Journal of Basic and Environmental Sciences 4 (2017) 318-328

ISSN
Online: 2356-6388
Print: 2536-9202

Research Article Open Access

Acrylamide grafting with Maltodextrin for adsorption of hazardous water pollutants Cu(II), Co(II) and Cr(III)

Alaa M.M. EL-Torky[1], **Gamal O. El-Sayed**[2], **Hanan A. Abdelwahed**[3]
[1] Department of chemistry, Faculty of science, Zagazig University, Zagazig, Egypt.
[2] Department of chemistry, Faculty of science, Benha University, Benha, Egypt.
[3] High Institute for Engineering and Technology AL-Obour.

Abstract

Maltodextrin was modified by grafting with acrylamide to improve the swelling characters. The conditions of grafting such as monomer concentration, initiator ratio and grafting temperature were evaluated. The grafting efficiency, the swelling characters as water retention values and sodium binding capacity were determined and nitrogen content were also evaluated for grafting maltodextrin. The structure of these compounds was investigated using FTIR. The optimum condition of grafting ratio of maltodextrin to acrylamide monomer1:6g/g, ratio of maltodextrin to initiator 1:0.03g/g, grafting time three hours and grafting temperature was 70^{o}C. The obtained graft copolymers were used as adsorbents for the removal of Cu(II), Co(II) and Cr(III) ions from an aqueous solution, each one alone. The effect of pH value, contact time, initial metal ion concentration and polymer dosage on metal ions uptake were reported.

Adsorption data for adsorbate concentration are most commonly described by adsorption isotherm, such as the Langmuir, Freundlish and Tempkin isotherms.

Received; 18 Aug., 2017, Revised form; 6 Sept. 2017, Accepted; 6 Sept. 2017, Available online 1 Oct, 2017

1. Introduction

Maltodextrins (MD) are non-sweet, non-toxic saccharide polymers having a dextrose equivalent value of less than 20. Maltodextrins are obtained from the acid and/or enzymatic controlled hydrolysis of starch. Maltodextrins are composed of D-glucose units connected by (1–4) glucosidic linkage to give D-glucose polymers of variable length and therefore different molecular weight. The number of the reducing sugar content is defined by the dextrose equivalent value (DE-value), which is calculated on a dry weight basis. [1]

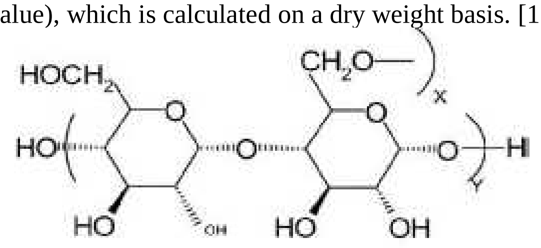


Fig (1): Chemical structure of maltodextrin

Maltodextrin is a hydrolysis product of starch and the process used have an important influence on the composition and the properties of final product and its gel [2]. Maltodextrins with different DE values have different physiochemical properties, including solubility, freezing temperature, viscosity, etc. However, the same DE value of maltodextrins may also have different properties. These depend on the hydrolysis procedure, on the source of starch (potato, maize, rice), and on the amylase to amylopectin ratio. Maltodextrins are widely used in food emulsions as stabilizers [3]. Maltodextrin (MD) is produced from starch with a wide use. Cornstarch has been widely used as raw matter in order to obtain MD [4]. Seven types of starch (waxy corn, normal corn, waxy rice, normal rice, waxy potato, normal potato, and tapioca) were selected to produce slowly digestible maltodextrins by enzymatic modification using a previously developed procedure [5].

Maltodextrin in specific length is of great interest because of its wide industrial applications. Previously hydrophilicity and its functional pendant groups, the possibility of large-scale continuous production of pure maltodextrins from β-cyclodextrin [6], In addition, the maltodextrin obtained from the microalgae biomass residues was resistant to enzymatic hydrolysis, in which this form of maltodextrin is usually denoted as resistant maltodextrin [7].

Not to mention that maltodextrins are odor-, color- and tasteless so they appear as the best option to be employed as encapsulating agents either by spray-drying or twin-screw extrusion. Now a days, maltodextrins are used as the main ingredient rather than additive for the elaboration of bio-based materials by melt extrusion [8-10].

