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New modified chitosan composites and nanocomposites for different applications

Taghreed H. Abdalla^{1,*}, Abir S. Nasr¹, Ghada Bassiuni², David R. Harding³, Nadia G. Kandile¹

¹ Chemistry Department, Faculty of Women for Art, Science and Education, Ain Shams University, Heliopolis Post Cod. No. 11757, Cairo, Egypt.

² Chemistry Department, Faculty of Engineering, Ain Shams University, Cairo, Egypt.

³ Chemistry Institute of Fundamental Science, Chemistry, Massey University, New Zealand.

Abstract

The present work focuses on the preparation of chitosan composite and chitosan nanocomposite derivatives for different applications. Chitosan was modified with bentonite or nano-bentonite to give chitosan composite and nanocomposite derivatives hydrogels I and II respectively, however chemical modification of chitosan with isonicotinic aldehyde via Schiff base formation in presence of bentonite or nanobentonite yielded chitosan composite and nanocomposite derivative hydrogels IIn and IIn respectively. The prepared hydrogels were characterized by Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (X-Ray), Thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC), Scanning electron microscopy (SEM), and swelling behavior. Adsorption studies for removal of heavy metal ions from aqueous media and the biological activity for the new hydrogels were studied. Results of evaluation of the prepared chitosan derivatives hydrogel for metal ions uptake showed that the maximum adsorption capacity amounted to 68 and 22 mg/l and the highest efficiency for adsorption of cobalt and mercuric ions from aqueous solution by hydrogel IIn at 10 h (93.2%) and (97.8%) respectively, whereas the adsorption capacity of hydrogel IIn increased with the increase of the initial concentration of heavy metals ions ranging from 0.4 to 1 g/l. However, modified chitosan derivative hydrogels I and IIn showed remarkable MIC and MBC towards Gram-positive (*B. subtilis*) (19.5, 38) µg/ml compared to the standard antibiotic Ciprofloxacin (19, 38) µg/ml respectively.

Keywords: Chitosan; Isonicotinic aldehyde; Bentonite; Nano-bentonite.

1. Introduction

Water is one of the most important needs for human and living organisms. Pollution of water resulted of various toxic contaminants such as heavy metals,

*Corresponding author: Taghreed H. Abdalla, Chemistry Department, Faculty of Women, Ain Shams University, Heliopolis 11757, Cairo, Egypt.

E-mail: [taghreedhassan41@gmail.com](mailto>taghreedhassan41@gmail.com)

organics, and oil, which become one of the world's most impactful environmental challenges [1]. Most heavy metal ions are highly toxic, non-degradable and have a tendency to bioaccumulate and cause dangerous impact to human health [2-4]. Adsorption methods are the most widely techniques used for removing metal ions and organic compounds from industrial effluents due to its simple use, cheap and the presence of different kinds of adsorbents [5-8]. In the recent years, widely various adsorbents have been used for treatment of water as geopolymers and clay-based adsorbents [9-11], chitosans [12,13], and nano-composites [14,15]. Several nanocomposite hydrogels have been developed to improve the antibiotic treatments by producing new antimicrobial agents or formulation of available antibiotics [16]. Antibiologicals are produced in nature by soil bacteria and fungi, are chemicals which can destroy or inhibit the growth of bacteria and similar microorganisms [17,18].

Chitosan is a high molecular weight cationic polysaccharide, is prepared by deacetylation of the N-acetyl groups from second most abundant biopolymer in nature chitin which is obtained from the extraction shells of crustacean exoskeleton, insects [19,20]. Chitosan has several advantages properties such as biodegradability, environmentally friendly, non-toxicity, abundance, biological activities such as antibacterial, antitumor and antifungal [21,22]. Due to of the amine and hydroxyl groups in the chemical structure of chitosan, that make it an effective biosorbent for the removal of many pollutants and environmental protection [23,24]. Due to some undesirable properties of chitosan as its solubility in acidic media, it has a limit uses in heavy metal adsorbent. Modifications of chitosan with various organic compounds under different conditions were proceed to improve its properties especially sorption performances [25-28]. Chitosan and its nanocomposite derivatives are used in a many field that interested in the life sciences and technology such as biomedical and pharmaceutical applications [29]. Moreover, many studies have shown that the modification of chitosan via Schiff bases condensation to enhance its biological activity [30].

