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Removal of heavy metals from water by adsorption on chitin derivatives

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ABSTRACT

Chitin, isolated from shrimp shell, was subjected to acid and alkali treatment. The effect of alkali and acid pretreatment of chitin on phosphorylation of chitin was investigated. Also the effect of alkali and acid pretreatment of chitin on the extent of phosphorylation in presence of cross-linker was illustrated. Acid pretreatment was found to be more efficient in increasing the reactivity of chitin toward phosphorylation than alkali pretreatment. The prepared chitin derivatives were investigated for heavy metal ions removal (Ni, Mg, Zn and Pb). Phosphorylated and also carboxylation of chitin (in presence of crosslinker) have increased capability toward heavy metal ions removal more than chitin. Also, phosphorylated cross-linked chitin treated with acid showed the highest heavy metal ion removal capability. Infrared spectroscopy (FTIR) was used to follow the molecular structure of chitin and its derivatives.

Keywords: Chitin, heavy metal ions removal, ion exchangers, crosslinking, phosphorylation, carboxylation.

INTRODUCTION

Chitin has been reported to be the second most abundant natural polysaccharide in nature and is widely distributed in marine invertebrates, insects, fungi and yeast [1-3]. After cellulose, it is the most common polysaccharide found in the nature. Like cellulose, chitin is a fiber, and in addition, it has been used in the pharmaceutical, environmental, cosmetic and agricultural industries for applications that include wound dressings, contacts, lotions, package film coatings, pesticides, and wastewater treatment [1]. Chitin, a polymer composed of linear repeating beta-1,4-linked *N*-acetyl-D-glucosamine monomers, thus chitin is properly poly (N-acetyl-2-amino-2-deoxy-β-D-glucopyranose) in which the N-acetyl-2-amino-2-deoxy-D-glycopyranose (or glucosamine) units are linked by (1-4)-β bonds. The repeating units contain two hexose residues and comprise one chitobiose unit [4, 5]. Purified chitin is a white material, it is insoluble in water, dilute acids, dilute and concentrated alkalis and all organic solvents, but is soluble in anhydrous formic acid, in hypochlorite solutions and in concentrated mineral acids. Chitin is most readily prepared from the shells of such crustaceans as crabs, lobster, shrimp, etc [6-8].

Removal of heavy metals from contaminated solutions is therefore essential [9-11]. It can be carried out by different methods, such as, precipitation, oxidation or reduction, ion exchange, electrochemical methods, filtration, coagulation, adsorption, osmosis, membrane operations, or evaporation [12]. To this end, chitin has been known to chelate heavy metal ions for wastewater treatment purposes [13, 2]. For instance, Yang and Zall [14] have studied the adsorption of various metal ions by chitin. Giles and Hassan [15] have investigated the adsorption of ionic species of sulfonated azo dyes and inorganic and organic acids onto chitin. Chitin showed high chelating ability in removal of trace metal ions, such as mercury, copper, zinc, chromium, cadmium, nickel, and lead, from contaminated effluents or sludge [16-18]. In another study, vanadate cations have been adsorbed by chitin [19]. The high capacity of chitin for adsorbing dyes and metal ions has been attributed to a combination of many factors such as its ionic nature, its affinity for water, and its porous polymer structure [20].

Chitin and the derivatives of chitin have played significant role in their capacity as adsorbent and complexing agent by virtue of their hydroxyl, acetate, amido and amino groups [21].

Compared with other polysaccharides, chitin is un-reactive so the incorporation of groups such as phosphate onto chitin by reaction of phosphorylating agent onto the amino groups is known to increase the chelating properties of chitin and could modify its solubility and increase the potential applications of chitin for pharmaceutical, veterinary, medicine, biomedical, and environmental fields [22-25].

The aim of this study was to prepare ion exchanger from chitin by incorporation of phosphate or carboxyl group onto chitin. Effect of crosslinking on the efficiency of the prepared ion exchanger toward metal ions sorption is investigated. Molecular structure of the produced resin from chitin is followed by using infrared spectroscopy.

MATERIALS AND METHODS

Materials

The raw material used in this study was shrimp shells.

Isolation of chitin from shrimp shells

Chitin was isolated from shrimp shells [26]. First, the shells were treated with hydrochloric acid to remove calcium carbonate then with sodium hydroxide to remove residual protein and finally washed thoroughly with water and left to dry in air. Pigments were removed with bleaching agents (chlorination, alkali extraction, and hypochlorite).

