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Utilization of Nitrogen Containing Pregelled Starch Derivatives as Biodegradable Polymers for Heavy Metal Ions Removal

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Abstract: Two type of nitrogen containing pregelled starch derivatives having amide groups ($CONH_2$) were used in heavy metal ions removal from its solutions. These pregelled starch derivatives were carbamated pregelled starch (CPS) and poly (methacrylamide)-pregelled starch graft copolymer (PMamPSGC). Different factors affecting adsorption of metal ions onto these substrates such as metal ion concentration, pH, treatment time and temperature as well as type of starch derivatives were studied. Results obtained reflect the following findings: (a) the adsorption values of both nitrogen containing starch derivatives in question increase by increasing the metal ion concentration up to 50 mmol L^{-1} then levels off, (b) poly (methacrylamide)-pregelled starch graft copolymer was selective adsorbent for Hg^{2+} at pH 0.5-1, (c) The adsorption values on these pregelled starch derivatives at different metal ions follow the order: $Hg^{2+} > Cu^{2+} > Zn^{2+} > Pb^{2+}$, (d) The adsorption efficiency % of metal ions in case of poly (methacrylamide)-pregelled starch graft copolymer is higher than that in case of carbamated pregelled starch irrespective of the metal ion used, (e) The adsorption values is higher at 30°C then decreases by raising the temperature to 50 and 70°C and (f) The adsorption values increase by increasing the treatment time up to 5 h then levels off.

Key words: Nitrogen containing pregelled starch, adsorption value, adsorption efficiency %, metal ions

INTRODUCTION

Environmental pollution caused by toxic heavy metals in industrial effluents is considered as one of the most important problems worldwide[1]. The use of synthetic resins for chelating toxic metal ions in wastewater is consider as a possible way for preventing environmental pollution. These resins are mostly based on petroleum synthetic polymers[2-7] at which secondary environmental pollution take place via their contamination on soil and air. In addition, these synthetic polymers are usually none renewable and non-biodegradable.

So, present research work has been directed to use modified starch products as an agriculture biopolymer, low cost as well as renew ability for heavy metal ion removals. This was done to replace the original starch duo to it has no chelating or interaction capacity for heavy metal ion removal. Hence, several trials have been made to utilize starch as a metal scavenger, by using modified starch containing carboxyl[8,9], phosphate[10], xanthate[11] as well as acrylamide[12]. In addition, removal of heavy metal ions was carried out via chelation by using cationic starches[13,14]. This work has been undertaken with studying the removal of some heavy metals via chelation on the aforementioned nitrogen containing pregelled starch derivatives having the same adsorbing amide groups and different backbone structure via different method of preparation. The different factors affecting adsorption of metal ions such as metal ion concentration, pH, treatment time and temperature as well as types of starch derivatives were studied. Beside, the work was further extended to study the durability for adsorption and desorption of different metal ions onto these substrate.

MATERIALS AND METHODS

Materials: Pregelled starch was kindly supplied by Egyptian starch and Glucose Manufacturing Company, Cairo Egypt.

Preparation of Poly (methacrylamide)-Pregelled starch Graft Copolymer having 820 mmol amide group/100 g sample (capacity): The graft polymerization reaction was carried out in 100 ml flasks containing an aqueous solution of monomer (10 g). The flask was stoppered and

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placed in a thermostatic water-bath until the required temperature (45°C) was reached. Nitrogen gas was purged through this solution to remove the dissolved oxygen. The pregelled starch (10 g) and ceric ammonium nitrate initiator (0.006 mol L^{-1}) were then added and the reaction mixture was mixed thoroughly. The contents were shaken occasionally during polymerization. After the desired reaction time (2 h), the flask contents were poured over 500 ml ethyl alcohol. At this end, a precipitate was formed which consisted of pregelled starch graft copolymer and the homopolymer. The homopolymer poly (methacrylamide) was removed from the reaction mixtures by washing the reaction mixture with 400 ml water-ethanol mixture (30:70) several times (for 15 min. each) at room temperature, filtered and finally dried in an electric oven at 60°C for 2 h. It was found experimentally that washing five times with a mixture of water/ ethanol (30:70, v/v) is quite enough for complete homopolymer removal in physical mixtures of pregelled starch/ poly methacrylamide. This was evidenced by measuring the nitrogen % after washing for each sample till constant nitrogen %, (three times measurement for each sample as well as their standard deviations were obtained). Finally, washed with pure ethanol and air-dried.