Bentonite or montmorillonite is a sedimentary rock with a permanent negative surface charge; this negative surface charge helps to attract the oppositely charge adsorbate molecules [31], also it has wide surface area so it can be potential adsorbent [32]. It is an inexpensive matrix and in addition to its low cost, it has several other

advantages that include its high chemical reactivity, low toxicity, high stability, its high cation exchange capacity, high adsorption and available so, it has been widely used in the field of adsorption and remove of contaminants [33-36].

Nanobentonite shows more and more homogeneity, specific surface area, a particle with small size and porous structure, more compact structure and more active absorption sites. Nanobentonite can be used as a nano-polymer filler material for nanocomposite materials [37-39].

Pyridine nucleus and their derivatives are important class of heterocyclic compounds include compounds exhibiting antimicrobial, antihypoxic activity, anti-inflammatory, and analgesic [40]. Functionalized pyridines are not only existing in a wide range of bioactive molecules, but also widely used as building blocks that can be transformed into a series of valuable structures in the preparation of ligands and functional materials [41,42].

The goal of the present work is preparation of new modified chitosan composite and nanocomposite derivatives hydrogels I, II, In and IIn to improve its physicochemical properties and increase its applications. Chitosan was modified with bentonite or nano-bentonite to give chitosan composite and nanocomposite derivatives hydrogels I and II respectively, however chemical modification of chitosan with isonicotinic aldehyde via Schiff base formation in presence of bentonite or nanobentonite yielded chitosan composite and nanocomposite derivative hydrogels In and IIn respectively. The prepared hydrogels were characterized and metal ions adsorption capacity for cobalt and mercury ions from aqueous media and biological activity towards different Gram-positive (*S. aureus & B. subtilis*) and Gram-negative (*E. coli & Proteus*) of microorganisms were evaluated.

2. Experimental

2.1. Materials

Chitosan (Cs) LMW (M.W. = 60 KDa, DD 91%) (Acros Organics), isonicotinic aldehyde (107.112 g/mol) (Alpha), bentonite (Sigma- Aldrich), nano-bentonite (Sigma-Aldrich), glacial acetic acid (60.052 g/mol) (Alpha), ethyl alcohol (46.07 g/mol) (Aldrich), dimethylsulphoxide (78.13 g/mol) (DMS) (Aldrich), and dimethylformamide (73.09 g/mol) (DMF) (Edwic).

2.2. Swelling behaviors

A. Soluble-gel fraction can be determined by weight sample of the hydrogels and heated for 1 h in 20 mL in the following: (acetic acid (99.85%), dimethyl sulphoxide, dimethyl formamide, and water). The swollen hydrogel was dried in an oven at 70 °C to get rid of the solvent [43]. the dry hydrogel gives constant weight (W_1). Calculation of the soluble and gel fraction by using the following Eq. (1, 2):

$$\text{Soluble fraction (SF \%)} = \frac{(W_0 - W_1)}{W_0} \times 100 \quad (1)$$

Where W_0 is the initial weight of hydrogel and W_1 is the weight of the oven dried hydrogel.

$$\text{Gel fraction (\%)} = 100 - \text{soluble fraction} \quad (2)$$

B. Calculation of the degree of swelling (DS) of chitosan and its modified at room temperature in different solvents (acetic acid (99.85%), dimethyl sulphoxide, dimethyl formamide, and water) by applying Eq. (3) [44, 45].

$$DS = \frac{(W_2 - W_1)}{W_1} \times 100 \quad (3)$$

Where W_1 is the weight of dry hydrogel and W_2 is the weight of swollen hydrogel.

2.3. Solubility

Chitosan composite and nanocomposite derivative hydrogels (0.1g) were immersed in different solvents (acetic acid (99.85%), dimethyl sulphoxide, dimethyl formamide, and water), and continuously shaken at room temperature and at 100 °C for 1h.

2.4. Instrumentation

FT-IR in the frequency range of 400 – 4000 cm⁻¹ (Ft-Ir Spectrometer 4100 Jasco – Japan Ultraviolet Shimadzu – 1650 Pc, X – ray diffraction using an X – ray powder diffractometer with Ni – filter and Cu K α radiation source. TGA using the instrument: SDT Q600 V20.9 Build 20. Differential scanning calorimetric (DSC) DSC131 Evo (SETARAM Inc., France. SEM, Model Quanta 250 FEG (Field Emission Gun) with accelerating voltage 30 kV Gun, FEI Company, Netherlands. The surface morphology of untreated and treated hydrogels was obtained by using scanning electron microscope (SEM) images.