Pretreatment of chitin with acid and alkali

Chitin was treated with 0.1N hydrochloric acid or 0.1N sodium hydroxide before phosphorylation for 3 hours at room temperature, then washed with distilled water till neutrality and finally air dried.

Phosphorylation

Chitin was phosphorylated according to the method of Lehrfeld [27, 28]; 5 gm of oven– dry chitin was suspended in 40 ml of pyridine and cooled to 8°C. 20 ml of dichloromethane containing 5 ml of phosphorus oxychloride was added to the previous mixture and heated at 115°C for 2h. The mixture was filtered and the phosphorylated material was washed with 0.1N HCl, distilled water, methanol and air-dried.

Crosslinking

Cross-linking of the phosphorylated chitin with epichlorohydrin was carried out by treating chitin with epichlorohydrin in presence of ammonium hydroxide at 60°C for 2 hours [29]**.** The cross-linked chitin was filtered, washed with ethanol and water, and finally vacuum dried at 65°C for 12 hr.

Determination of phosphorous

Phosphorylated material (0.2g) was digested in 10 ml of concentrated nitric acid. After digestion, the solution was diluted to 100 ml with de-ionized water in a measuring flask. Phosphorus was determined using an Induced Coupled Plasma spectrophotometer ICPAES Jobin Yvon J4 185 spectrometer.

Preparation of crosslinked carboxylated chitin [30]

Crosslinking of chitin

5g of chitin was crosslinked using epichlorohydrin (100ml) under reflux for 3hr. The crosslinked chitin was filtered, washed with ethanol and water, and finally vacuum dried at 65°C for 12 hr.

Crosslinked oxy-chitin

Crosslinked chitin (5g) was mixed with 100 ml of aqueous 10% $NaIO_4$ solution. The mixture was stirred gently at room temperature for 24 hr. The product was further treated with 50 ml of 0.4 M sodium chlorite solution in 2M acetic acid at room temperature for 48 hr. The produced oxy-chitin was thoroughly washed with water and left to air dry [31].

Infrared spectroscopy

Infrared spectra of chitin and its derivatives were obtained by using JASCO FTIR 800E spectrometer. The samples were measured using the KBr disc technique.

Adsorption of heavy metal ions

The phosphorylated and carboxylated chitin derivatives (0.2gm) were stirred with 25 ml of the aqueous solution of the metal chlorides of nickel, magnesium, lead and zinc. The suspension was filtered and the metal ions were determined in the filtrate using ICP-AES Jobin Yvon J4 185 spectrometer. The pH value was adjusted using 0.01 N NaOH solutions.

RESULTS AND DISCUSSION

FTIR spectra of chitin and its derivatives

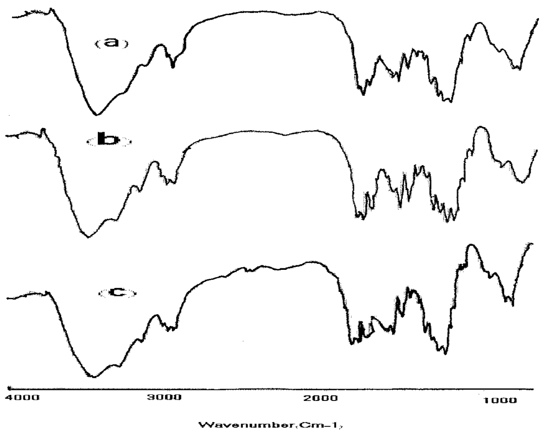
Acid treatment can remove residual calcium carbonate and other containments present in chitin and thus increased the porosity of chitin and make the penetration of chemicals easier during the reaction. Acid treatment could also cause degradation of chitin chain and consequently increased the number of hydroxyl end groups available for the phosphorylation. On the other hand, treatment with alkali causes swelling and decrease of crystallinity of chitin as shown in table (1) and interrupts the hydrogen bonding between chains resulting in increasing the accessible hydroxyl groups for reaction. Acid treatment of chitin increased the reactivity towards phosphorylation more than the alkali treatment. This may be due to the increase of the number of hydroxyl end groups due to the acid treatment as mentioned above. FTIR spectra of acid –treated, alkali- treated, and untreated chitin is shown in figure (1). The figure shows a decrease in the relative absorbance of the ether linkage band in case of acid treatment due to cleavage of the ether bonds between chitin units and formation of more hydroxyl groups and appearance of O-H bending bands. Due to phosphorylation of chitin a new bands appeared at 1200 and 980 Cm^{-1} which are characteristic to C-O-P.

