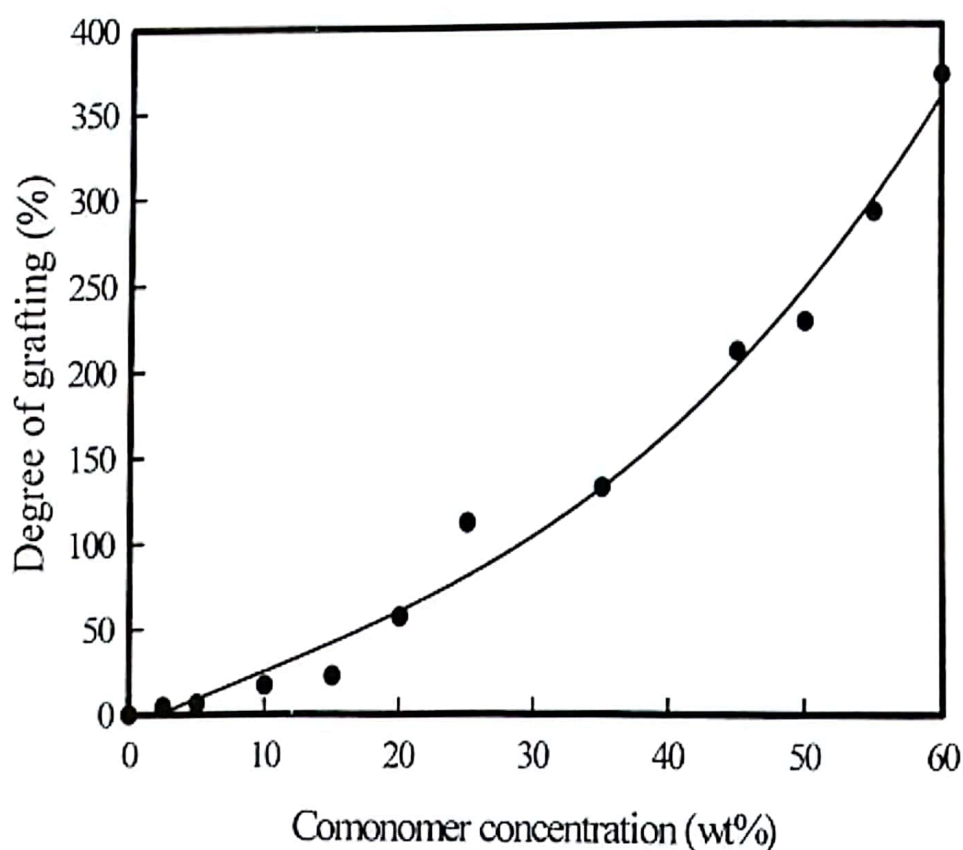

Fig. (2). Effect of (4-VP/AAm) binary comonomer concentration in H₂O/MeOH on the grafting degree of 4-VP and AAm onto PP fibers.

Effect of comonomer composition

In the present work, the use of binary comonomer system is a pathway to enrich the functionality of the inert PP substrate by introducing two functional groups of different chemical nature and behavior. The presence of more than one monomer may lead to the retarding or the enhancement of the grafting process. The grafting of (4-VP/AAm) binary system of different relative compositions investigated and illustrated in figure (3), shows that the use of comonomer feed solution rich in 4-VP resulted in a higher grafting degree as compared to that prepared using AAm rich comonomer feed solution i.e. the increase in the AAm content in the comonomer feed solution reduced the grafting degree to reach minimum in case of pure AAm. These results could reveal the high ability of the AAm for homopolymerization and crosslinking via the conversion of monomer molecules into polymer and the mutual termination between two growing macroradical chains forming long slowly moving chains which could be entangled and easily crosslinked. Such homopolymerization leads to the increment in the reaction medium viscosity and consequently to restrict the movement of the free radical to reach the active sites on the polymeric substrate, resulting in lower degree of grafting obtained.
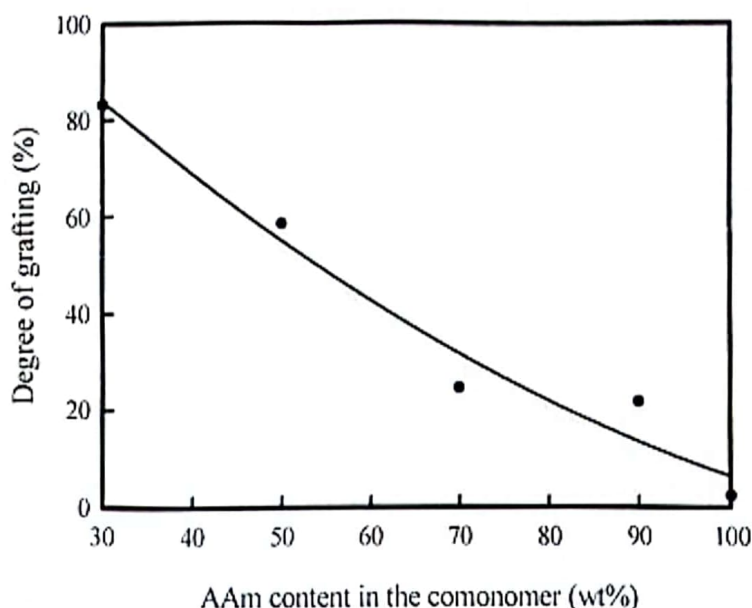

Fig. (3). Effect of (4-VP/AAm) binary comonomer composition in H$_2$O/MeOH on the grafting degree of 4-VP and AAm onto PP fibers.

Characterization of the prepared functionalized polymer
pH-dependent swelling of grafted PP fibers

Figure (4) demonstrates the equilibrium swelling of PP-g-(4-VP/AAm) of different degrees of grafting as a function of pH at room temperature (25°C) where NaOH and HCl were used to adjust the pH value

of the swelling medium. The Figure shows that all the tested grafted fibers achieved higher equilibrium swelling degree at low pH values than that which occurred at high pH values. The Figure also shows that the equilibrium swelling degree at low pH values increases by increasing the degree of grafting. Such results can be directly attributed to the ionic nature of the graft chain functional groups. In acidic pH values, nitrogen atom of the pyridine ring is protonated and as a result the hydration ability of pyridine ring increases and consequently the swelling degree increases. The hydration ability of the grafted fibers with increasing the degree of grafting due to the increase in the number of pyridine rings.
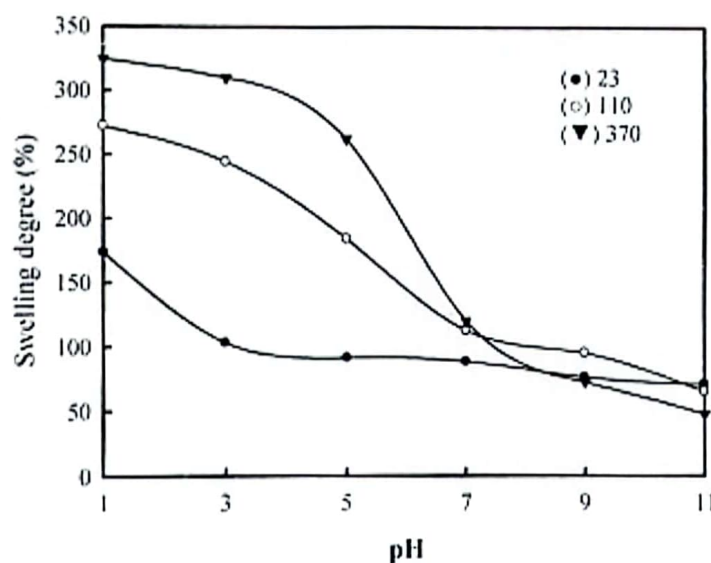

Fig. (4). pH dependent swelling of PP-g-(4-VP/AAm) fibers of different degrees of grafting (%).