2.5 Metal ions uptake study

Adsorption studies were proceeding by a concentration of 100 mg/L of hydrogel in water with stirrer. The equilibrated hydrogels were withdrawn and immersed in aqueous solution [cobalt acetate, and mercuric acetate] (0.025 g in 25 ml water) which equals 1000 mg/l at (pH 7, and 25 °C) under studied conditions. Metal ion concentration in solution can be calculated using UV-visible apparatus and the efficiency of metal ions uptake of hydrogels was calculated using Eq (4) [46].

$$F = \left[1 - \frac{C}{C_0} \right] \times 100 \quad (4)$$

Where F is the efficiency (%), C is the concentration of M⁺² in the solution after a certain time period and C₀ is the initial concentration of M⁺² in solution.

2.6. Biological activities

2.6.1. Bacterial inhibition zone activities

The disc diffusion procedure [47] was used for assessing the antibacterial activity of the hydrogels. Briefly, discs of 10 mm diameter were cut from the hydrogels. The 10mm discs of hydrogels were placed onto the surface of inoculated plates. The plates were incubated at 37 °C for 48 h. (National Research Centre, Egypt).

2.6.2. Minimum inhibition concentration and Minimum bactericidal concentration

Minimal inhibitory concentration (MIC) and minimal bactericidal concentration(MBC) of the hydrogels were evaluated according to broth tube dilution method with slide [48].

2.7. Methods

2.7.1. Synthesis of hydrogel (I)

A mixture of clear solution of chitosan (0.25g) dissolved in (39 mL) of 1% acetic acid and bentonite (1g) dispersed in (12.5 mL) distilled water was heat at 70 °C for 9 h (Table 1) [49,50]. The reaction mixture then centrifuged to remove excess bentonite. The solution was poured in petri dish, the hydrogel formed after evaporating the solvent in air at room temperature, and then washed with 1% acetic acid solution

and distilled water. Dry at room temperature, to give modified chitosan composite hydrogel (I).

2.7.2. Synthesis of hydrogel (In)

A mixture of clear solution of chitosan (0.25g) was dissolved in (39 mL) of 1% acetic acid solution and (1g) of bentonite dispersed in (12.5 mL) distilled water was left under stirring at room temperature for 2 h. Subsequently, isonicotinic aldehyde (0.57g, 0.5ml) was added dropwise in this mixture, and reflux for 23 h at 60 °C (Table 1) [51]. The reaction mixture then centrifuged to remove excess bentonite. The solution was poured in petri dish. After evaporating the solvent in air at room temperature, the hydrogel was formed and then washed using 1% acetic acid solution and distilled water. Dry the hydrogel at room temperature, to give composite hydrogel (In).

2.7.3. Synthesis of hydrogel (II)

A mixture of clear solution of chitosan (0.25 g) dissolved in (39 mL) of 1% acetic acid solution and nanobentonite (1g) dispersed in (12.5 mL) distilled water was heat at 70 °C for 9 h (Table 1) [49]. Centrifuge the produced mixture for the removal of excess nanobentonite. The solution was poured in petri dish. After evaporating the solvent in air at room temperature the hydrogel was formed and then washed using 1% acetic acid solution and distilled water. Dry the hydrogel at room temperature, to give the nanocomposite hydrogel (II).