From Table (1), it is clear that the relative absorbance (intensity of any band/intensity of band at 1325 Cm^{-1}) [14, 31] of acid treated chitin is higher than untreated and that of alkali treated chitin due to the increase of the end group of degraded chitin. On the other hand, the relative absorbance of CH_2 group of alkali treated was higher than that in case of untreated and acid treated chitin due to the dissolution of protein and $CaCO_3$ in chitin. On the other hand, the mercerization depth (ratio of band intensity at 1375 to band intensity at 1325) [32] of alkali treated chitin is higher than in case of treated chitin with acid. This can be confirmed by the higher crystallinity index (ratio of band intensity at 1425 Cm^{-1} to band intensity at 900 Cm^{-1}) of acid treated chitin than untreated and alkali treated chitin.

Figure (1) shows the infrared spectra of chitin, acid treated chitin and alkali treated chitin. The bands at 3264 and 3106 Cm^{-1} are characteristic to vibrational mode of NH amide (intramolecular hydrogen bonding C=O-NH and H-bonded of NH group) [33].

Table (1): The values of some properties of chitin which calculated from the infrared spectra

Materials	Acetyl content %	Mercerization depth	Crystallinity index	Relative absorbance of groups		
				A1115/A1325	A1650/A1325	A3110/A1325
chitin	98	1.33	1.10	1.76	1.1	1.3
chitin treated with acid	62	1.26	1.2	1.56	1.6	0.75
chitin treated with soda	55	1.51	1.01	1.61	1.5	0.66



Figure(1) FTIR spectra of chitin (a) ,chitin treated with acid (b) and chitin treated with soda (c).

Generally, the incorporated phosphate groups in phosphorylated treated chitin are higher than that in case of phosphorylated untreated chitin (Table 2). This can be attributed to that; acid removes residual $CaCO_3$ and other contaminated materials present in chitin. This treatment increases the porosity of chitin which enhances the penetration of chemicals through chitin. Also, acid increases the degradation of C-O-C between the chitin chains causing an increase in the end groups of chitin chain causing an increase in the reactivity of chitin toward phosphorylation process. On the other hand, treatment of chitin with alkali increases the swelling of chitin chains and consequently the crystallinity index of alkali treated chitin decreases and this increase the phosphorylation of chitin. Phosphorylation of acid treated chitin is higher than alkali treated chitin. This can be explained by increasing of chitin degradation by acid which increases the end groups of chitin chains.

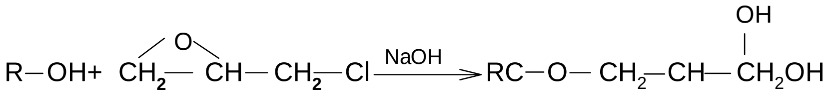
Table (2): Phosphate groups incorporated in phosphorylated of untreated and treated chitin with acid or alkali

Materials	Phosphate group (microgram/gm)
Untreated chitin	40
Acid treated chitin	88
Alkali treated chitin	80

Chitin incorporated with different functional groups

Incorporation of different functional groups e.g. phosphate and carboxylic groups onto chitin was carried out. Also chitin was crosslinked with epichlorohydrine to improve its efficiency toward phosphorylation and to improve its efficiency toward metal ion uptake.

Table (3) shows that, the incorporated phosphate group onto chitin increased by acid treatment and crosslinked chitin. This is indicated by the calculated relative absorbance of C-O-P of incorporated phosphate group onto chitin. It was found that the phosphate crosslinked chitin has higher efficiency toward phosphorylation than treatment of chitin with acid. This is attributed to that, the crosslinking increased OH groups of chitin and increased the extent of phosphorylation.



$$R{-}OH + \underset{\text{O}}{CH_2{-}CH}{-}CH_2{-}Cl \xrightarrow{NaOH} RC{-}O{-}CH_2{-}\overset{\text{OH}}{\overset{|}{CH}}{-}CH_2OH$$