Maltodextrins are great film forming and texturizing agents, as they can increase viscosity, retard crystallization or decrease stickiness and hygroscopicity of a mixture but also improve shelf-life stability of food matrices [11].

Maltodextrins are popular in the food industry not only for all the previous reasons but also because they are highly soluble in water and non-sweet compared to classical sugars [12].

As maltodextrins have ability to form gels, they could be used in producing emulsions as texture modifiers, bulking agents and particularly in food emulsions to certain extent for substitution of fat [13].on spray drying of bayberry juice [14], MD was used as a carrier agent at different concentrations in pineapple juice[15]. Freeze-dried strawberry powder studying the effect of the addition of maltodextrin and arabic gum. Both compositional and physicochemical analyses of strawberry pulp were performed [16].

Resistant maltodextrin is a water soluble fiber and short chain polymer of glucose that are resistant to digestion in the human digestive system. For the confirmation of newly developed analytical method several samples of juices were also analyzed. The method given specifically measures resistant maltodextrin [17].

Dietary intake of probiotic bacteria has been shown to impart health effects, however, maintaining viable cells in foods and during passage of the adverse conditions in the upper gastro-intestinal tract is often a problem. The objective of this research was to develop and characterize novel food-grade phase-separated gelatin–maltodextrin (G-MD) microspheres, presents a new protein based microencapsulation method, which using all food-grade ingredients protects probiotic lactic acid bacteria during exposure to adverse environmental conditions [18].

Investigation the antioxidative and antimicrobial activities of liquid smoke (LS) nanocapsules from coconut shell using chitosan and maltodextrin as encapsulants and its effective preservative agent for fresh tuna fish [19].

Thermal aggregation of whey proteins is a challenge for applications in clear food products with acidity around their isoelectric points (pH 5.0). Glycating whey proteins with sufficient maltodextrins by the Maillard reaction effectively prevents thermal aggregation [20].and Heating the powder of whey protein isolate (WPI)-maltodextrin (MD) mixture [21].

MD is a D-glucose polysaccharide with hydrophilic properties. In the horse, MD has been suggested to reduce pain and swelling and to stimulate granulation tissue production and epithelialization when compared with conventional topical antimicrobials [22].In horse diets, MD can be added to equine diets in replacement of starch with good results in digestibility. Complete substitution of dietetic starch by maltodextrin provides more glucose for longer, increasing energetic balance [23].

Chemical grafting is one of the most effective methods for modifying structure and properties of natural polymers [24,25]. Graft copolymerization of natural polysaccharides is becoming an important resource for developing advanced materials as it can improve the functional properties of natural polysaccharides. grafting of polyacrylamide to dextrin was synthesized by microwave assisted [26].

As an important aspect of starch modification, graft copolymerization of starch with a variety of vinyl monomers is initiated either by a chemical free radical initiator (e.g. ceric ammonium nitrate or ammonium persulfate) [27] . Corn starch graft copolymers were prepared from acrylamide/dimethyl diallyl ammonium chloride binary monomers (AM/DMDAAC) by a simultaneous radiation grafting method [28].

Heavy metal ions in the environment arise from both natural and industrial emissions. Not only they can be non-degradable, but also will be bio-accumulated in animals, plants and human body, causing serious disorders [29].

Langmuir, Freundlich and Temkin isotherms were used to describe the behaviour of equilibrium adsorption. The equilibrium adsorption of the studied mercury ions is best fitted using the Freundlich isotherm. However, due to the small particle size of nanoparticle, nanomaterials have difficulty in separating from solution which limits the application in water treatment [30].

Graphene oxide (GO) and its composites have attracted widespread attentions as novel adsorbents for the adsorptionof various heavy metal contaminants. Because of the unique physicochemical characteristics, they might become an excellent and most potential adsorbent. This review summarizes the application of GO and its composites as a superior adsorbent for the removal of heavy metal ions from water. The adsorption affinity and mechanisms, affecting factors and regeneration are highlighted. Moreover, the challenges for the commercial uses are discussed [31].