2.7.4. Synthesis of hydrogel (IIn)

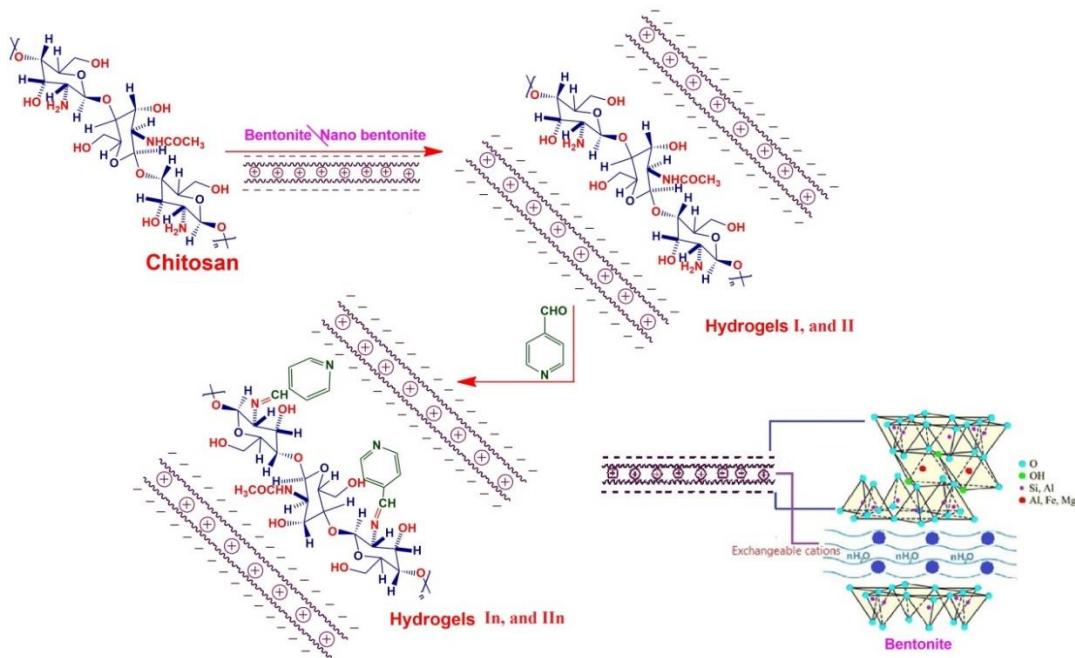
A mixture of chitosan (0.25 g) was dissolved in (39mL) of 1% acetic acid solution by stirring at room temperature until the solution became clear and nanobentonite (1g) dispersed in (12.5 mL) distilled water left under stirring at room temperature for 2 h. Isonicotinic aldehyde (0.57g, 0.5ml) was added dropwise to the reaction mixture and refluxed for 23 h at 60 °C (Table 1) [51]. The reaction mixture then centrifuged to remove excess nanobentonite. The solution was poured in petri dish, the hydrogel formed after evaporating the solvent in air at room temperature, and then washed using 1% acetic acid solution and distilled water. Dry the hydrogel at room temperature, to give the nanocomposite hydrogel (IIn).

Table 1. Compositions of the hydrogels I, In, II, and IIIn

Hydrogel code	Compositions		
I	Chitosan	Bentonite	-
In	Chitosan	Bentonite	Isonicotinic aldehyde
II	Chitosan	Nanobentonite	-
IIIn	Chitosan	Nanobentonite	isonicotinic aldehyde

3. Results and Discussion

In the current study, preparation of composite and nanocomposite hydrogels from abundant and low-cost materials such as chitosan, bentonite and nanobentonite with heterocyclic compound isonicotinic aldehyde to improve its physicochemical properties and to evaluate its applications. Chitosan was modified with bentonite or nanobentonite to give the composite and nanocomposite hydrogels I and II respectively. However, chemical modification of chitosan with isonicotinic aldehyde via Schiff base formation from the reaction of chitosan amine groups with the aldehydic groups of isonicotinic aldehyde in presence of bentonite or nanobentonite to yield chitosan composite and nanocomposite derivative hydrogels In and IIIn respectively as shown in Scheme 1.

**Scheme 1.** Synthesis of I, In, II, and IIIn hydrogels

3.1. The Swelling Behaviors

3.1.1. Soluble-gel fraction

The swelling behavior of chitosan and new hydrogels I, In, II and IIIn were characterized by studying of soluble- gel fraction for different solvents (acetic acid (99.85%), dimethyl sulphoxide, dimethyl formamide, and water) and heated for 1 h. The soluble fraction of the synthesized hydrogels showed low values in weight loss whereas gel fraction increased by decreasing soluble fraction indicated increase of the degree of polymerization as shown in Fig.1. It observed that the nanocomposite hydrogel IIIn had the highest gel fraction reached 99% using acetic acid.

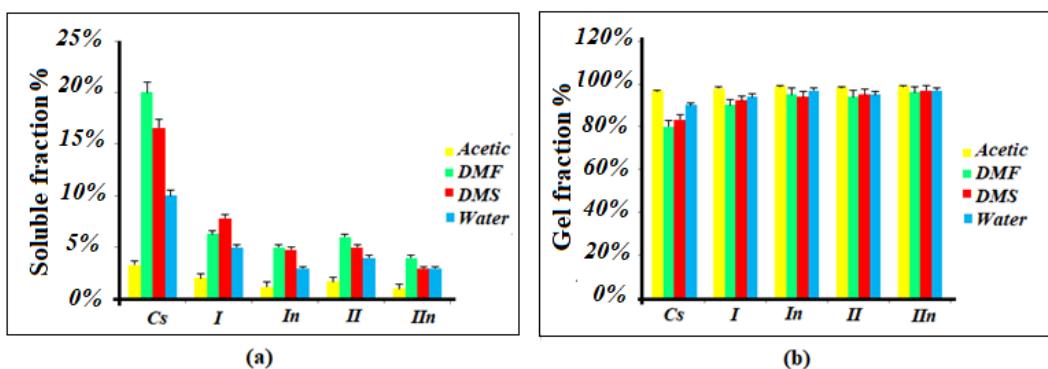


Fig. 1. (a) Soluble fraction (b) Gel fraction by heating of Cs, hydrogels I, In, II and IIIn for 1h in the different solvents