Chitin Epichlorohydrine

Table (3): The relative absorbance of different derivatives of chitin

Material	Relative absorbance of groups						Acetyl content %	Degradation
	C-O-P	COOH	CH_2	$NHCOCH_3$	OH	NH_2		
chitin	---	---	1.20	1.40	1.20	1.10	98	1.30
phosphorylated chitin.	1.20	---	1.11	1.33	1.28	1.83	60	122
phosphorylated chitin treated with acid	1.31	---	1.25	1.30	1.28	1.30	50	1.18
carboxylated chitin	---	1.41	1.34	---	1.26	1.40	54	1.20
Phosphorylated crosslinked chitin treated with acid	1.43	---	1.40	1.20	1.32	1.42	56	1.15

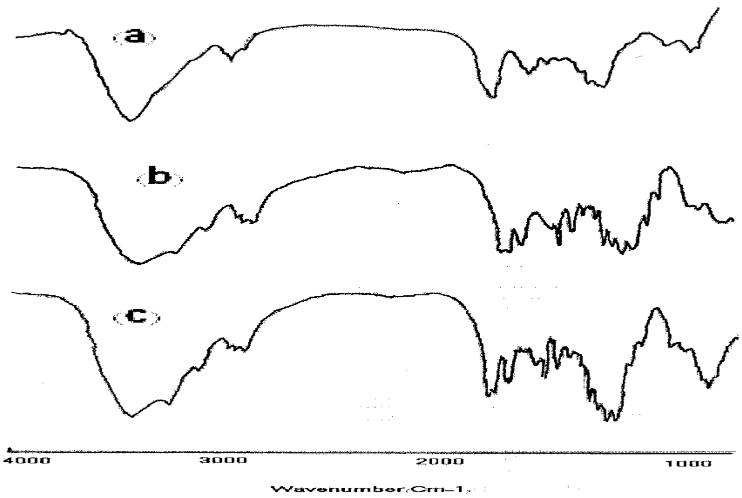


Fig (2): FTIR of phosphorylated chitin (a), phosphorylated crosslinked chitin treated with acid (b) and phosphorylated chitin treated with soda (c).

Also the crosslinked acid treated chitin is more active toward phosphorylation than the crosslinked untreated chitin. This is due to acid treatment of chitin degraded the chitin chains and thus increasing the end groups of chains beside the crosslinking. On the other hand the relative absorbance of band at 1200 Cm^{-1} which attributed to C-O-P band of phosphorylated acid treated chitin is higher than that of phosphorylated untreated chitin (Figure 2). From infrared spectra it is shown that the acetyl percent is decreased by acid, crosslinking, carboxylation and phosphorylated chitin. This is due to that, during the treatment process of chitin, the acetyl amine groups will be hydrolysed .Due to this, the relative absorbance of amino group at 3120 Cm^{-1} increased by this treatment.

Figures 3 (a, b) show a decrease in the relative absorbance of the ether linkage band in case of phosphorylated crosslinked chitin and phosphorylation of crosslinked (chitin treated with acid) due to cleavage of the ether bonds between chitin units and formation of more hydroxyl groups and appearance of O-H bending bands. In case of carboxylated chitin Figure (3c) shows a clear increase in the carboxyl group absorption bands at about 1715Cm^{-1} and 1690 Cm^{-1} due to the introduction of the COOH group.

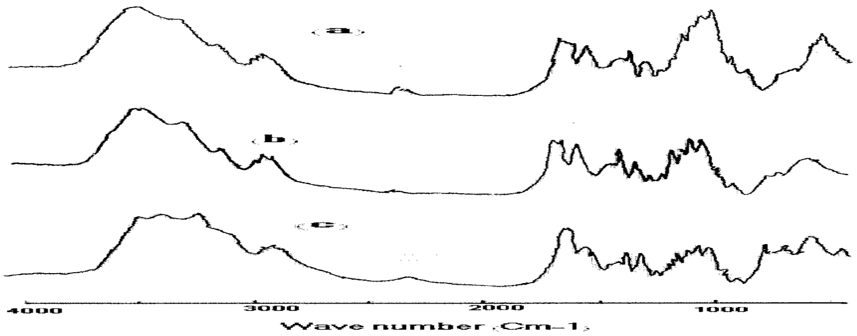


Fig (3): FTIR of phosphorylation of crosslinked chitin (a), phosphorylated crosslinked acid treated chitin (b) and carboxylated chitin (c)

Figure (4a) shows a decrease in the relative absorbance of the ether linkage band in case of crosslinked chitin treated with soda due to cleavage of the ether bonds between chitin units and formation of more hydroxyl groups and appearance of O-H bending bands. Due to phosphorylation of crosslinked chitin treated with soda**,** new bands appeared at 1200 and 980 Cm^{-1} which is attributed to C-O-P.