Preparation of carbamated pregelled starch having 530 mmol amide group/100 g sample (capacity): Pregelled starch (10 g) was mixed well with (5g urea) and 0.2 g-cupper chloride catalyst using electric mixer. The mixture was transferred to a petri dish and covered, then heated for 30 min at 160°C. After the desired reaction time, the thermally treated mixture was poured over 500 ml of ethanol for precipitation and then washed several times with ethanol: water mixture (80:20) for 10 min. for each wash on magnetic stirrer at room temperature. It was found experimentally that 3-5 times washing with the latter mixture is quite enough to remove the contaminants (unreacted substances). This was evidenced by measuring the nitrogen % after washing for each sample till constant nitrogen %, (three times measurement for each sample as well as their standard deviations was obtained). Finally, washed with pure ethanol and air-dried.

Metal salts: Hg $(NO_3)_2$, Cu $(COOCH_3)_2.2H_2O$, Zn $(COOCH_3)_2$ and Pb $(COOCH_3)_2.3H_2O$. were of analytical reagent grade.

Adsorption of metal ions: Aqueous solutions of 0.01 M of different metal salts were prepared and its pH was adjusted to the specified values. The pregelled starch derivatives (0.1 g) were put into a glass bottle containing 100 ml of the metal salts solution and the mixture was occasionally shaken for the desired treatment time. The adsorption value was calculated by estimating the metal ion concentration before and after treatment with pregelled starch derivatives by titration against standard EDTA.

Desorption of metal ions: The treated pregelled starch derivatives with metal ions was stirred with 50 ml of 0.1N nitric acid for 2 h at room temperature and then filtered. Then the metal ion in the filtrate was estimated.

The adsorption efficiency%: It was calculated as follows:

$$\text{The adsorption efficiency \%} = \frac{\text{The adsorption value}}{\text{Pregelled starch derivatives capacity}} \times 100$$

RESULTS AND DISCUSSION

Effect of metal ion concentration: Figure 1 and 2 show the adsorption values (expressed as mmol/100 g sample) of different metal ions concentration in case of poly (methacrylamide)-pregelled starch graft copolymers and carbamated pregelled starch. It is shown Fig. 1 and 2 that:

- The adsorbed amounts of metal ions increase by increasing metal ions concentration from 10-50 mmol L^{-1} then levels off.
- The maximum adsorption value was 800 mmol/100g sample for Hg^{2+} and the minimum was 425 mmol/100g sample for Pb^{2+} in case of poly (methacrylamide)-pregelled starch graft copolymer. While that in case of carbamated pregelled starch were 400 and 240 mmol/100 g samples for Hg^{2+} and Pb^{2+}, respectively.
- The adsorption values depend on the metal ion used and follow the order: $Hg^{2+} > Cu^{2+} > Zn^{2+} > Pb^{2+}$

This is in accordance with Irving-William's series[15] for the stability of various ligands with nitrogen or oxygen as coordinating atoms for divalent metal ions.

Effect of pH: Figure 3 and 4 represent the adsorption values (expressed as mmol/100 g sample) of different metal ions at different pH values (0.5-6.5) of poly (methacrylamide)-pregelled starch graft copolymer and carbamated pregelled starch. The results obtained reflect the following findings:

- The adsorption values of metal ions in question increase by increasing the pH values within the range studied.

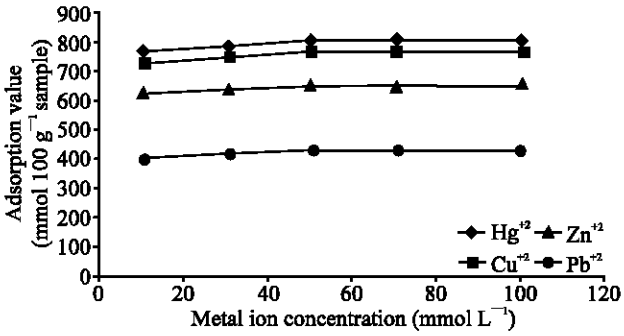

Fig. 1: Effect of metal ion concentration on the adsorption value (expressed as mmol/100 g sample) of different metal ions in case of poly (methacrylamide)-pregelled starch graft copolymer
Reaction conditions: Poly (MAam)-pregelled starch graft copolymer, 0.1 g; total volume of metal ion, 100 ml; pH, 6.5, treatment time, 24 h and temperature, 30°C

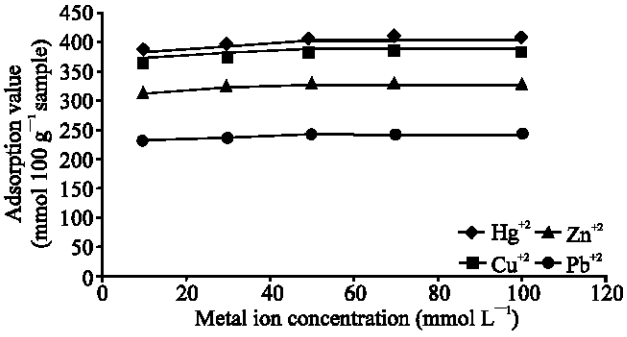

Fig. 2: Effect of metal ion concentration on the adsorption value (expressed as mmol/100 g sample) of different metal ions in case of carbamated pregelled starch
Reaction conditions: Carbamated pregelled starch, 0.1 g; total volume of metal ion, 100 ml; pH, 6.5, treatment time, 24 h and temperature, 30°C