3.1.2. Solvent uptake at different solvents

The swelling behavior of chitosan and synthesized hydrogels I, In, II and II_n were determined gravimetry by studying of solvent uptake for different solvents (acetic acid (99.85%), dimethyl sulphoxide, dimethyl formamide, and water) at room temperature. The hydrogels showed high values of swelling ratio, the highest degree of swelling was observed with water for chitosan and the synthesized hydrogels due to intermolecular hydrogen bonding and the presence of high porosity in their structures [52], shown in Fig 2.

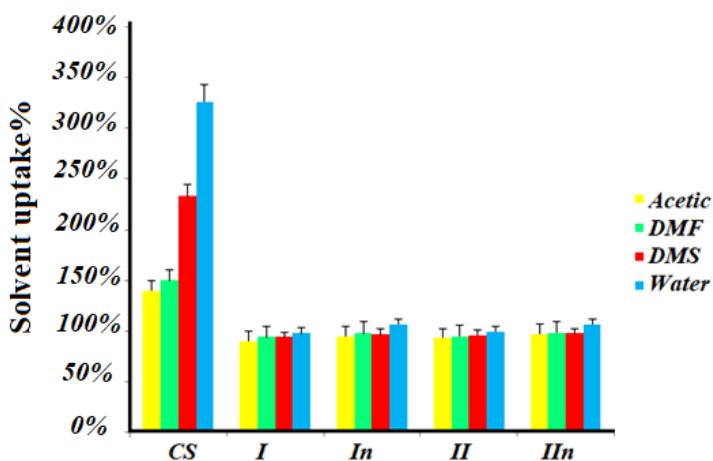


Fig. 2. Solvent uptake of Cs, hydrogels I, In, II, and II_n at room temperature in different solvents

3.2. Solubility

Chitosan is soluble in 1% glacial acetic acid solution; however, hydrogels I, In, II and II_n were insoluble in different solvents (water, acetic acid, dimethyl sulphoxide, and dimethyl formamide) at room temperature and by heating, confirmed the modification of chitosan and formation of the new modified chitosan composite and nanocomposite hydrogels.

3.3. Characterization of hydrogels

The prepared hydrogels were characterized by FTIR, X-Ray, DSC, TGA, and SEM.

3.3.1. FTIR Spectra

FTIR of chitosan (Cs) and its modified hydrogels I, In, II and II_n was shown in (Fig. 3). Chitosan exhibited a strong broad absorption at 3441 cm⁻¹ due to O-H implied

to the N-H stretch, absorption peak at 2869 cm^{-1} assigned to (C-H stretch), 1590 cm^{-1} (N-H bend), and 1149cm^{-1} (bridge-O stretch) [53]. In addition, chitosan composite and nanocomposite derivatives hydrogels spectra showed some shifts of vibration bands characteristic of the corresponding hydrogels I, In, II and IIn differ than native chitosan. The absorption bands of O-H and N-H groups corresponding to the following wave numbers 3424cm^{-1} , 3427cm^{-1} , 3424cm^{-1} , and 3425 cm^{-1} , and C-H stretch band at 2925 , 2922 , 2924 , and 2921 cm^{-1} respectively. The Si–O stretching vibration band in hydrogels I, In, II and IIn are observed at 670 , 772 , 663 , and 778cm^{-1} respectively. The characteristic band of Schiff base, showed strong stretching absorption band of imine ($\text{C}=\text{N}$) at 1606 , and 1615 cm^{-1} , for hydrogels In, and IIn respectively.