Thermogravimetric analysis (TGA)

Figure (5) shows the results of thermogravimetric curves for the ungrafted PP fibers compared with those of the grafted fibers of different AAm ratio. The data show that AAm rich grafted fibers possess higher thermal stability, even more than ungrafted PP itself. However, the increment in 4-VP content in the graft chains leads to the decrease in the thermal stability of the grafted fibers. Thermal degradation of PAAm takes places via losses in NH_2 in the form of ammonia, whereas the lower degradation temperature of P4-PV at about 240°C could be attributed to the high electron density which may provoke a weakening of chemical bonds in the pyridine ring and polymeric back bone (Lyons *et al.*, 1990; Khairou 1994).
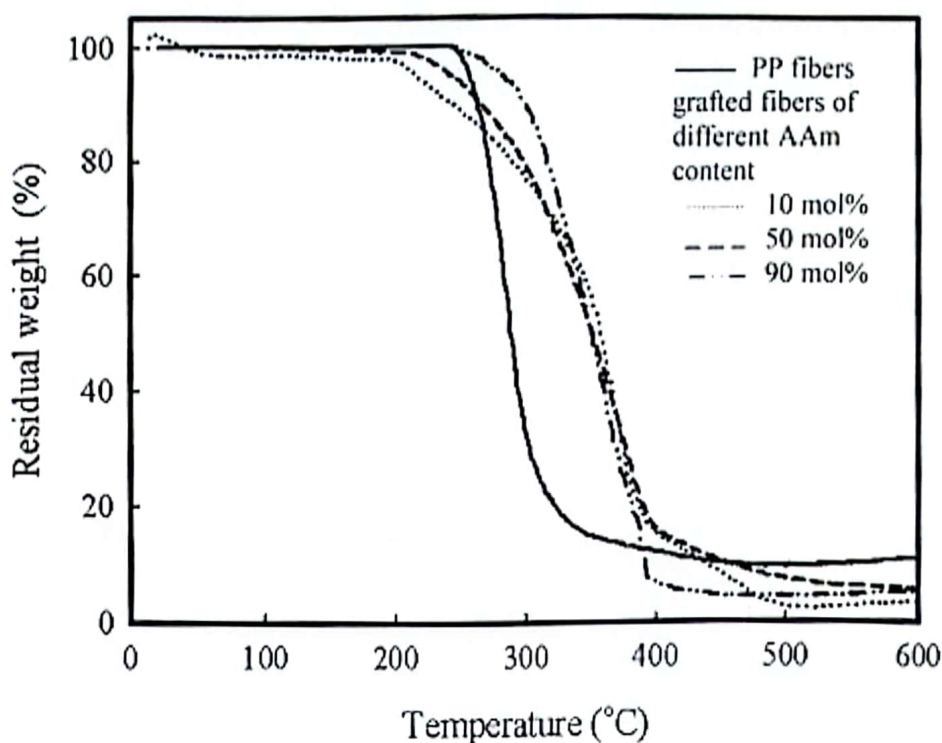
Fig. (5). TGA thermo grams.

Metal sorption characteristics
Effect of pH on the Metal ion adsorption process

Metal solution pH is an important controlling parameter in the adsorption process. Variation in the pH value of metal solution would not only affect the electronic status of the present functional groups (protonation / deprotonation of the basic groups and / or dissociation/association of the acidic groups) but it may also affect or alter the form of the metal ions present in the medium. The effect of pH on the adsorption amount of Pb(II), Cd(II), Zn(II), Cu(II), Fe(III), Mn(II), Sr(II) and Al(III) on PP-g-(4-VP/AAm) was investigated within pH ranges between 1 and 5.

pH-dependent metal ion adsorption data, (Figure 6), shows that at low pH values, PP fuctionalized fiber acquire very low adsorption. By increasing pH of the medium (> pH 2), the adsorption amount increased to reach maximum amount at pH values which depend on the metal ion type. The observed data at low pH values (pH <2) could be referred to the electrostatic repulsion between the metal ions in the medium (M⁺) and the positive charges accumulated on the surface of the fiber as a result of the protonation of the pyridine moieties. Such repulsion prevents the approach of the metal ions to the fiber surface (Kornicker and Morse, 1991; Park and Huang 1989). At higher pH, such positive charge density decreases allowing the metal ions to approach the sorbent fiber surface which result in higher adsorption

values. Further increase in the pH value would transform the dissolved metal into precipitated hydroxide form which as a result minimizes adsorption values resulting in a minimization of the adsorption values.
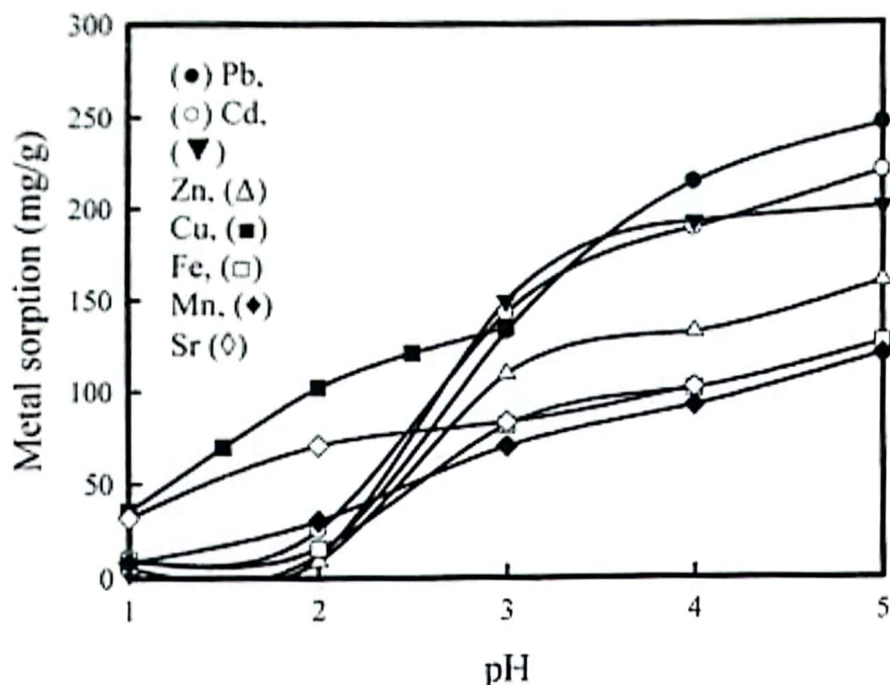

Fig. (6). pH-dependent metal uptake of different metal ions.