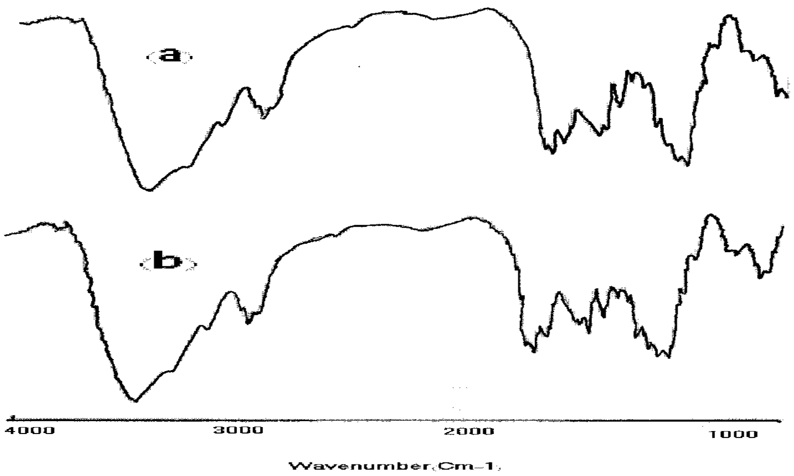
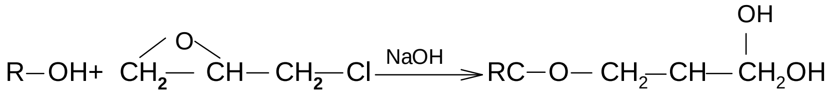


Fig (4): FTIR of crosslinked chitin treated with soda (a) and phosphorylated crosslinked chitin treated with soda (b)

Effect of crosslinking of phosphorylated chitin on their ion exchange capacity

Crosslinking of chitin is usually carried out to avoid its dissolution in water in case of its modification with hydrophilic groups such as phosphate. The effect of crosslinking of phosphorylated chitin on their ion exchange capacity toward some heavy metal ions (at 20µg) is shown in Figures (5, 6). As shown in the Figure, the adsorption of the heavy metal ions is generally higher for phosphorylated chitin (treated with acid) than that treated with alkali. This could be attributed to the presence of higher phosphorus content of phosphorylated chitin (treated with acid). Although crosslinking using epichlorohydrine reduces the number of hydroxyl groups but it adds news hydroxyl groups that have larger ability for adsorption due to their presence onto the introduced ethyl side chain (as shown in the following equation).



$R{-}OH + CH_2{-}CH{-}CH_2{-}Cl \xrightarrow{NaOH} RC{-}O{-}CH_2{-}CH{-}CH_2OH$

Chitin Epichlorohydrine

From Table (4), it is clear that the phosphorylated acid treated chitin has the higher affinity toward metal ions uptake due to its higher incorporated phosphate groups, on the other hand, treatment of chitin with acid eliminated the pigments and traces protein formed in chitin, thus increasing the porosity of chitin causing an increase in the penetration of chemicals through chitin chains and consequently the contact between phosphorylated acid treated chitin and metal ions increases.

From Table (4), it is clear that Mg ion is more adsorbed by resin than the others. In contrast Ni is the lowest metal ions adsorped by resin. This is depending on the electron negativity and radius of the ions. On the other hand, the phosphorylated alkali treated chitin has a higher metal ions uptake more than untreated one.

Table (4): Metal ions uptake (µ mole/ gm) by Phosphorylated treated chitin

Material	Metal ions uptake µ mole/ gm				
	Mg	Ni	Zn	Pb	Phosphate groups
Phosphorylated chitin	27.82	0.43	31.24	11	60
Phosphorylated acid treated chitin	38.5	2.60	32	11.74	78
phosphorylated alkali treated chitin	35	1.20	31.62	11.50	70