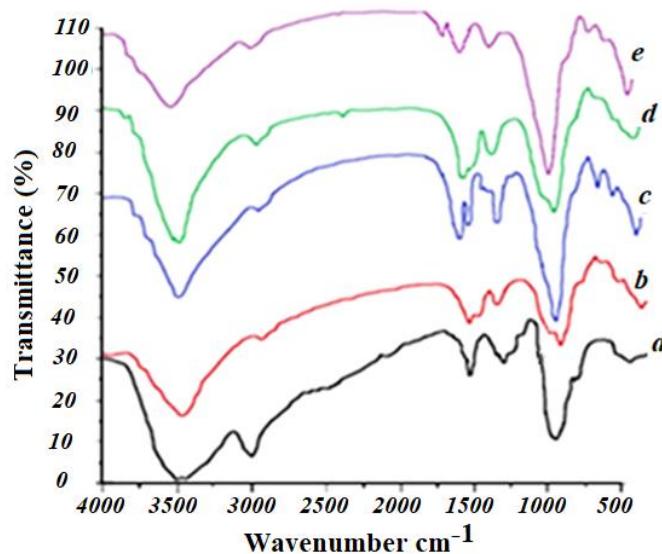


Fig. 3. FTIR spectra of (a) Cs, hydrogels (b) I, (c) In, (d) II and (e) IIn

3.3.2. X-ray diffraction

X-ray patterns of chitosan (Cs) and hydrogels I, In, II and IIn are exhibited in Fig. 4. The X-ray diffraction pattern of chitosan shows characteristic semi crystalline peaks observed at 2θ at 20^0 [54]. Hydrogels In and IIn were revealed higher crystallinity than hydrogel I and II. The peaks of hydrogels In and IIn showed reflections at different angles in their diffractograms. By comparing with chitosan, the new hydrogels showed weaker beaks than chitosan [25], which indicating lower crystallinity due to modification of chitosan with bentonite and nanobentonite and isonicotinic aldehyde.

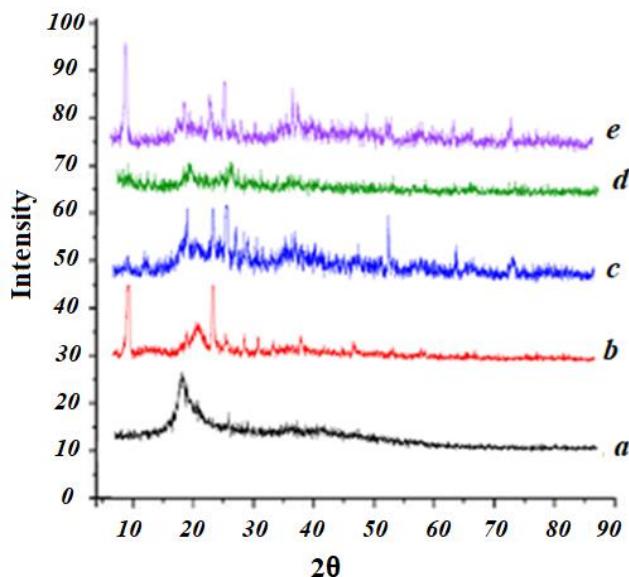


Fig. 4. X-ray diffraction of (a) Cs, hydrogels (b) I, (c) In, (d) II and (e) IIIn

3.3.3. Thermal stability

3.3.3.1. Thermogravimetric analysis (TGA)

The thermograph of chitosan, hydrogels I, In, II and IIIn displayed three steps of thermal degradation, as shown in Fig. 5.

The first step of chitosan started from 49.5 °C to 200 °C accompanied by the weight loss of 12.2%, due to the presence of moisture. Step two of degradation of 40.7% for Cs was observed between 200-400 °C referring to degradation of acetylated groups and the end loss of 12.7% at 400-900 °C due to degradation of backbone [55].

The first step of hydrogels I, In, II, and IIIn showed the weight loss 7.3% from 104 °C to 213 °C, 8.9% from 118 °C to 237 °C, 11.9% from 180 °C to 256 °C, and 6.9% from 200 °C to 288 °C respectively. The second step showed weight loss 12% from 213 °C to 378 °C for hydrogel I, 8.3% from 237 °C to 500 °C for hydrogel In, 18.9% from 256 °C to 375 °C for hydrogel II, and 7.2% from 288 °C to 550 °C for hydrogel IIIn. The third step of hydrogels I, In, II, and IIIn represented high temperature due to the degradation of backbone, which showed weight loss 12.4% from 378 °C to 1000 °C and 12.6% from 500 °C to 1000 °C respectively. These results indicated that the modified hydrogels were more thermal stability than native chitosan [56], and showed variation in weights loss at different temperature which indicated variation in residual weights at 1000 °C due to the different in the composition of each hydrogel.

Hydrogel IIIn had the highest thermal stability, due to strong interactions between the reactive groups of chitosan with isonicotinic aldehyde, and nanobentonite.

