

## Evaluation and Characterization of Magnetic Carboxymethyl Chitosan Nanocomposite for Removal of Zinc and Lead from Waste-water

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**Abstract:** The human and animal health is jeopardized by water pollutants such as Zinc and lead which are considered globally attention. Herein magnetic carboxymethylchitosan nanocomposites were synthesized for zinc and lead removal from industrial waste-water. The particles sizes were varied according to concentration and pH. The transition electron microscope (TEM) and zeta seizer were employed for nanocomposites characterization. Also, the adsorption of Zinc and Lead on nanocomposite from waste-water were evaluated by atomic absorption. The results clearly demonstrated that, the nanocomposites have size in the range of 30-100nm, and maximum adsorption of lead, and zinc were 20.4mg/g, & 36.6mg/g respectively.

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### 1. Introduction

Heavy metals such as lead (Pb) and zinc (Zn) have fetal effects on the life creatures. There are many approaches for waste water treatment such as physical, biological and chemical [1-5]. One of the best technological approaches in the field of waste water treatment is chemical methods via using natural polymers, metal polymers and chemical additives. The using of natural polymers are a promising tools in industrial waste-water treatment. One of the best natural polymers is chitosan which is degradable, safe, has antibacterial effects, and inexpensive which has been introduced successfully in many applications such as drug delivery, tissue engineering, surface treatment and heavy metal removal [5]. Chitin extracted from crustacean shells [6] and simply deacetylated to chitosan and carboxymethylated to carboxymethylchitosan [7], but the adsorption of heavy metals by chitosan derivatives are considered time consuming with limited capacity [1,8]. The carboxymethylchitosan nanocomposites have unambiguous effect on heavy metals removal from waste water [9-10]. Magnetic nanoparticles (MNPs) have unique physical and chemical properties and have been successfully introduced in many applications such as drug delivery, [11] cancer therapy[12] imaging, dyes, catalysis[13] and waste-water treatment. Magnetic nanoparticles MNPs are synthesized by co-precipitation, spray co-precipitation[14], sol gel [15], thermal decomposition[16] and electro chemical methods.

In this investigation we developed simple, inexpensive, fast, and safe method for removal of

Zn and Pb from industrial waste water. MNPs were prepared by chemical co-precipitation method and carboxymethyl chitosan have been synthesized by carboxymethylation. Additionally, the adsorptions of Zn and Pb on magnetic nanocomposites were evaluated by atomic absorption. The magnetic carboxymethylchitosan nanocomposites were characterized by (TEM) and zeta seizer.

### 2. Materials and Methods

#### 2.1. Chemicals.

Ferrous chloride (FeCl<sub>2</sub>, 98%), ferric chloride (FeCl<sub>3</sub>, 98%), chitosan, cyanamide, and monochloroacetic acid were provided by Sigma Aldrich, Chemie GmbH (Munich, Germany). Hydrochloric acid (HCl), Nitric acid (HNO<sub>3</sub>), isopropanol and sodium hydroxide were provided by El Gomhoria Co., Cairo Egypt. Double deionized distilled water (DDI) with a resistivity of 18MΩcm were obtained from our mille pore unite Milli-Q™ system (Direct-Q 3, Model ZRQS0P0WW, Millipore Corporation, Billerica, MA) with a resistivity of 18 MΩcm. All purchased Chemicals were used without additional purification.

#### 2.2. Synthesis of magnetic nanoparticles (MNPs)

(MNPs) were prepared by chemical co-precipitation method. Briefly, 200 ml of (DDI) was bubbled by nitrogen gas for 30 minutes then 5.2gm of FeCl<sub>3</sub>, 2gm of FeCl<sub>2</sub> were dissolved by mechanical stirring under protection of the nitrogen gas, 1.5M NaOH solution was added drop wise on to the above mixture under vigorous stirring till

black precipitate of magnetic nanoparticles is formed at pH 8 then the stirring is stopped, after settling of nanoparticles the precipitate is isolated via external magnetic field of 6000G the supernatant is decanted to obtain the pure and neutral products, the precipitate were rinsed with DDI water 3 times. Different concentrations of  $\text{FeCl}_3$  with  $\text{FeCl}_2$  and reaction pH were used as tabulated in table 1.