Metals sorption by functionalized polymer

Total sorption capacity of the prepared functionalized chelating polymer presents evaluating property in determining the amount needed for the removal of certain amount of polluting metal ion. Figure (7) shows the maximum sorption capacity of the chelating PP-g-(4-VP-AAm) fibers towards eight different individual metal ions at their respective optimum pH value. The data show that the affinity of the chelating fiber towards the under investigation metal ions proceeds in the following order Pb> Cd > Zn> Cu> Fe> Mn> Sr> Al

The mechanism of metal ion removal by the prepared functionalized polymer can be suggested in four steps (Shawky *et al.*, 2006).

1-*Bulk diffusion:* metal ion transfer from the bulk solution to the boundary film bordering the sorbent surface.

2- *Film diffusion:* metal ion transport from the boundary film to the surface of the sorbent.

3- *Intraparticular diffusion:* transfer of the metal ion from the surface to the intraparticular active sites.

4- *Chemical reaction:* uptake of the metal ion on the active sites, via chelating, ion-exchange or complexation.

Regarding to the first two steps, it has been demonstrated that they could be neglected if a sufficient speed of stirring was used (>400rpm). For this reason, intraparticular diffusion or chemical reaction (chelating or ion-exchange) would be the rate-limiting step of sorption kinetics.
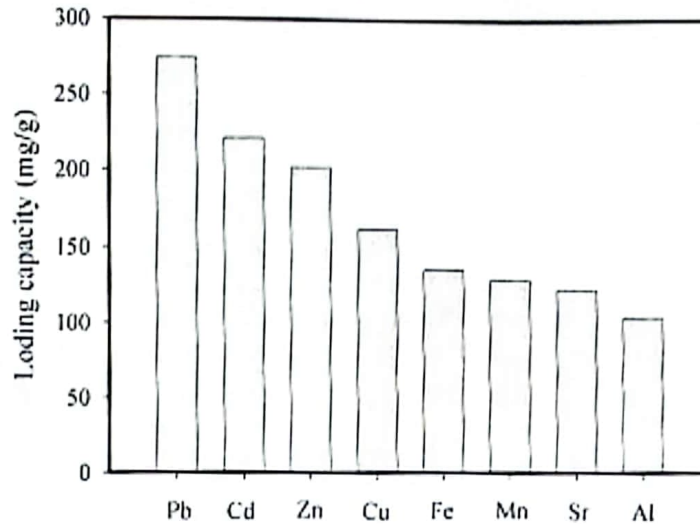
Fig. (7). Maximum sorption capacity of the chelating PP-g-(4-VP/AAm) fibers towards eight different individual metal ions.

Effect of initial metal feed concentration

The efficiency of the chelating sorbent at different pollution concentrations is also a good evaluating property for the prepared chelating PP-g-(4-VP/AAm) fibers. Figure (8) shows the effect of metal ion concentration on the adsorption process. Generally, the increase in the metal ion concentration increases its adsorption in fast rates at first then tends to slow down up to reach equilibrium depending on the type of metal ions.

Fig. (8). The effect of the individual metal ions concentration on their adsorption.

Sorption isotherm studies

The adsorption data of eight contaminant metal ions were analyezed by a regression analysis to fit the Freundlich and Langmuir isotherms models (Kinniburgh, 1986; Hasany *et al.*, 2000). The coefficients of these two models were computed with linear square fitting of the plot of metal ion concentration at equilibrium versus the metal ion concentration at equilibrium.
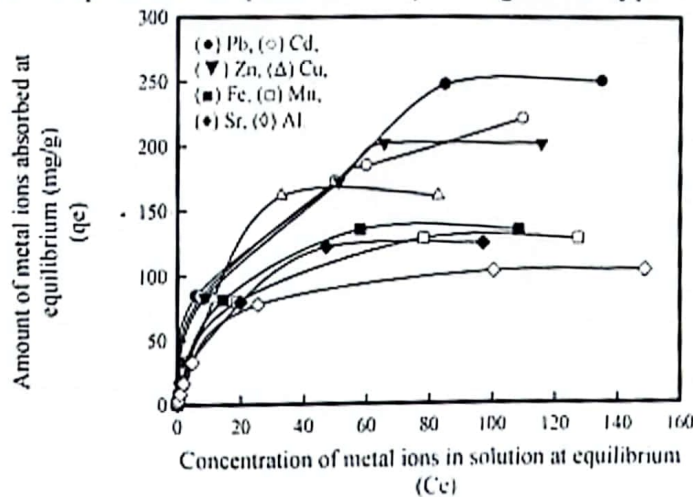
Langmuir model is the best known model to study and determine the chemisorption parameters on well defined localized sorption sites of the same energy independent of surface coverage (Rutheven, 1984). Langmuir sorption isotherm was used to fit the experimental sorption data. Langmuir equation can be described by the linearized form:

$$C_e/q_e = (1/Q_0 . K_L) + (1/Q_0)C_e$$

Where: C_e is the concentration of metal ions in solution at equilibrium, q_e is the amount of metal ions adsorbed at equilibrium (mg/g), K_L is the equilibrium adsorption constant which is related to the affinity of the binding sites in the functionalized polymer and Q_0 (mg/g) represents a practical limiting adsorption capacity of metal ions per unit weight of functionalized polymer, i.e. the maximum adsorption capacity of the fiber towards particular metal ion. The linear plot of *(C_e/q_e)* against C_e, (Figure 9) of the metal ions under investigation shows that the adsorption obeyed the Langmuir model. The Langmuir constants were evaluated and reported in table (1).
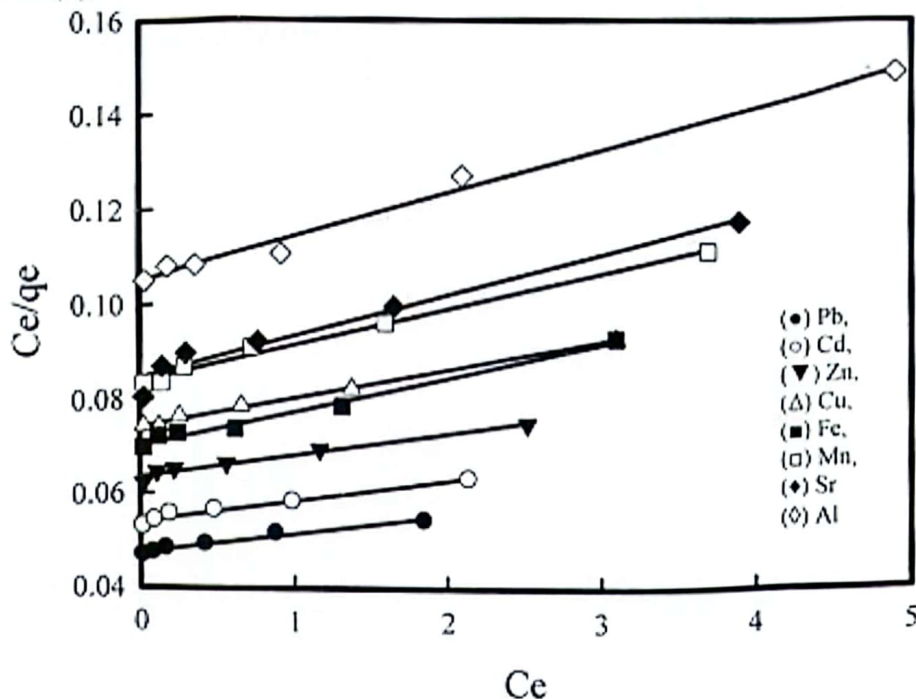

Fig. (9). The linear plot of *(C_e/q_e)* against C_e for different metal ions.