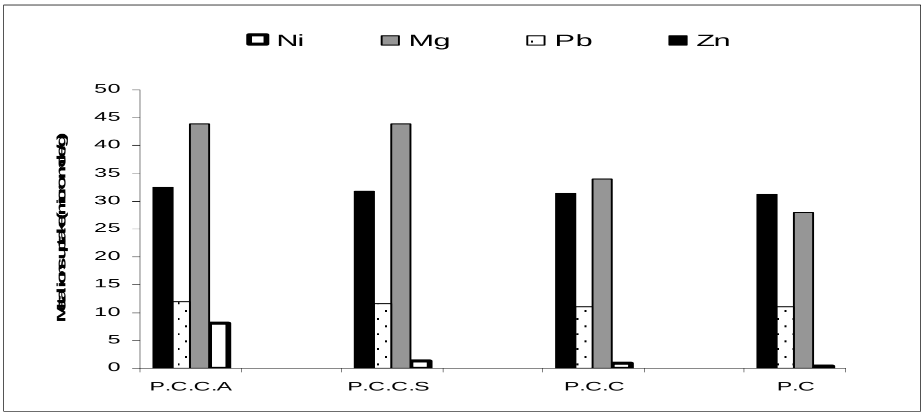


Figure (5): Effect of different treatment of chitin on their metal ions uptake capacity, where, P.C.C.A is considered as phosphorylated crosslinked chitin treated with acid, P.C.C.S is phosphorylated crosslinked chitin treated with soda, C.C.P is phosphorylated crosslinked chitin, and P.C is phosphorylated chitin

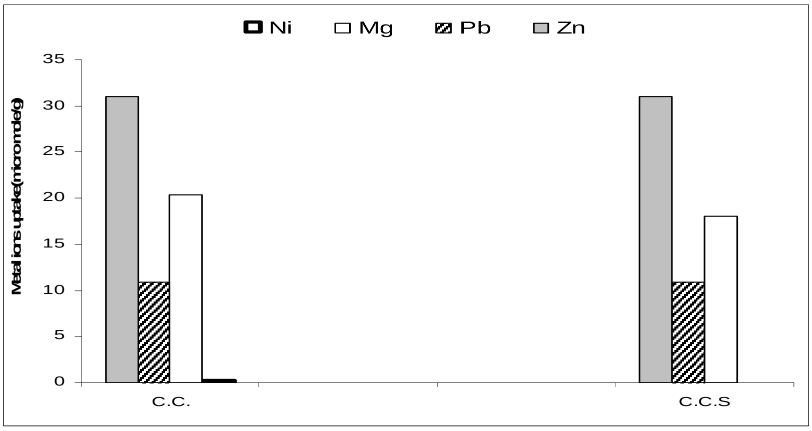


Figure (6): Effect of carboxylated chitin (C.C.) and crosslinked chitin treated with soda (C.C.S.) on their metal ions uptake capacity

Effect of crosslinking

Table (5) shows the Metal ions uptake (µ mole/ gm) by phosphorylated chitin, phosphorylated crosslinked chitin, phosphorylated crosslinked acid treated chitin and phosphorylated crosslinked alkali treated chitin. Crosslinking using epichlorohydrine reduces the number of hydroxyl groups but it adds new hydroxyl groups which have larger ability for adsorption due to their presence onto the introduced ethyl side chain. As shown in table the phosphorylated crosslinked acid treated chitin has a higher metal ions uptake than the other prepared ions exchangers.

Also in Figures (7, 8) the adsorption of heavy metal ions in case of phosphorylated crosslinked chitin (treated with acid or alkali) is generally higher than that of phosphorylated crosslinked chitin, phosphorylated chitin (in absence of crosslinker), carboxylated chitin, and chitin (treated with soda) in presence of crosslinker respectively. There are different factors affect the adsorption of heavy metal ions onto different functional groups such as charge of metal ion, its atomic radius, and softness of its charge. The charge of the metal ion is an important factor.