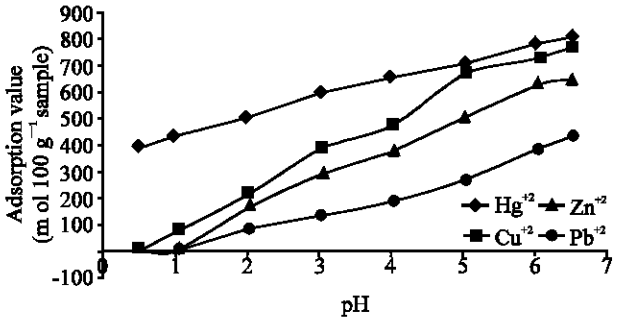

Fig. 3: Effect of changing pH on the adsorption value (expressed as mmol/100 g sample) of different metal ions in case of poly (methacrylamide)-pregelled starch graft copolymer
Reaction conditions: Poly (MAam)-pregelled starch graft copolymer, 0.1 g; metal ion concentration, 50 mmol L^{-1}; total volume of metal ion, 100 ml; pH, 6.5, treatment time, 24 h and temperature, 30°C

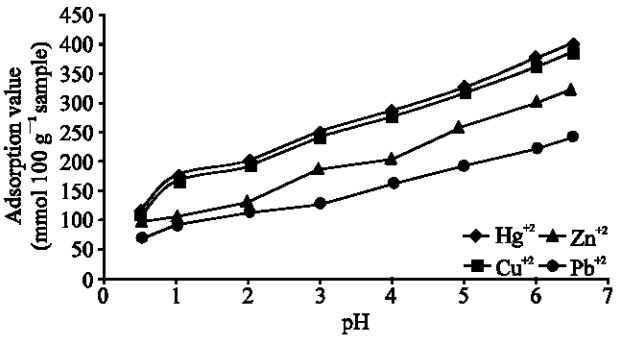

Fig. 4: Effect of changing pH on the adsorption value (expressed as mmol/100 g sample) of different metal ions in case of carbamated pregelled starch
Reaction conditions: Carbamated pregelled starch, 0.1 g; metal ion concentration, 50 mmol L^{-1}; total volume of metal ion, 100 ml; pH, 6.5, treatment time, 24 h and temperature, 30°C

- At pH value 0.5 only Hg^{2+} metal ion adsorbed and the adsorption value was 385 mmol/100 g samples in case of poly (methacrylamide)-pregelled starch graft copolymer. While in case of carbamated pregelled starch all metal ions were adsorbed. This reflects the role of using poly (methacrylamide)-pregelled starch graft copolymers as selective adsorbent for Hg^{2+} at pH 0.5.
- At pH value 1 the adsorbed metal ions were Hg^{2+} and Cu^{2+} and the adsorption values were 430 and 70 mmol 100 g^{-1} samples, in case of using poly (methacrylamide)-pregelled starch graft copolymer and carbamated pregelled starch.

- At pH range 1.5-6.5 all metal ions used were adsorbed with different values depending on the nature of metal ion and;
- The adsorption values depend on the metal ion used and follow the order: $Hg^{2+} > Cu^{2+} > Zn^{2+} > Pb^{2+}$.

Effect of treatment time (duration) and temperature: Table 1 and 2 represent the adsorption of metal ions at

Table 1: Effect of changing treatment time and temperature on the adsorption value (mmol/100 g sample) of different metal ions in case of poly (MAam)-pregelled starch graft copolymer

	Adsorption value (mmol/100 g sample)														
	30°C					50°C					70°C				
Metal ion	½ h	1 h	3 h	5 h	24 h	½ h	1 h	3 h	5 h	24 h	½ h	1 h	3 h	5 h	24 h
Hg^{2+}	450	530	760	800	800	420	500	730	760	760	380	460	700	680	680
Cu^{2+}	400	430	590	760	760	380	410	560	720	720	360	370	520	600	600
Zn^{2+}	375	415	560	645	645	350	385	520	600	600	315	350	430	465	465
Pb^{2+}	210	230	350	425	425	190	200	310	395	395	160	175	215	250	250

Reaction conditions: Poly (MAam)-pregelled starch graft copolymer, 0.1 g; metal ion concentration, 50 mmol L^{-1}; Total volume of metal ion, 100 ml; pH, 6.5