Table (1). Langmuir and Freundlich adsorption constants associated to adsorption isotherms of different metal ions on PP-g-(4-VP/AAm).

Metal	Langmuir constants			Freundlich constants		
	Q_o (mg/g)	K_L	r	K_F	n	r
Lead	250.2	21.3	0.97	3.15	1.24	0.96
Cadmium	234.3	18.5	0.97	2.97	1.27	0.97
Zinc	217.4	15.8	0.97	2.8	1.26	0.97
Cupper	171.0	13.5	0.99	2.74	1.15	0.99
Iron	141.4	14.3	0.98	2.66	1.27	0.97
Manganese	134.4	12.5	0.99	2.48	1.31	0.97
Strontium	116.6	11.9	0.96	2.48	1.25	0.98
Aluminum	110.7	9.5	0.99	2.24	1.35	0.96

Meanwhile. Freundlich isotherm is a characterizing model used to estimate the surface homogeneity and active site distribution empirically using the following equation:

$$\log q_e = \log K_F + (1/n) \log C_e$$

Where; K_F and n are the Freundlich constants characteristics on the system. K_F and n are indicators of adsorption capacity and adsorption intensity, respectively. The linear plot of $\log q_e$ versus $\log C_e$ shows the applicability of the Freundlich model (Fig. 10), from which Freundlich constants K_F and n were calculated and reported in table (1). Values of $1 < n < 10$ show the positive sorption of metal ion (McKay et al.. 1982).
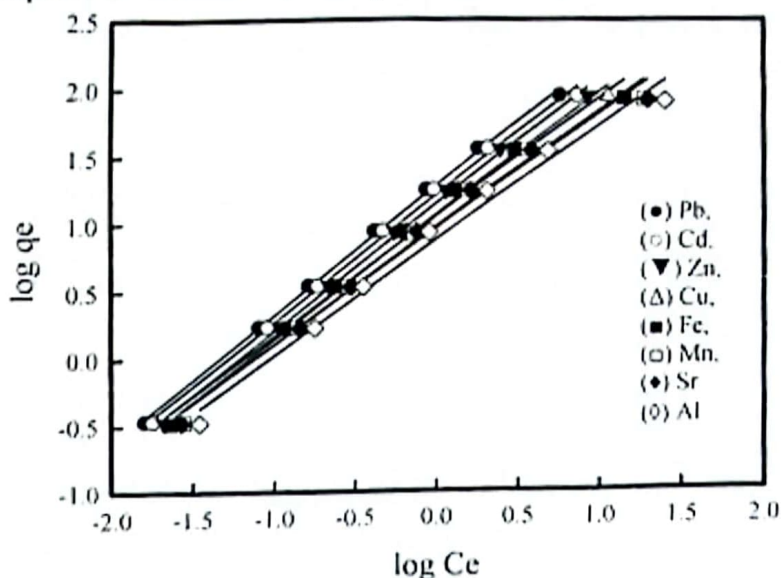

Fig. (10). The linear plot of $\log q_e$ versus $\log C_e$ for different metal ions.

Sorption kinetics of metal ions

The rapid adsorption of metal ions by the adsorbent is an important characteristic for practical use which indicates shortening the time needed for water purification. Figure (11) shows the result of kinetic experiments conducted to determine the equilibrium time required for the uptake of metal ions by the prepared PP-g-(4-VP/AAm). A two-stage kinetic behavior is evident: a very rapid initial sorption over a few minutes, followed by a long period of much slower uptake. The equilibrium time needed for the different metal-polymer systems ranged from about 45-180 min. depending on the type of metal ion.

The result suggested that, at the beginning of the process, the adsorption occurs on the polymer surface, so, a fast adsorption rate was found (Fritz *et al.*, 1981 and Lee *et al.*, 2002). After that; the adsorption takes place at the functional groups located in inner structure of the polymer, so, the adsorption rate was slow due to the pore diffusion of metal ions into the polymer matrix.

The metal adsorption by functionalized polymer is a reversible sorption-desorption process which can be described by Langmuir according to the following equation:

$$-\ln(1-F_{(t)}) = Kt + C$$

Where; $F_{(t)} = C_o - C_t / C_o - C_e$, K is the equilibrium constant and C_o, C_t are the concentrations of metal ions at the beginning and at time (t), respectively.
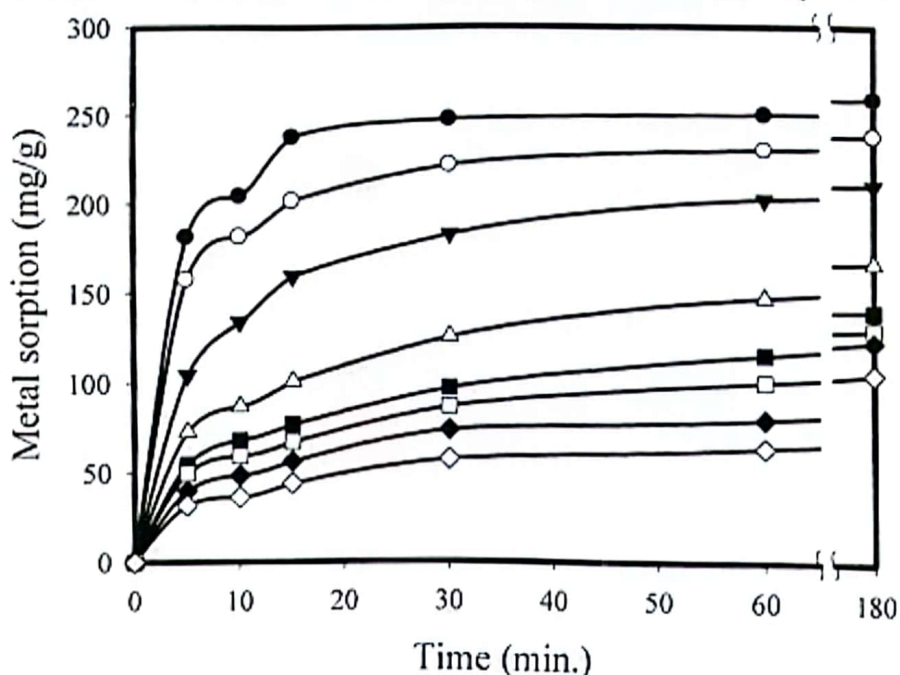
Fig. (11). The change in amount of adsorbed metal ions with time for PP-g-(4-VP/AAm).