A novel crosslinked starch-graft-polyacrylamide-*co*-sodium xanthate (CSAX) was synthesized by grafting copolymerization reaction of corn starch, acrylamide (AM), and sodium xanthate using epichlorohydrin (EPI) as cross-linking reagent and ceric ammonium nitrate (CAN) as initiator in aqueous solution [32].

The produced copolymers of MD-g-AC was used for removal of (Cu(II), Co(II) and Cr(III) metals from aqueous solutions by adsorption. The effects of pH value, contact time, initial metal ion concentration and polymer dosage were reported.

2. Experiments and Materials

2.1. Materials

Maltodextrin, Acrylamide, Potassium Persulfate PPS, Sodium Hydroxide, and salts of Cu, Co, Cr ($CuSO_4.5H_2O$, $CoSO_4.7H_2O$ and $Cr_2(SO_4)_3$) obtained from EL-Nasr Company, Egypt.

2.2. Grafting of acrylamide onto Maltodextrin

Graft copolymerization of acrylamide onto Maltodextrin was carried out with $K_2S_2O_8$ (PPS) as an initiator under vacuum. In a nicked 250 mL flask, PPS is added to Maltodextrin with a definite volume of distilled water(liq.ratio 1:25), then make activation in water bath at 100 ^oC for 15 minutes, leave it till cool then added aqueous solution of acrylamide,put it in a water bath for experimental time with a shaking from time to another after close it .The reaction product was precipitated in methanol and dry it at 50 ^oC to obtain constant weight. The homopolymer of acrylamide coated polymer was removed with distilled water for 24 hours then dry it.

2.3. Determination of metal uptake (Adsorption experiments)

Sorption was carried out by stirring 0.05 g of grafted Maltodextrin as adsorbents in 25ml solution containing different concentrations (5,10,15and 20) ppm ions of (Cu^{+2}, Co^{2+}, and Cr^{3+}) at 90 min. Then after filtration, the remaining metal ions in the filtrate were determined using Atomic Absorption (AA) spectrophotometer.

The adsorption capacity was calculated from the following Eq.(1).

$$q_e = (C_o - C_e)V/m \qquad (1)$$

where $q_e$is the adsorption capacity of adsorbent (mg/g), C_0andC_e(mg/L) are the initial and final concentration of each heavymetal ion in the solution, and V (L) and m(g) are the volume of theadsorption solution and the dose of each adsorbent, respectively.

Which will be used to apply Langmuir, The Freundlich and Tempkin isotherm's models.

3. Results and Discussions

3.1. Effect of polymerization condition on grafting parameters of maltodextrinand its derivatives.

Maltodextrin was chemically modified by grafting with acrylamide in a homogenous aqueous phase by using potassium persulfate (PPS) as initiator.

The grafting parameters (Grafting Efficiency (%G.E), Grafting (%G), Polymerization (%P), Water Retention Value (%WRV), Sodium Hydroxide Retention Value (%NaOH RV) and % N2 Content) were studied by changing grafting process conditions as reaction temperature, Potassium persulphate (PPS) concentration, monomer and time of grafting to maltodextrin ratio to reach the optimum conditions for grafting process.

3.1.1. Effect of reaction Temperature on grafting parameters.

While maintaining reagents and other fixed variables the grafting reaction was performed at different temperatures ranging from 50 to 80 ° C.

Table (1) and figure (2) illustrate the effect of grafting reaction temperature on the grafting parameters which shows that the grafting efficiency increased with an increase in grafting temperature from 50°C to 70°C, it could due to better decomposition of the reaction system giving more free radical, and higher rate of initiation of the graft chain [33]. This effect is attributed the increase of the rate of diffusion of acrylamide through maltodextrin molecules, swelling maltodextrin, as well as an increase of the rate of initiation and propagation of the grafting process.

The results show the grafting efficiency decreased with increasing the grafting temperature (above 70°C) enhances the oxidation of free radicals and mutual termination of growing macro radicals favors more homopolymer formation over the grafting reaction. This observation indicates that the optimal reaction temperature for produce high grafting efficiency is 70°C. Also from table (1) and figure (2) it is clear that the water retention value and NaOH retention value of the produced grafted Maltodextrin highly increases by increasing temperature at 80°C due to increase the space between chains of grafting polymer.