Table 2: Effect of changing treatment time and temperature on the adsorption value (mmol/100 g sample) of different metal ions in case of carbamated pregelled starch

	Adsorption value (mmol/100 g sample)														
	30°C					50°C					70°C				
Metal ion	½ h	1 h	3 h	5 h	24 h	½ h	1 h	3 h	5 h	24 h	½ h	1 h	3 h	5 h	24 h
Hg^{2+}	265	300	350	400	400	235	270	330	385	385	200	230	275	300	300
Cu^{2+}	250	280	340	385	385	220	250	300	340	340	185	210	235	260	260
Zn^{2+}	225	250	300	325	325	200	230	260	300	300	170	190	210	230	230
Pb^{2+}	185	200	210	240	240	170	190	210	230	230	150	170	190	210	210

Reaction conditions: Carbamated pregelled starch, 0.1 g; metal ion concentration, 50 mmol L^{-1}; Total volume of metal ion, 100 ml; pH, 6.5

Table 3: The adsorption efficiency % of different metal ions of poly (methacrylamide)-pregelled starch graft copolymer and carbamated pregelled starch using the optimum condition for each substrate

	Adsorption efficiency %	
Metal ion	Poly (methacrylamide)-pregelled starch graft copolymer	Carbamated pregelled starch
Hg^{2+}	97.6	75.5
Cu^{2+}	92.7	72.6
Zn^{2+}	78.7	61.3
Pb^{2+}	51.8	45.3

Table 4: The adsorption of different metal ions on the poly (methacrylamide)-pregelled starch graft copolymer and carbamated pregelled starch (adsorption and desorption)

	Adsorption value (mmol/100 g sample)									
	Poly (MAam)-pregelled starch graft copolymer					Carbamated pregelled starch				
Metal ion	0 cycle	1 cycle	2 cycles	3 cycles	4 cycles	0 cycle	1 cycle	2 cycles	3 cycles	4 cycles
Hg^{2+}	800	760	680	560	460	400	250	150	60	-
Cu^{2+}	760	700	610	510	420	385	230	120	50	-
Zn^{2+}	645	600	500	400	300	325	210	100	40	-
Pb^{2+}	425	330	260	200	110	240	110	70	10	-

different duration (0.5-24 h) and temperatures (30-70°C) in case of poly (methacrylamide)-pregelled starch graft copolymers and carbamated pregelled starch.
The data show that:

- The adsorption of metal ions increases by increasing treatment duration to reach a maximum value then levels off. The maximum adsorption values occur after 5 h at 30 and 50°C and 3 h at 70°C, respectively.
- The adsorption values of metal ions decrease by increasing the treatment temperature from 30-70°C. This can be explained in terms of higher stability of formed chelates at lower temperatures as generally observed for low molecular weight complexes. This observation is in agreement with that obtained with Nakamora *et al.*[16].

Adsorption efficiency%: Table 3 shows the adsorption efficiency % of different metal ions in case of poly (methacrylamide)-pregelled starch graft copolymer and carbamated pregelled starch. This was done to examine the difference in efficiency between the above two substrates.

From Table 3, the adsorption efficiency % of poly (methacrylamide)-pregelled starch graft copolymer is higher than that carbamated pregelled starch irrespective of metal ions used. This may be explained in terms of:

- The difference in backbone structure (i.e. method of preparation via grafting or carbamation),
- The available surface area and,
- The distribution of the adsorbing groups ($CONH_2$) on the backbone structure.

Durability: Both poly (methacrylamide)-pregelled starch graft copolymer and carbamated pregelled starch were used in adsorption and desorption of different metal ions several times (4 cycles) to examine their durability.

Table 4 shows the adsorbancy of different metal ions on the above two substrate after four cycles (adsorption and desorption).

It is seen from the Table 4 that:

- The adsorbed metal ions were easily desorbed by treatment with 0.1 M HNO_3 at room temperature,
- The adsorbed amount of the different metal ions decreases after each cycle and the decrement observed depends on the substrate used,
- The stability of these substrate towards adsorption and desorption shows the privilege of Poly (methacrylamide)-pregelled starch graft copolymers over carbamated pregelled starch.

In other word, the decrement in adsorption capacity of latter two substrate in question may be duo to solubility of some highly substituted derivatives after each cycle.

It was found that the higher adsorption value of different metal ions obtained when using metal ion concentration, 50 mmol L^{-1}; pH, 6.5; treatment time, 5 h; treatment temperature, 30° as well as using a metal ion solution of 100 ml. Beside, the newly prepared poly (methacrylamide)-pregelled starch graft copolymers shows a privilege in metal ion adsorption than carbamated pregelled starch as well as its selectivity to adsorb Hg^{2+} at pH 0.5-1.

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