A plot of $-\ln(1-F_{(t)})$ against t (Fig. 12) as conducted from the experimental results of figure (11), shows that the reaction rate of sorption (K_s) and rate of desorption (K_d) of PP-g-P(AAm/4VP) can be determined (Table 2) from the slope and intercept of Figure 12 as follow:

$$K_d = k(C_e/C_o) \text{ and } K_s = K - K_d$$
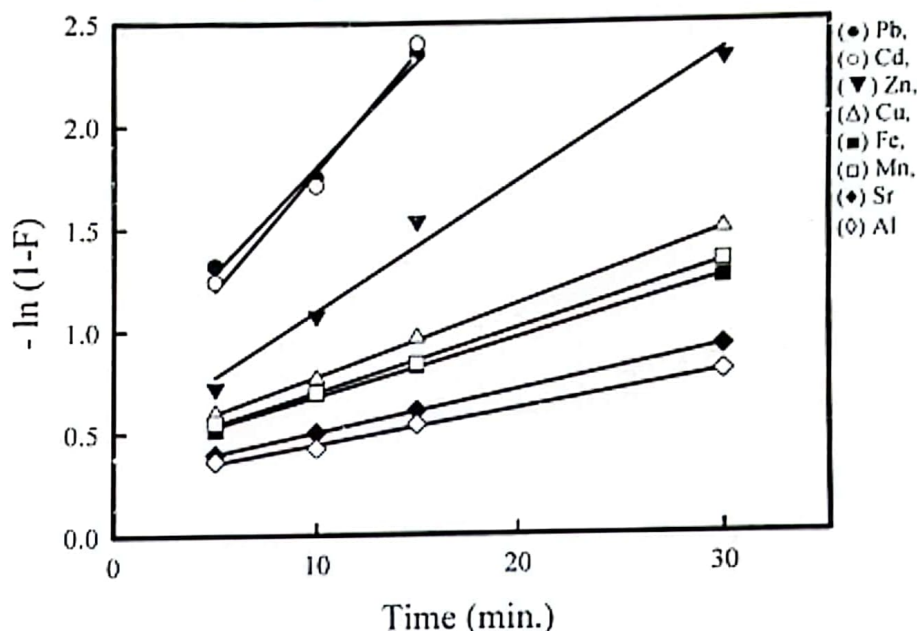
Fig. (12). Plots of *-ln (1-F)* versus t for different metal ions.

Table (2). Adsorption rate constant for different metals on PP-g-P(AAm/4VP).

Metal	$K(s^{-1}) \times 10^{-4}$	$\left(\dfrac{C_e}{C_o}\right)$	$K_d (s^{-1}) \times 10^{-4}$	$K_s (s^{-1}) \times 10^{-4}$	r
Lead	17.13	0.047	0.8	16.32	0.99
Cadmium	19.3	0.147	2.84	16.46	0.99
Zinc	10.6	0.22	2.33	8.27	0.98
Cupper	5.9	0.37	2.18	3.72	0.99
Iron	4.8	0.47	2.25	2.55	0.99
Manganese	5.23	0.5	2.615	2.614	0.99
Strontium	3.45	0.52	1.79	1.66	0.99
Aluminum	2.91	0.59	1.71	1.2	0.99

Effect of temperature on the adsorption of metal ions.

It is well known that temperature has a great influence on any chemical process so that it may enhance or retard such dependence on the nature of the reactants and/or the products. The effect of temperature on the

adsorption of the under investigation metal ions was studied at 25, 40, 55 and 70°C. From figure (13), it has been observed that the adsorption of metal ions from aqueous solution is affected by the reaction temperature. The figure shows an unexpected result as the metal adsorption decreased remarkably with increasing temperature.
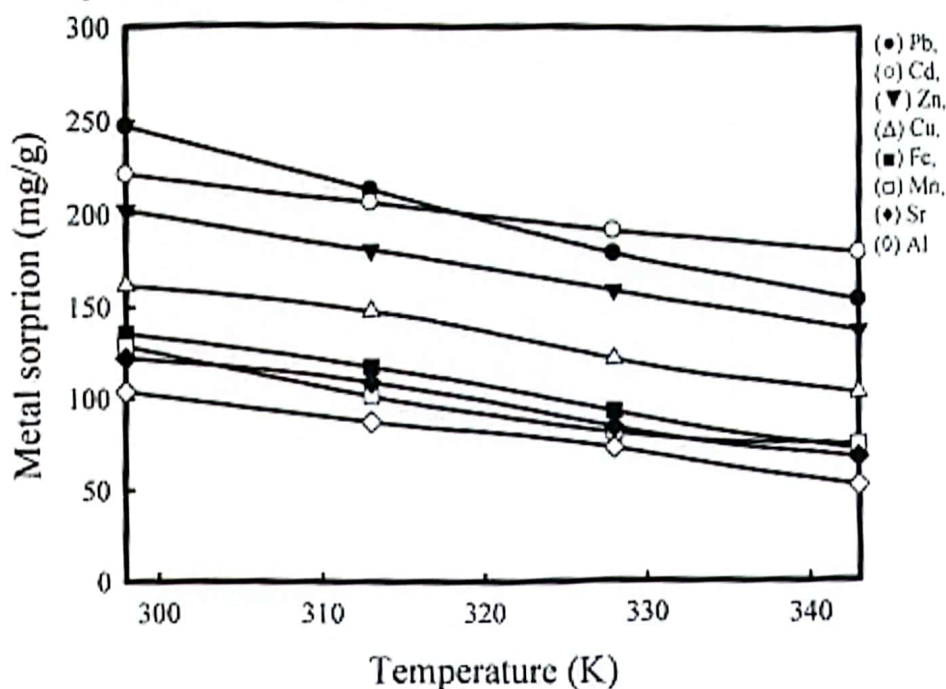
Fig. (13). Effect of temperature on the adsorption of different metal ions.

Thermodynamic studies

The effect of temperature on the adsorption process can be explained by calculating the thermodynamic parameters such as changes in free energy ΔG, enthalpy (ΔH) and entropy (ΔS) according to the following equations:

$$D = q_e/C_e$$
$$Log\ D = -(\Delta H/2.303\ RT) + (\Delta S/R)$$
$$\Delta G = \Delta H - T\Delta S$$

Where D is the distribution ratio between metal ions and the adsorbent in aqueous solution and R is the gas constant

The relationship between *log D* verses *1/T* for the prepared chelating fiber is shown in figure (14). According to the mentioned equations, the slopes and intercepts of linear lines in figure (14), thermodynamic parameters were calculated, and are shown in table (3).
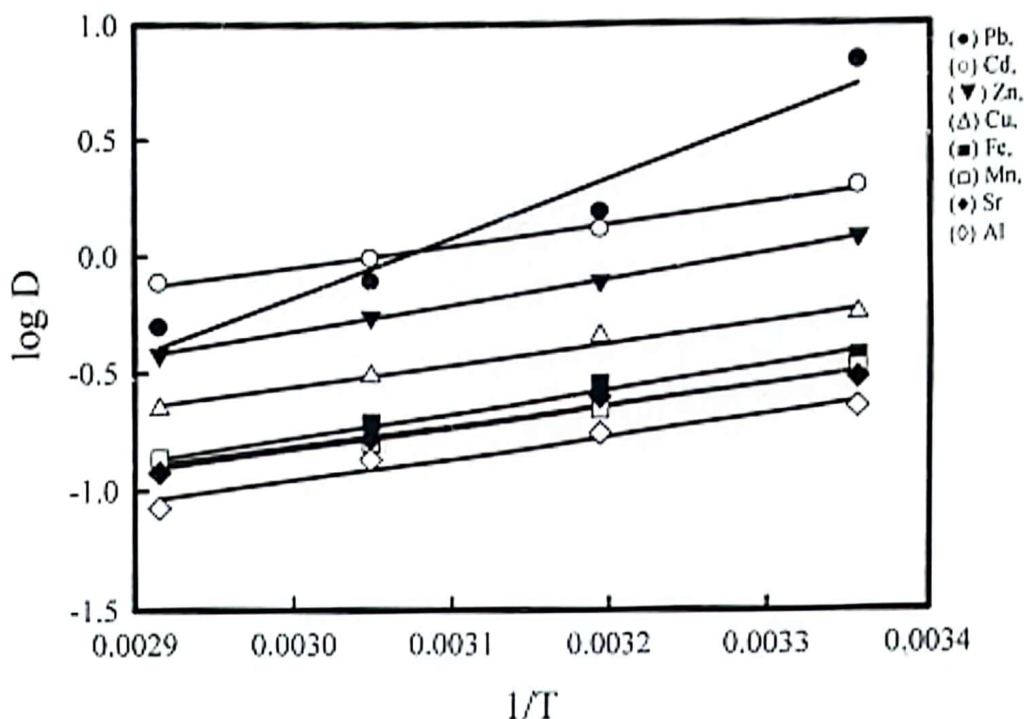
Fig. (14). The relationship between *log D* and *1/T* for the prepared chelating fiber for different metal ions.