Table (1): Effect of grafting reaction temperature on the grafting parameters

No.Exp.	Temperature ^oC	P %	G %	G.E%	WRV	NaOH RV	N_2%
1	50	722	614	85.04	1571.7	78.55	14.4
2	60	639.5	562.5	87.96	1673.5	85.36	13.3
3	70	632	603	95.49	1830.43	96.8	13.7
4	80	650.5	546	83.95	2933.3	556	13.8

Condition: 1:25 Liq. ratio, 1:6 maltodextrin/acrylamide, 0.03g pps/g maltodextrin 3 hrs, under vacuum.

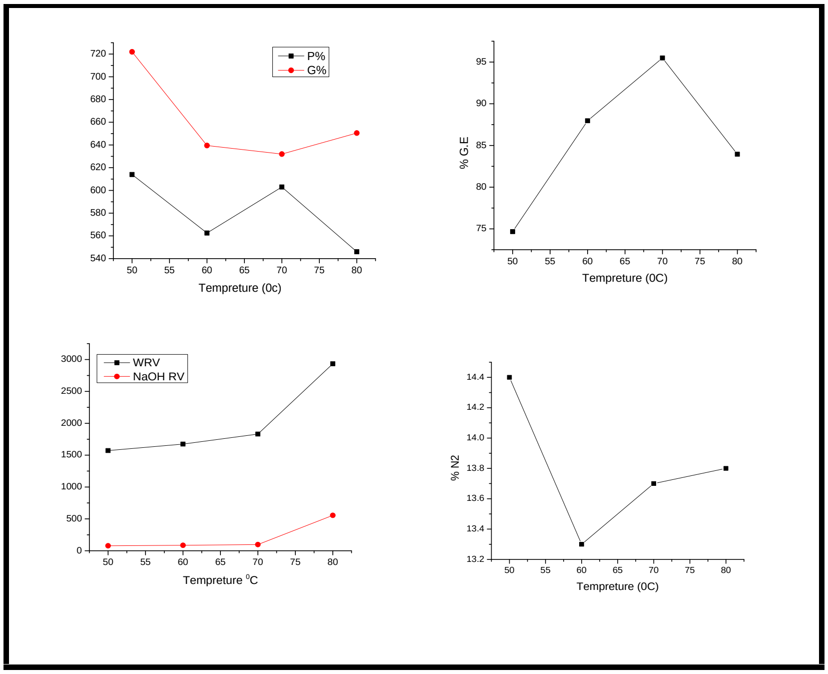


Fig (2): Effect of temperature on grafting parameter, swelling properties, and N_2 content

3.2.2. Effect of reaction monomer concentration on grafting parameters

The effect of different concentration of acrylamide on the grafting parameters, P%, G%, G.E.%, WRV, NaOH RV and N_2 content , with the constant of other conditions of grafting process were listed in table (2) and figure (3).

It is clear that increasing monomer ratio increased the grafting, grafting efficiency, swelling behavior WRV and NaOH RV this is because the acrylamide ions increase around the active sites of the maltodextrin molecules that increase the formation of the copolymer and lengthening the acrylamide polymerized residue of grafting products.

It is clear from table (2) and figure (3) that increasing monomer concentration (2,4,6 g monomer /1g maltodextrin) causes a significant increase in the grafting efficiency then increase slowly up (8 g monomer /1g maltodextrin) then decrease again, thus the optimal monomer concentration for produce high grafting efficiency is (6g monomer /1g maltodextrin).

Table (2): Effect of monomer concentration on grafting parameters.

No.Exp.	Monomer(g)	P %	G %	G.E %	WRV	NaOHRV	N2 %
5	2	177	105.5	59.7	1334.38	60.42	5.9
6	4	420	367	87.42	1605.77	64.42	8.3
3	6	632	603	95.49	1830.43	96.8	13.7
7	8	870	868	99.79	2938.9	108.2	14.3
8	10	1170	1073	90.93	3472.27	116.1	14.7

Condition: 1:25 Liq. ratio, 1g maltodextrin, 0.03g pps/g maltodextrin, 3hrs under vacuum at 70°C.