**Table (1):** Concentrations of ferric chloride ( $\text{FeCl}_3$ ) and ferrous chloride ( $\text{FeCl}_2$ ) and pH values of reaction

Samples	$\text{FeCl}_3$	$\text{FeCl}_2$	pH
1	0.02	0.01	8
2	0.01	0.05	8
3	0.2	0.1	8
4	0.2	0.1	9.5
5	0.2	0.1	11

### 2.3. Synthesis of carboxymethyl chitosan (CMCh).

Chitosan (10 g) was suspended in 20ml 50 % NaOH solution and kept at  $-20^\circ\text{C}$  for 16 hrs. The frozen alkali chitosan was transferred to 2-propanol (100 mL), and (20 ml) monochloroacetic acid isopropanol solution (1:1 wt/wt) was added drop wise to the suspension with mechanical stirring at room temperature for 2 hrs, and then heat was applied to bring the reaction mixture to a temperature of  $60^\circ\text{C}$  for another 6 hrs. The solid product was then filtered, resuspended in 150mL of methanol and neutralized with glacial acetic acid. The product was washed with 80% ethanol till the washing alcohol produced became chloride free. The product was vacuum dried at room temperature.

### 2.4. Synthesis of Magnetic carboxymethyl chitosan nanoparticles (MCMCh NPs)

(MCMCh NPs) were prepared by adding 100 mg of  $\text{Fe}_3\text{O}_4$  nanoparticles to 2 ml of buffer A (0.003 M phosphate, pH 6, 0.1 M NaCl), and mix with 0.5 ml of cyanamide solution ( $0.025 \text{ g ml}^{-1}$  in buffer A). Then, the reaction mixture was sonicated for 10 min via propb sonicator (Model GM 2200, Bandelin Electronic, Berlin, Germany). Finally, 2.5 ml of carboxymethyl chitosan solution ( $50 \text{ mg ml}^{-1}$  in buffer A) was added and the reaction mixture was sonicated for 60 min. The carboxymethyl chitosan-bound  $\text{Fe}_3\text{O}_4$  nanoparticles were recovered from the reaction mixture by placing the bottle on a permanent magnet with a surface magnetization of 6000 G. The MNPs were settled within 1–2 min and then washed with water and ethanol. NaCl was used for

the flocculation of magnetic nanoparticles to accelerate the magnetic separation.

## 3. Characterization of Nanocomposites.

### 3.1. Transmission electron microscopy

The size and morphology of MNPs and MCMCh NPs samples were studied using Transmission electron microscopy TEM (JEOL Model JEM-1200EX, Japan) with accelerating voltage in the range of 40-120 kV and magnification ranged between 100-300kx.. Briefly, 50  $\mu\text{L}$  of the samples were dropped on TEM grids, and dried for two hours in grid box before imaging.

### 3.2. Particle size analyzer

Mean particle size diameter and polydispersity index of the MNPs, and MCMCh NPs were measured in solution directly after synthesis, using photo correlation spectroscopy (Malvern Instruments Ltd, Worcestershire, UK) (Malvern ZEN2600 Zetasizer Nano Z). Briefly, two mL of MNPs and MCMCh NPs were mounted on quartz cells and all measurements were taken at  $90^\circ$  to the incident light source. Additionally, for Zeta Potential Measurements 5ml of MNPs, and MCMCh NPs were placed in 50 ml DDI at ionic strength of  $2 \times 10^{-2}$  M NaCl then pH was adjusted between 3 and 11. The samples were shaken for 30 minutes. After shaking, the equilibrium pH was recorded and the zeta potential of the mineral particles was measured. A zeta potential was used to determine the electro kinetic surface potential of MCMCh NPs. The samples were diluted to 2.5 mM in water, and the zeta potential was analyzed at  $25^\circ\text{C}$ .