Table (5): Metal ions uptake (µ mole/ gm) by Phosphorylated chitin, Phosphorylated crosslinked chitin, Phosphorylated crosslinked acid treated chitin and Phosphorylated crosslinked alkali treated chitin

Material	Metal ions uptake µ mole/ gm				
	Mg	Ni	Zn	Pb	Phosphate groups
Phosphorylated chitin	27.82	0.43	31.24	11	60
Phosphorylated crosslinked chitin	33.94	0.96	31.49	11.07	66
Phosphorylated crosslinked acid treated chitin	43.97	8.16	32.5	11.94	90
Phosphorylated crosslinked alkali treated chitin	43.87	1.29	31.74	11.66	84

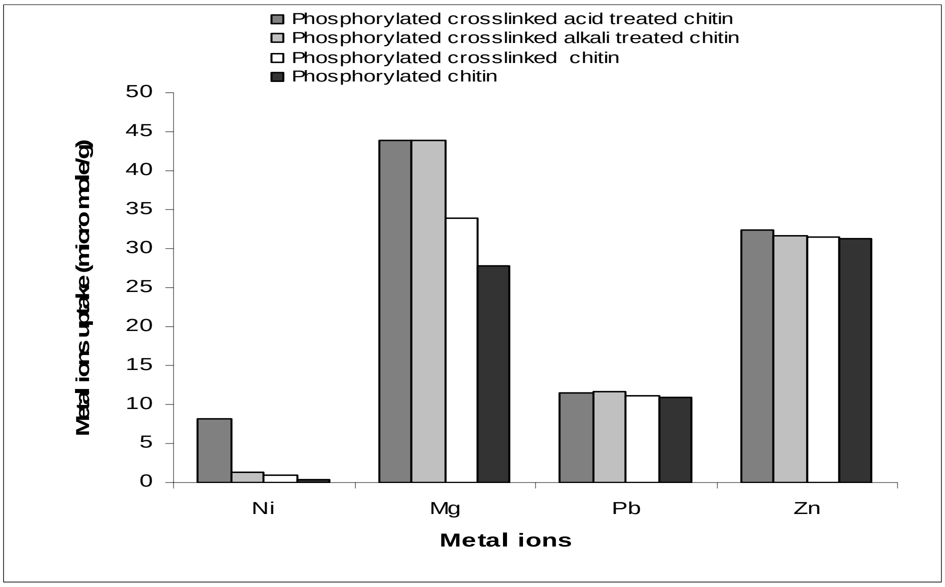


Figure (7): Effect of crosslinking of phosphorylated chitin on their metal Ions uptake capacity

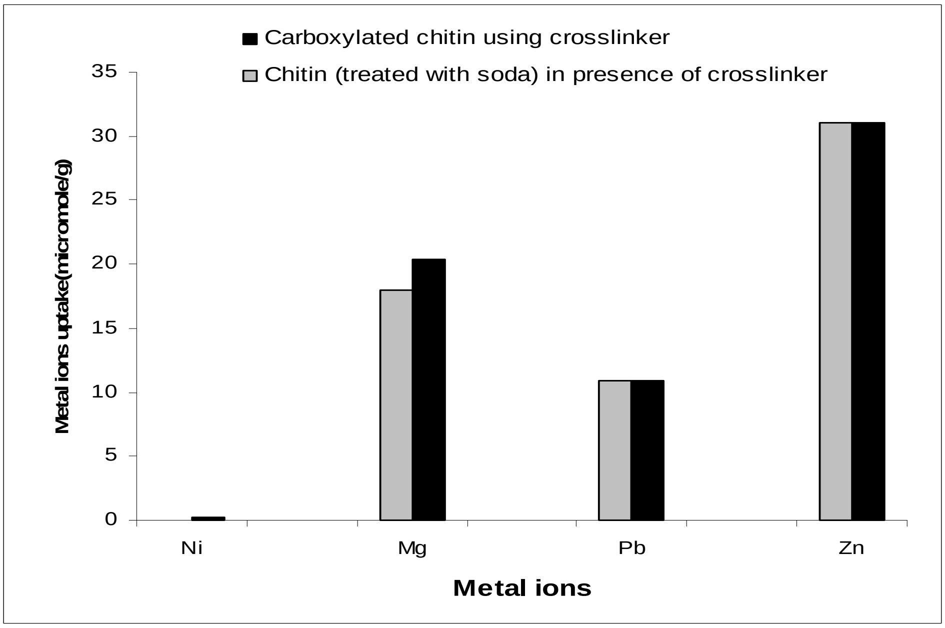


Figure (8): Effect of treatment of chitin (without phosphorylation) on its metal ions uptake capacity

CONCLUSION

Acid pretreatment of chitin was more efficient in increasing its reactivity toward phosphorylation than alkali pretreatment. Chemical modifications of chitin by phosphorylation, crosslinking and carboxylation increased its capability toward heavy metal ions removal. Also, Phosphorylated crosslinked chitin treated with acid gave the best results.

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