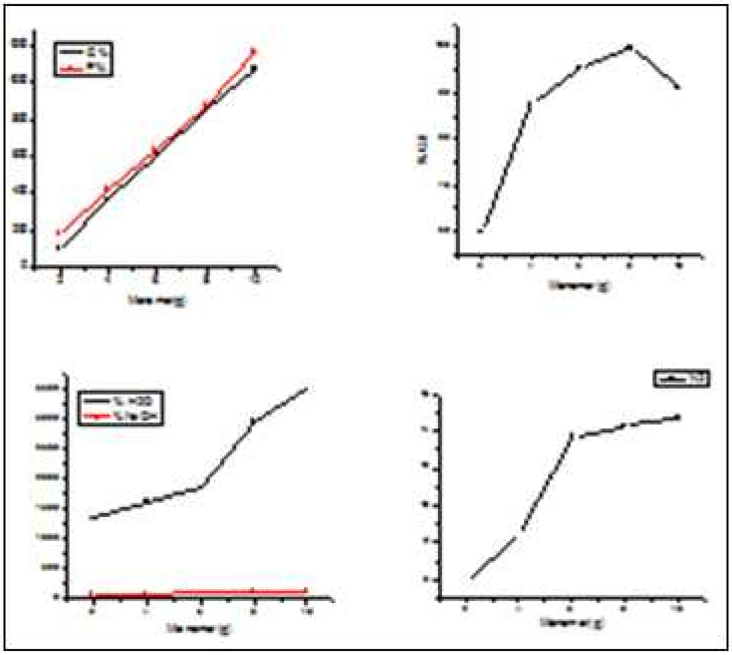


Fig (3): Effect of monomer concentration on grafting parameter, swelling properties and N_2 content.

3.2.3. Effect of reaction Initiator Concentration on grafting parameters

Potassium persulphate was used as initiator for grafting process with the concentration of 0.03to 0.07 g/g maltodextrin. The effects of increasing the initiator concentration on the grafting parameters were illustrated in Table (3) and Figure (4).

Table (3): Effect of initiator concentration on the grafting parameters.

No.Exp.	pps	P%	G%	G.E%	WRV	NaOHRV	N_2%
9	0.01	-ve	-ve	-ve	-ve	-ve	-ve
3	0.03	632	603	95.49	1830.42	96.8	13.7
10	0.05	640.5	615.5	96.17	2066.7	109.4	13.9
11	0.07	655	634	96.84	2887.5	155.9	14.1

Condition: 1:25 Liq. ratio, 1g maltodextrin, 6g monomer, 3hrs under vacuum at 70°C.

It is clear from table (3) that initiator concentration (0.03g PPS/1g maltodextrin /6g monomer) causes a significant increase in the grafting parameters. This is because the presence of free radicals on maltodextrin molecules which enhances the grafting process. At 0.05,0.07g PPS/1g maltodextrin /6g monomer, G.E.% increase by small value that may be due to the enhancing of the homopolymerization reaction [34,35]. This observation indicates that the optimal pps concentration is (0.03g PPS/1g maltodextrin /6g monomer). All this was illustrated in fig (4) .

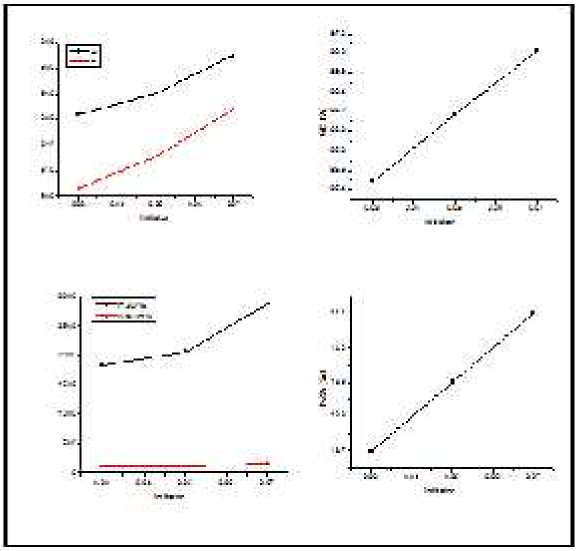


Fig (4): Effect of initiator concentration on grafting parameters, swelling properties and N2 content.