The negative values of ΔH reflect that adsorption is an exothermic process and is responsible for the reduction in adsorption rate with the increase in temperature. The higher negative values of ΔH suggest the possibility of weak bonding between the adsorbate and adsorbent (Yigitoglu et al., 1998). The negative values of ΔS suggest more order in the reaction between the adsorbate and adsorbent (more order in the structure between the adsorbate and adsorbent). The values of ΔG increase with increasing temperature, demonstrating a decrease in the feasibility of adsorption at higher temperatures.

Selectivity of the chelated polymer towards different Metals

It is hoped that in the presence of different metal ions, one metal ion could be selectively adsorbed by the prepared chelating fibers. Adsorption capacity of a polymeric ligand towards the metal ions, effect of pH of the feed metal solution, adsorption equilibrium time are important factors over the selectivity properties of ligand in competitive adsorption (Senkal et al., 2004).

Table (3). Thermodynamic parameters for adsorption of different heavy metals on PP-g- (4-VP/AAm).

Temp. (°C)	Metal	Thermodynamic Parameters		
		ΔG (kj/mol)	ΔS (j/mol)	ΔH (25-70) (kj/mol)
25	Lead	29.84	64.55	
40		28.27	66.46	-49.08
55		27.48	65.84	
70		26.89	64.66	
25	Cadmium	10.96	23.79	
40		10.52	24.05	-18.06
55		10.2	23.95	
70		9.88	23.82	
25	Zinc	12.54	31.04	
40		12.06	31.07	-21.79
55		11.63	30.97	
70		11.13	31.07	
25	Cupper	9.68	28.5	
40		9.41	28.01	-18.18
55		8.89	28.29	
70		8.42	28.43	
25	Iron	10.49	33.25	
40		10.14	32.8	-20.41
55		9.61	32.92	
70		9.0	33.24	
25	Manganese	8.74	29.41	
40		8.21	29.68	-17.51
55		7.7	29.81	
70		7.44	29.35	
25	Strontium	9.1	30.97	
40		8.82	30.37	-18.33
55		8.26	30.7	
70		7.73	30.88	
25	Aluminum	8.84	32.13	
40		8.47	31.77	-18.42
55		8.06	31.57	
70		7.36	32.23	

To investigate such items, competitive adsorption of (Cd(II) and Pb(II)), (Cu(II) and Zn(II)), (Fe(III) and Mn(II)), (Fe(III) and Sr(II)) and (Cd(II), Fe(III) and Pb(II)) ions by the prepared PP-g-P(AAm/4VP) fibers from their mixture solutions was carried out (Fig. 15). The concentration of each metal ion in the mixture was 250 mg/l. The pHs of this solutions were adjusted to either 3 or 5 by addition of dilute HNO_3. A fixed amount of polymer was equilibrated with the mixture of metal ion solutions and the adsorption of each metal ion was followed up to 3h contact time. The metal ion removing capacity is expressed as mg/g and the percentages given on top

of the bars are selectivities found from adsorption ratios. From the results it can be seen that the prepared functionalized PP fiber show some selectivity towards Cd(II), Fe(III) and Cu(II) metal ions.
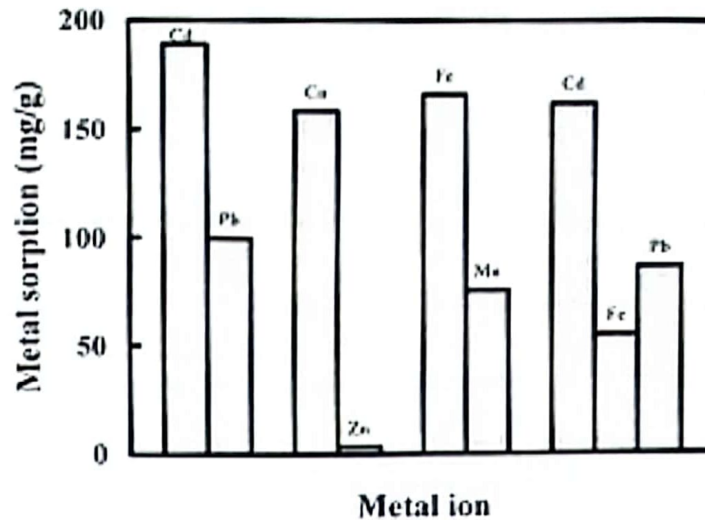
Fig. (15). Competitive adsorption of ions by the prepared PP-g- (4-VP/AAm) polymer from their mixture solutions.

Regeneration of functionalized fiber

Regeneration of the chelating fiber after metal sorption process without damaging the capacity is a very important factor for the success of sorption technology development. Recovery of different metal ions adsorbed on PP-g-P(AAm/4VP) was carried out by 0.1 M HNO₃ for 2h, at room temperature. The regeneration stability was tested by applying the adsorption and desorption processes several times. The test shows that almost no decrease in the sorption capacity even after 10 repeating as shown in figure (16).

Groundwater treatment

Groundwater has historically been assumed to be safe for use without treatment. Layers of soil act as a natural filter, removing microbes and other particles as water seeps through. Water percolating through soil and rock dissolves minerals including iron and manganese that are common of the most metallic elements found in the earth's crust. Iron and manganese are not considered as health risk, but at concentrations above 0.3 mg/l, iron can stain laundry and plumbing fixtures and cause undesirable tastes. The precipitation of excessive iron imparts an objectionable reddish-brown colour to the water. Iron may also promote the growth of certain microorganisms, leading to the deposition of a slimy coat in piping. Also, at levels exceeding 0.15 mg/l, manganese stains plumbing fixtures and laundry and causes undesirable tastes. Its presence in water may lead to microbial

growths. Even at concentrations as low as 0.02 mg/l, manganese will form coatings on piping that may slough off as black precipitates.