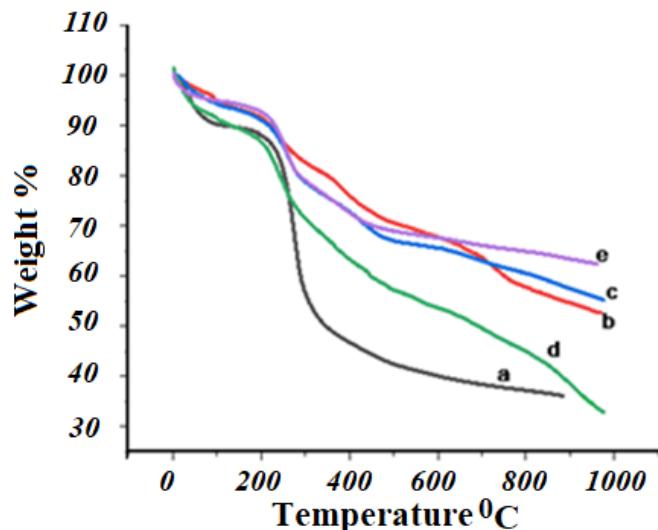


Fig. 5. TGA of (a) Cs, hydrogels (b) I, (c) In, (d) II and (e) IIIn

3.3.3.2. Differential Scanning Calorimetry (DSC)

The glass transition temperature (T_g) of chitosan at $89\text{ }^{\circ}\text{C}$, and the decomposition temperature (T_d) at $247.9\text{ }^{\circ}\text{C}$ due to the degradation of backbone [57]. The glass transition temperature (T_g) of the hydrogels I, In, II, IIIn showed at $139\text{ }^{\circ}\text{C}$, $144\text{ }^{\circ}\text{C}$, $139\text{ }^{\circ}\text{C}$, and $142\text{ }^{\circ}\text{C}$ respectively, while the decomposition temperatures of hydrogels I, In, II, and IIIn showed at $301\text{ }^{\circ}\text{C}$, $303\text{ }^{\circ}\text{C}$, $266\text{ }^{\circ}\text{C}$, and $300\text{ }^{\circ}\text{C}$ respectively, as shown in Fig. 6. The modified chitosan composite and nanocomposite hydrogels presented higher glass transition and decomposition temperatures than that of native chitosan, which increases with the formation of Schiff base and bentonite and nanobentonite content of the sample.

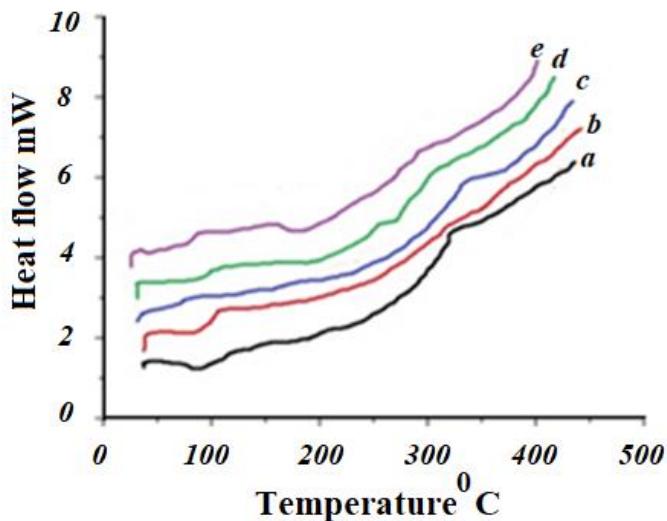


Fig. 6. DSC of (a) Cs, hydrogels (b) I, (c) In, (d) II and (e) IIIn

3.3.4. Morphological analysis

3.3.4.1. Scanning Electron Microscope

The surface morphology of chitosan and new hydrogels I, In, II, and IIIn was determined by scanning electron microscopy technique as shown Fig. 7, the surface morphology of chitosan showed rough with some clefts in the surface [25]; while the morphology of new hydrogels I, In, II and IIIn showed massifs surface of different particles sizes in the surface of hydrogel I, whereas hydrogel In showed smooth surface area of large rocks with some clefts. Large number spot rocks and small holes with some rocks in the surface of hydrogel II, and small rocks surface with straps and small caves in surface of hydrogel IIIn. SEM images of hydrogels I, In, II, and IIIn indicated that the changes in the shape and surface morphology than chitosan, due to the formation of modified chitosan composite and nanocomposite hydrogels.