3.2. Infrared spectra of the maltodextrin and graftedsamples.

IR-spectra of grafted maltodextrin with acrylamide exhibited the new absorption band in 3340 cm^{-1} and 1649 cm^{-1} which attributed for –N-H band of (–NH2), carbonyl groups (C=O) of the amide group.

Figure (5) show the FT-IR of ungrafted maltodextrin and acrylamide – maltodextrin grafting. In ungrafted maltodextrin the absorption at 3301 cm^{-1} for OH group and 1148, 1107 and 1034 cm^{-1} were attributed to C-O band stretching. Asmall share peak at 807 Cm^{-1}, corresponding to the glucosidic C-H deformation with Ring vibration contributions and OH bending. Additional characteristic adsorption band appeared at 681 cm^{-1}, were done to anhydroglucose ring stretching vibrations.

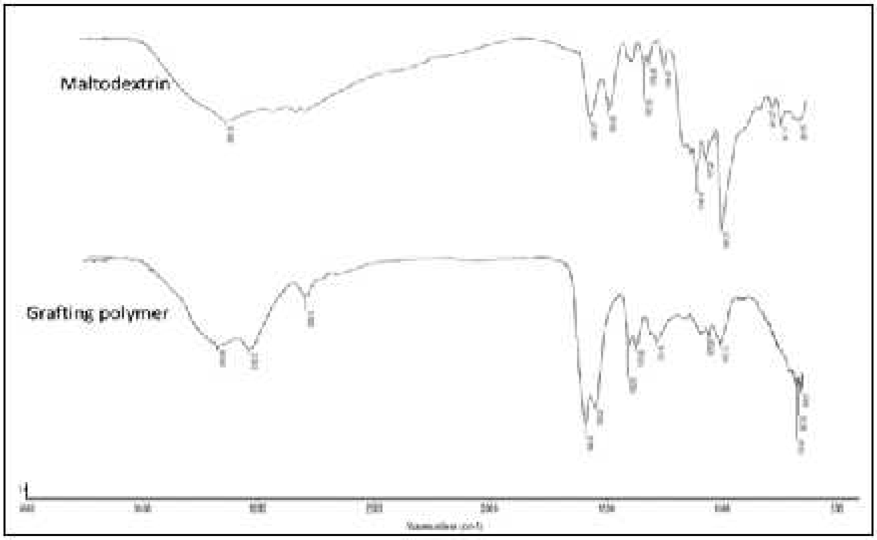


Fig (5): FTIR spectra of maltodextrin and grafted maltodextrin-acrylamide copolymer,

3.3. Analytical Applications

The ability of the resulting polymer to remove Cu^{2+}, Co^{2+} and Cr^{3+} ions from aqueous media was examined and optimized by considering the following parameters.

3.3.1. pH

The pH of the aqueous solution of metal ion is an important operational parameter in the adsorption process as it affects the solubility of the metal ion, concentration of the counter ions on the functional groups of the adsorbent as well as the degree of ionization of the adsorbate during reaction [36]. The effect of pH on Cu^{2+}, Co^{2+} and Cr^{3+} adsorption was investigated in the pH range 1.8 to 6 to prevent the precipitation of metal ions as hydroxides. As shown in Fig.6, the uptake of all metal ions increases with increasing pH. This behavior is expected [37-39] and may be due to the electrostatic attraction between metal ions and the functional groups on the adsorbent surface which increases with decrease of H^+ ions as the solution acidity decreased. The low removal values found at acidic solutions may be attributed to the competition between H^+ and metal ions for the same adsorbing sites [40].