In Egypt, many localities depend on groundwater as the only water supply for different uses. El Dakhla Oasis which is located at the western Desert of Egypt is considered as one of these localities which depend on groundwater for water supply. Although, the groundwater at this area is considered as fresh water (having salinity less than 1500 mg/l), it suffers from high iron and manganese concentrations.
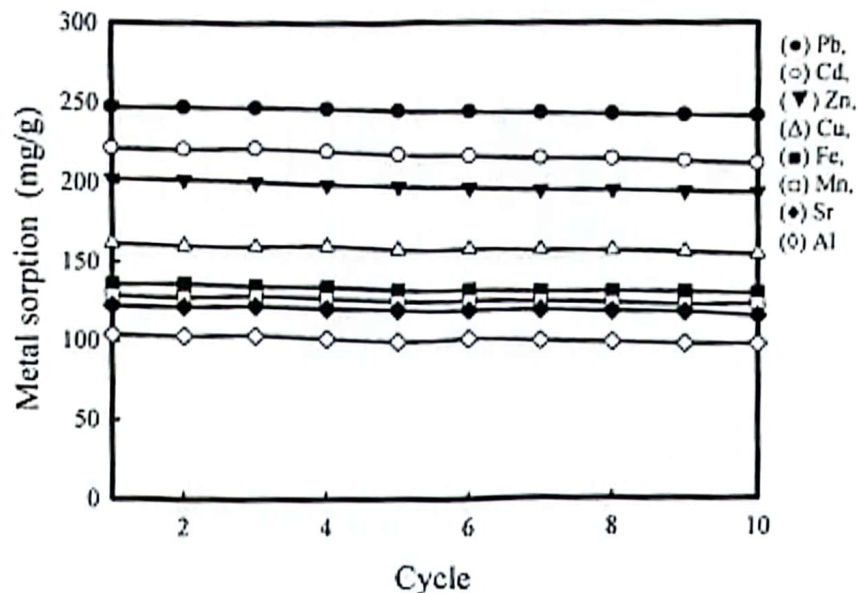
Fig. (16). **Effect of adsorption and desorption operations on the efficiency of PP-g-P (4-VP/AAm) towards different metal ions.**

The groundwater in El Dakhla oasis is obtained from three successive confined aquifers at different depth within the Nubia sandstone formation. They are defined from top to base as; Taref, Sabaya and SixHills water bearing units locating at depths 150 to 300, 300 to 600 and 600 1200 m, respectively. The calculated storage of the groundwater in the three formations estimates about 12×10^{11} m^3, with a production rate of approximately 650,000 m^3/day. Water salinities are ranged from 194 to 2677, 163 to 470 and 133 to 206 mg/l, with mean values of 701, 240 and 161 mg/l in Taref, Sabaya and SixHills formation, respectively. Although this represents a very good water quality, a higher concentrations of iron and manganese found in the three formations. The values of iron concentrations are estimated to rang from 0.001 to 72.04, 0.001 to 13.64 and 0.0009 to 7.66 mg/l, with mean values of 14.6, 6.46 and 4.11 mg/l in the above mentioned three formations, respectively. On the other hand, higher concentrations of manganese also exist in the three formations which is ranging from; 0.11 to

4.6, 0.1 to 0.46 and 0.07 to 0.46 with mean values of 0.08, 0.31 and 0.21, respectively.

So, a trial has been made in this work to treat this groundwater using the prepared PP-g- (4-VP/ AAm) fiber.

Fourteen samples involving all the groundwater types including individual and mixed formations and collected from different localities in the study area were chosen for the treatment process. The efficiency of the treatment was measured by a complete chemical analysis of such groundwater samples before and after the process (Table 4)

The results of the analysis before the process show that; the salinity of these water samples as well as the concentrations of major cations and anions (Ca^{2+}, Mg^{2+}, Na^+, K+, HCO_3^-, SO_4^- and Cl⁻) are all in the acceptable limits for drinking according to WHO guideline (with the exception of sample no 113). On the other hand, higher concentrations of iron and manganese are found in these samples. But after the treatment process it is found that the prepared functionalized fibers were able to remove 91 to 98 % of iron and 0.3 to 95 % of manganese and almost removing all of the other heavy metals found. The analysis also showed a decrease in the calcium and magnesium concentration, due to the affinity of the chelated fibers towards alkaline earth metals as that for transition metal ions. Such changes in salts type of the groundwater are accompanied by a decrease in the pH of most of the samples.

The decrease in the concentrations of iron, manganese, calcium and magnesium is accompanied by an overall decrease in the salinity of the water which ranged from 5 to 40 %. It can be therefore suggested that the chelating fiber could be used for water desalination and treatment techniques.

CONCLUSIONS

New metal chelating functional polymer was synthesized by γ-radiation induced graft copolymerization of AAm and 4-VP onto PP fibers. The suitable preparation conditions were estimated to obtain reasonable grafting yield. The sorption capacities of the chelating hydrogel towards some selected elements were studied. The adsorption process was found to be dependent on the pH, time interval, initial concentration, and temperature, following both the Freundlich and Langmuir isothermal adsorptions. Moreover, the study reveals that the adsorption process is favored with lowering temperature, indicating that the process is exothermic. The applicability of the prepared PP-g-P(AAm/4VP) fibers for the treatment of natural groundwater samples of higher iron and manganese concentrations were examined. The treatment process of such groundwater using the prepared functionalized fibers showed a removing efficiency up to 98 and

95% of iron and manganese, respectively resulting in an improvement of the groundwater quality.

Table (4). Chemical analysis data for groundwater samples before and after the treatment process.

(a) Major constituents

Sample*		EC (µS/cm)	TDS	pH	Major anions (ppm)				Major cations (ppm)			
					CO$_3^{--}$	HCO$_3^-$	SO$_4^{--}$	Cl$^-$	Ca^{++}	Mg^{++}	Na$^+$	K$^+$
2	Before	480	278	8.0	0	46.48	80	64.80	30.36	9.93	38	10
	After	290	209	7.6	0	46.48	36	64.80	13.50	9.93	38	10
	%	39.58	24.73		0	0	55	0	55.53	0	0	0
45	Before	732	364	3.8	0	8.48	160	60.00	30.36	19.86	36	15
	After	386	257	6.4	0	8.48	100	60.00	17.30	13.95	36	15
	%	47.26	29.53		0	0	37.5	0	43.01	29.75	0	0
83	Before	1372	941	3.2	0	0	520	88.80	109.7	51.51	60	33
	After	790	558	5.6	0	21.19	280	88.80	27.30	44.75	60	30
	%	42.41	40.66		0	0	46.2	0	75.11	13.12	0	9.1
113	Before	2210	1358	3.0	0	42.39	450	388.8	121.5	46.83	240	18
	After	1190	1063	5.6	0	42.39	280	371.3	78.00	32.12	240	18
	%	46.15	21.69		0	0	37.8	4.51	35.78	31.41	0	0
50	Before	630	307	8.2	0	77.47	55	84.00	23.36	14.19	46	19
	After	378	271	7.7	0	63.59	55	74.25	15.60	12.58	46	19
	%	40.00	11.49		0	17.91	0	11.60	33.21	11.34	0	0
32	Before	480	290	7.9	0	54.22	74	72.00	23.36	11.35	50	7
	After	291	231	7.4	0	50.87	44	69.30	11.80	9.50	50	7
	%	39.37	20.26		0	6.17	40.5	3.75	49.48	16.29	0	0
42	Before	433	260	7.9	0	58.10	64	61.87	23.36	9.93	40	10
	After	260	198	3.7	0	50.87	28	61.87	9.52	6.83	40	10
	%	39.95	23.92		0	12.44	56.3	0	59.24	31.21	0	0
73	Before	289	163	8.0	0	61.97	23	33.60	16.35	5.67	20	10
	After	176	122	7.7	0	55.11	21	17.32	9.60	2.37	20	10
	%	39.10	25.41		0	11.06	8.6	48.45	41.28	58.20	0	0
80	Before	504	265	7.9	0	54.22	40	88.80	37.41	13.63	26	7
	After	299	202	7.6	0	42.39	30	74.25	23.40	9.47	26	7
	%	40.67	23.67		0	21.81	25	16.38	37.44	30.52	0	0
111	Before	260	162	7.5	0	56.27	24	33.60	17.40	6.06	14	14
	After	144	115	7.7	0	54.22	6	27.22	4.90	6.06	14	14
	%	44.61	29.04		0	3.64	75	18.98	71.83	0	0	0
1	Before	231	167	8.3	0	50.35	19	28.80	7.00	5.67	13	24
	After	192	159	7.5	0	50.35	19	28.80	7.00	5.12	13	24
	%	16.88	4.75		0	0	0	0	0	9.70	0	0
55	Before	259	153	8.1	0	54.23	20	33.60	11.68	7.09	15	17
	After	162	115	7.7	0	42.39	9	27.32	3.90	4.74	15	17
	%	37.45	24.44		0	21.83	55	18.69	66.60	33.14	0	0
91	Before	222	176	7.6	0	75.03	21	33.60	24.94	7.57	8	17
	After	164	118	7.5	0	72.07	10	12.37	7.80	7.10	8	17
	%	26.12	33.07		0	3.94	52.4	63.18	68.72	6.20	0	0
108	Before	260	150	7.3	0	77.47	18	24.00	14.01	9.93	12	10
	After	152	115	7.5	0	63.59	4	24.00	7.80	7.11	12	10
	%	41.53	22.89		0	17.91	77.8	0	44.32	28.39	0	0