### 3.4. The capacity of heavy metal removal

The capacities of lead and Zinc removal by (MCMCh NPs) samples were measured by using atomic absorption spectrophotometer (Z-5000, Hitachi, Japan). Briefly, the solution was processed at  $120^\circ\text{C}$  two hours with Zn, Pb lamp. The percentage was calculated as follows:

$$\% \text{ metals} = [(W_t - W_s) / W_t] \times 100.$$

Where  $W_t$  is the initial (Zn or Pb) content in the water and  $W_s$  is the (Zn, or Pb) content in the water after treatment with nanoparticles the data presented in fig. 2.

## 4. Results and Discussion.

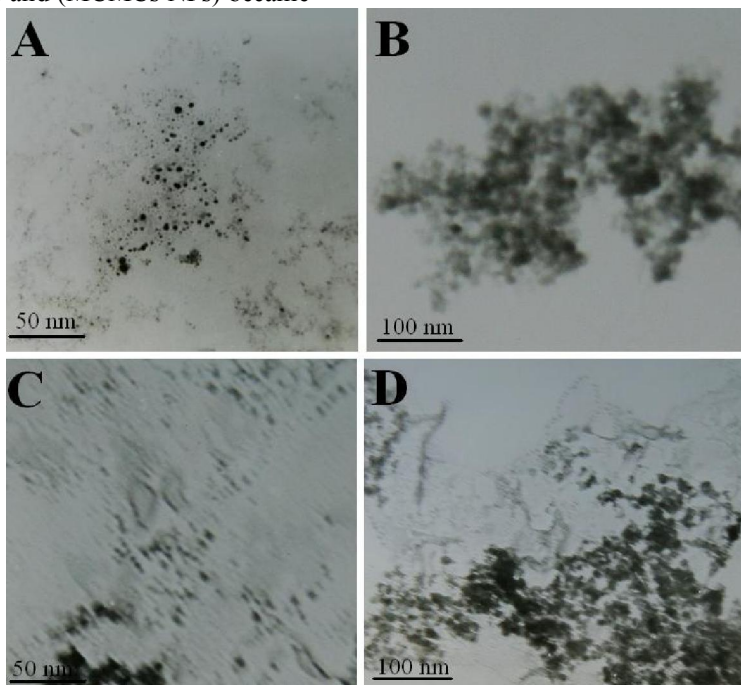
### 4.1. Transmission electron microscopy.

The size and morphology of the (MNPs) and (MCMCh NPs) were studied using transmission electron microscopy TEM. Particle size was reported as the mean diameters as shown in figure

1 which were selected randomly. MNPs were in a spherical form with a well controlled particle size which subsequently is preparation conditions dependent. Also, MCMCh NPs were in a spherical form with a well distributed size and shape with lack of aggregation. The particles size distribution of (MNPs) and (MCMCh NPs) became

narrower with an average particle size in the range of 10-60nm and 30-80 nm respectively.

The result clearly demonstrated that, the particle size and morphology are in agreements with the preparation methods as reported elsewhere [13].



**Fig (1):** TEM of (A,C) (MNPs), &, (B,D) (MCMCh NPs).

#### 4.2. Particle size analyzer

The particle size and granulometric for both of (MNPs) ,and (MCMCh NPs), have been recorded in table 2. The data illustrated that the size of the (MNPs and (MCMCh NPs) having size in the range of 15-50 nm and 27-78nm respectively. The results

revealed that, the presence of the synthesized nanostructures with mono size distribution as tabulated in table 2). The size distribution was in concurrence with other nanosystems described before. Also, the results were in agreement with the TEM

**Table (2):** The Particle size distribution of the (MNPs) and (MCMCh NPs).using Malvern ZEN2600 Zetasizer

Sample	(MNPs)	Polydispersity	(MCMCh NPs)	Polydispersity
1	15	0.1	27	0.02
2	28	0.02	42	0.090
3	47	0.04	78	0.31
4	42	0.03	67	0.80
5	36	0.03	59	0.68