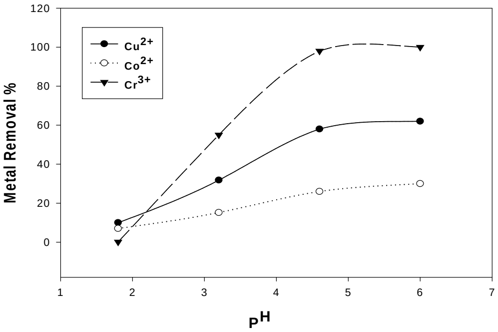


Fig (6): Effect of solution pH on the removal efficiency of Cu^{2+}, Co^{2+} and Cr^{3+} by grafted polymer**.**

3.3.2. Contact time

The effect of contact time was depicted in Figure (7). As can be seen from the figure, the adsorption increased with increasing contact time. The rapid adsorption at the initial stage is probably due to the abundant availability of active sites on the surface of grafted polymer. The adsorption capacity of metal ions becomes less and the equilibrium was achieved within 90 min, so an equilibration period of 90 min was selected for all further experiments.

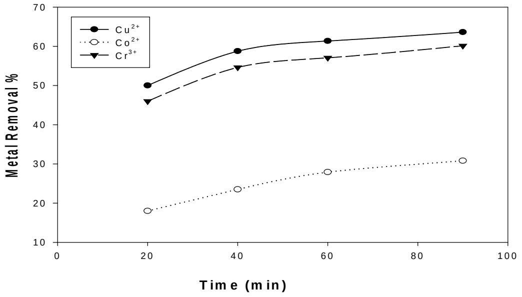


Fig (7): Effect of contact time on removal efficiency of Cu^{2+}, Co^{2+} and Cr^{3+} by grafted polymer

3.3.3. Initial metal ion concentration

The initial concentration of metal ions is an important factor for effective adsorption process. The removal percent of metal ions Cu^{2+}, Co^{2+} and Cr^{3+} at different metal ion concentration (5-20 mg/L) were performed by keeping all other parameters constant. As shown in Fig (8), the removal percent decreased for all metal ions by increasing the initial metal concentration.

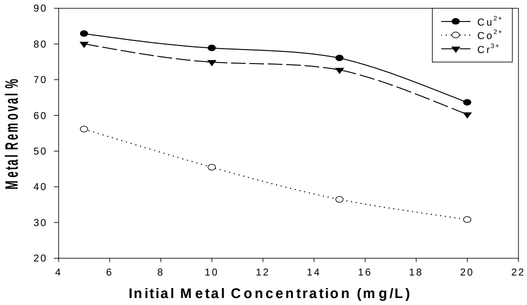


Fig (8): Effect of contact initial metal concentration on removal efficiency of Cu^{2+}, Co^{2+} and Cr^{3+} by grafted polymer.

3.3.4. Polymer dosage

The effect of adsorbent dosage on Cu^{2+}, Co^{2+} and Cr^{3+}adsorption was investigated by changing the adsorbent dosage from 1to 4 g/L. The results (Fig 9)show that The removal percent of metal ions Cu^{2+}, Co^{2+} and Cr^{3+} at were performed by keeping all other parameters constant, the removal percent increased for all metal ions by increasing the Polymer dosage concentration, when increased adsorbent surface and availability of more adsorption sites with a fixed amount of metal ions.

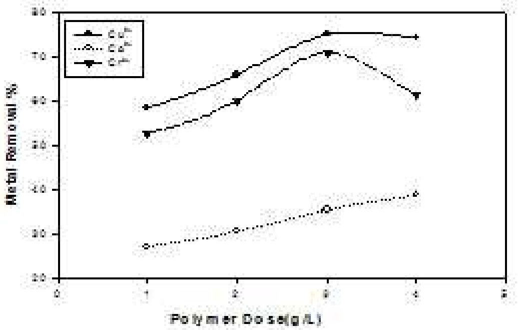


Fig (9): Effect of contact polymer dosage on removal efficiency of Cu^{2+}, Co^{2+} and Cr^{3+} by grafted polymer.

3.4. Adsorption isotherms

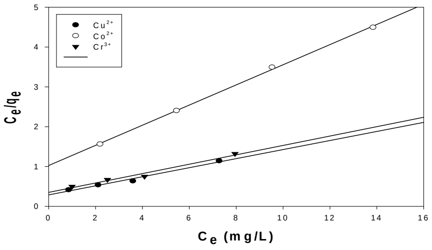
Adsorption data for adsorbate concentration are most commonly described by adsorption isotherm, such as the Langmuir, Freundlish or Tempkin isotherms. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The Langmuir model assumes a homogeneous surface with respect to the energy of adsorption, in which there is no interaction existed between adsorbed species, and all the adsorption sites are equally available to the adsorbed species [41]. Langmuir adsorption model can be described as Eq (1):

$$1/q_e = 1/Q_o + (1/b\,Q_o)\,(1/C_e) \qquad (1)$$

Where C_e is the concentration of solute remaining in solution at equilibrium (mg/L); q_e is the amount of solute adsorbed per weight unit of solid adsorbent at equilibrium (mg/g); and Q_o and b are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively.