* Samples 2, 45, 83 and 113 collected from Taref formation, 50 from Taref and Sabaya formation, 32, 42, 73 and 80 Sabaya formation, 111 from Sabaya and Six hills formation and 1, 55, 91 and 108 from Six hills formation.

(b) Heavy metals

Sample*		Heavy metal ions (ppm)					
		Al	Cu	Fe	Mn	Sr	Zn
2	Before	0.247	0	5.97	0.345	0.153	0.087
	After	0.078	0	0.384	0.026	0.152	0.031
	%	68.45	0	93.56	92.38	0.91	64.19
45	Before	0.259	0.019	26.70	1.218	0.175	0.077
	After	0.131	0	0.430	1.214	0.173	0.075
	%	49.42	100	98.38	0.328	1.48	2.724
83	Before	0.459	0.026	45.23	2.934	0.175	0.486
	After	0.100	0	2.59	0.139	0.155	0.030
	%	78.13	100	94.25	95.23	11.50	93.79
113	Before	0.222	0.023	55.12	4.197	0.165	0.202
	After	0.092	0	4.719	2.834	0.161	0.161
	%	58.39	100	91.44	32.47	2.18	20.52
50	Before	0.232	0.017	7.868	0.213	0.220	0.061
	After	0.177	0	0.454	0.058	0.200	0.039
	%	23.72	100	94.22	72.71	9.17	35.58
32	Before	0.090	0	7.854	0.052	0.144	0.132
	After	0.066	0	0.186	0.048	0.144	0.050
	%	26.44	0	97.63	6.95	0.208	61.86
42	Before	0.146	0	6.627	0.195	0.125	0.055
	After	0.057	0	0.258	0.017	0.118	0.026
	%	61.29	0	96.09	91.18	5.59	52.17
73	Before	0.129	0.332	8.506	0.328	0.092	0.097
	After	0.069	0	0.458	0.051	0.085	0.022
	%	46.87	100	94.62	84.38	7.57	76.71
80	Before	0.289	0.044	10.07	0.381	0.163	0.065
	After	0.122	0.008	0.359	0.151	0.157	0.031
	%	57.66	81.96	96.43	60.37	3.86	52.22
111	Before	0.174	0.015	7.602	0.094	0.079	0.063
	After	0.068	0	0.544	0.011	0.073	0.016
	%	61.19	100	92.8	88.49	7.12	75.55
1	Before	0.151	0.021	6.239	0.223	0.129	0.109
	After	0.053	0.005	0.333	0.024	0.123	0.028
	%	65.12	76.89	94.65	89.35	4.57	74.64
55	Before	0.126	0.013	3.705	0.035	0.120	0.054
	After	0.052	0	0.302	0.007	0.106	0.037
	%	59.16	100	91.84	79.66	11.78	31.97
91	Before	0.237	0.034	5.916	0.163	0.123	0.089
	After	0.043	0	0.322	0.078	0.120	0.003
	%	82.09	100	94.55	52.02	2.28	96.64
108	Before	0.132	0	3.483	0.049	0.138	0.086
	After	0.020	0	0.252	0.014	0.130	0.016
	%	84.72	0	92.77	72.12	5.79	81.37

* Samples 2, 45, 83 and 113 collected from Taref formation, 50 from Taref and Sabaya formation, 32, 42, 73 and 80 from Sabaya formation, 111 from Sabaya and Six hills formation and 1, 55, 91 and 108 from Six hills formation.

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التخليق بالأشعاع لألياف البولى بروبلين الفعالة واستخداماتها فى معالجة المياه الجوفية فى واحة الداخلة – الصحراء الغربية – مصر

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تم تحضير الياف البولى بروبلين الفعالة باستخدام التطعيم الاشعاعى للاكريلاميد و٤ فينيل بيريدين. كما تم دراسة ظروف التطعيم المختلفة مثل نـوع للمــذيب المــستخدم ونــسب زوج المونيمرات المستخدمة وتركيزها للحصول على أعلى وأفضل نسب تطعيم لاستخدامها كمــواد فعالة فى مجال إزالة العناصر الملوثة ، كذلك تم دراسة تأثير درجة الاس الهيدروجينى على نسبة ازالة العناصر الملوثة كلا على حدا لتحديد أنسب قيمة للاس الهيدروجينى لكل عنــصر ليعطى أعلى نسبة ازالة.

أيضا وجد أن أعلى نـسبة امتـصاص هـى ٢٧٤٫٣ ، ٢٢١٫٣ ، ٢٠٢٫١ ، ١٦١٫٥ ، ١٣٥٫٤ ، ١٢٨٫٩ ، ١٢٢٫٠٦ ، ١٠٤٫١ ملليجرام / جرام من المادة الفعالة لكل من: الرصاص ، الكادميوم ، الزنك ، النحاس ، الحديد ، المنجنيز ، الاسترانشيوم ، الالمونيوم على التوالى.

أيضا تم دراسة تأثير الحرارة على عملية امتصاص العناصر حيث وجد أن الامتــصاص يقل مع زيادة درجة حرارة التفاعل ، كما أعطت الالياف الفعالة المحضرة كفاءة فى امتصاص العناصر الملوثة مع اعادة استخدامها لاكثر من ١٠ مرات متتالية.

بعد ذلك تم التطبيق العملى لتلك الالياف المحضرة فى ازالة الحديد ، المنجنيز الموجــود بالمياه الجوفية التى تم جمعها من واحة الداخلة التى تعانى من زيادة تركيز تلك العناصــر فــى مياهما.

أوضحت النتائج أن تلك الالياف الفعالة المحضرة تعتبر ذات أستخدام واعد فــى مجــال تحسين جودة مصادر المياه.