#### 4.3. Zeta potential

The stability of the obtained nanoparticles has been determined by Zeta potential measurements that indicate the tendency of the particles to associate or sediments. The results revealed that the Zeta potential distribution for (MCMCh NPs) ranged between +35 and -38mV which is a mono modal one. Also the (MCMCh NPs) were positively charged at pH 3 and 5 while they were negatively charged at pH7,9 and 11. The presence

of an electric charge on the particles surfaces, make particles interact across long distances via electrostatic repulsion forces. Additionally, the particles stability is electric charges dependent. The results clearly indicated that, the particles with their electrical charges are stable enough with fewer tendencies to aggregation which subsequently are in agreements with TEM results and preparation

conditions. Also, the results are in agreements with the preparation methods as reported elsewhere.

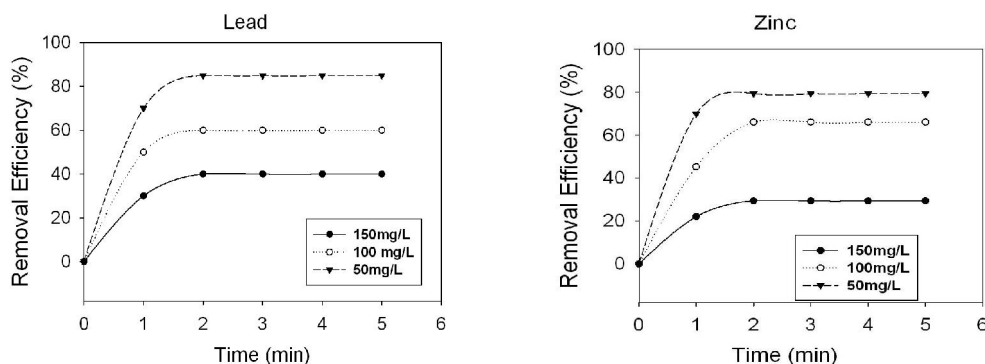
**Table (3)** The zetapotential of the (MCMCh NPs) using Malvern Instruments

Samples	pH	Zeta potential mV
1	3	35±2
2	5	28±1
3	7	-10±0.5
4	9	-21±0.8
5	11	-38.1±3

#### 4.4. The capacity of heavy metal removal

The efficiency removal of Zn and Pb from industrial waste water were examined by atomic absorption. Briefly, 20mL of 50,100 and 150 mg/L lead nitrate/ and or zinc acetate solution and 5g/L MCMCh NPs were mixed separately at pH 2.5, the removal efficacy of Pb and Zn and plotted against time as figured 2 . It can be seen that the rate of Pb

and Zn, absorbtion were initially steady increased from 0 up to 80% through duration experiment after 6 minute. The results demonstrated that, the removal Pb increased steady from 25-65% after 1 minute with varying concentration of MCMCh NPs from 50-150mg respectively and 38-80% at after 2 minute then it became constant after 3 minute. Also, the removal Zn increased steady from 18-65% after 1 minute with varying concentration of MCMCh NPs from 50-150mg respectively and 25-78% at after 2 minute then it became constant after 3 minute. The results clearly demonstrated that the removal efficiency of Zn and Pb were higher at the first minute of experiments until reach to equilibrium constant after 3 minute due to the solution may saturated after 3 minute or the MCMCh NPs may saturated with Zn and Pb which hindered their absorbance. The results are in agreements with data reported elsewhere [10]



**Figure (2):** The capacity of heavy metal removal for lead and zinc

#### 5. Conclusion

The (MNPs) and (MCMCs NPs) having size in the range of 15-50 nm and 27-78 nm with mono size distribution .The particle in a spherical shape and the size depend on the varying amount of precursor and pH. The zeta potential show the particle are coated with negatively charged ranged from +35 and – 38mV which strong enough to hinder aggregation. The nanocomposites have high capacity for lead and zinc removal from industrial waste water and the capacity ranged from 71-87%.

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