These values can be obtained from the plot of $1/q_e$ against ($1/C_e$).

The Langmuir linearrelation for maltodextrin grafted polymer is shown representatively in Fig. (10).



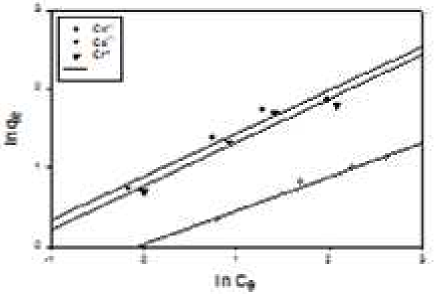
	Langmuir isotherm		
	R^2	Slope	Intercept
Cu^{2+}	0.98252	0.113754	0.287982
Co^{2+}	0.999076	0.253008	1.025347
Cr^{3+}	0.9751704	0.1178204	0.351401

Fig (10): Langmuir isotherm plot for adsorption of metal ions onto MD grafted polymer.

The Freundlich isotherm assumes that the adsorption of metal occurs on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with increase in concentration [42]. The Freundlich equation is represented as:

$$\ln q_e = \ln K_f + (1/n) \ln C_e \qquad (2)$$

Where, Kf is the freundlich constant (mg/g) which represent the relative adsorption capacity of the adsorbent. (1/n) is the heterogeneity factor which indicates of the intensity of the adsorption process.



	Freundlich isotherm		
	R^2	Slope	Intercept
Cu^{2+}	0.93727	0.544002	0.898603
Co^{2+}	0.984169	0.4273855	0.0351623
Cr^{3+}	0.940946	0.553589	0.7682795

Fig (11): Freundlich isotherm plot for adsorption of metal ions onto MD grafted polymer.

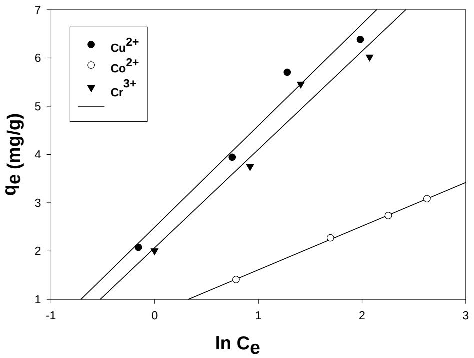
Tempkin isotherm considers the effects of some indirect adsorbate/adsorbate interaction on adsorption processes. The Temkin adsorption isotherm assumes that the heat of adsorption decreases linearly with the sorption coverage because of these interactions [43]. The Temkin isotherm equation is given as:

$$q_e = RT/b \ln(K_T C_e)$$

This Equation can be expressed in its linear form as:

$$q_e = B \ln K_T + B \ln C_e$$

Where B = (RT/b), b is the Temkin constant related to heat of sorption, A is the Temkin isotherm constant, R is the gas constant, and Tis the absolute temperature. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy). The Temkin isotherm was applied by a linear plot of q_e against ln (C_e) shown in Fig. (12). and the constants B and A were calculated from the slope and intercept respectively. The Temkins isotherm parameters A, B and $R^2$are presented. Again, looking at the regression R^2obtained, it is seen that this isotherm is not appropriate to use as a model to predict the adsorption isotherms of metal ions investigated for the entire adsorption period.



Metals	Tempkin isotherm		
	R^2	Slope	Intercept
Cu^{2+}	0.96652	2.1042996	2.493666067
Co^{2+}	0.999206	0.9043606	0.706073459
Cr^{3+}	0.960806	2.0366594	2.0674671754

Fig (12): Tempkin isotherm plot for adsorption of metal ions onto MD grafted polymer.

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