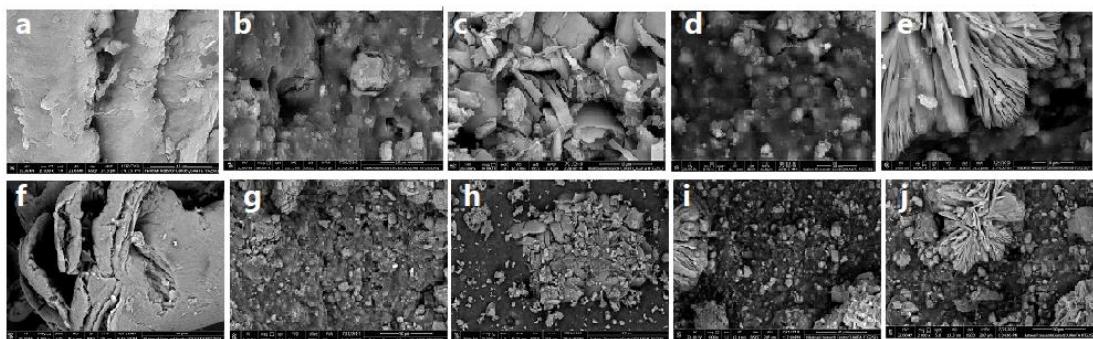


Fig. 7. SEM at 10 μ m of (a) Cs, hydrogels (b) II, (c) In, (d) II, (e) IIIn, and at 50 μ m of (f) Cs, hydrogels (g) I, (h) In, (i) II, (j) IIIn

3.4. Evaluation of the new hydrogels for different applications

3.4.1. Metal ions uptake study for the hydrogels

3.4.1.1. Effect of contact time:

Chitosan and modified hydrogels I, In, II and IIIn were evaluated for their efficiency to remove heavy metal ions such as Co^{+2} and Hg^{+2} from aqueous medium.

The results showed that the adsorption capacity values increased with increasing time of immersion of Cs and hydrogels I, I, II and IIIn, as shown in Fig. 8a [58]. The data indicated that the maximum adsorption capacity amounted to (80 ,68) mg/l and (40 ,22) mg/l, and the highest efficiency for adsorption of cobalt and mercuric ions was observed for composite hydrogels In, and IIIn at 10 h reached (92%, 93.2%) and (96%, 97.8%) respectively. These high results of the adsorption capacity due to the presence of heterocyclic moiety in isonicotinic aldehyde which have nitrogen atom carrying free lone pair of electrons thus increase the chelation of metal ions.

3.4.1.2. Effect of initial metal ions concentration

The effect of initial metal ions Hg^{+2} and Co^{+2} concentrations on the adsorption capacity of hydrogel IIIn was studied. According to Fig. 8b, the adsorption capacity sharply increased with the increase of the initial concentration of heavy metals ions ranging from 0.4 to 1 g/l. The results indicating that the highest adsorption capacity of hydrogel IIIn using 1 g/l of metal ions [59].

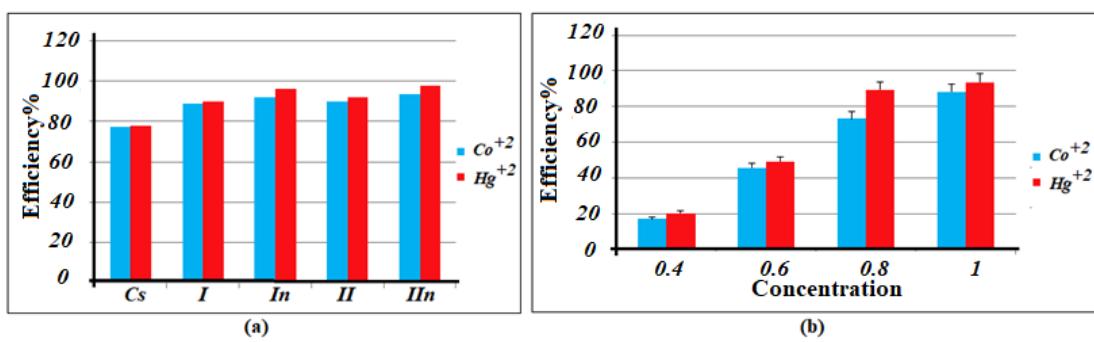


Fig. 8. (a) Efficiency of Cs, different hydrogels for metal ions uptake at 10 h (pH 7, and 25 °C), (b) Efficiency of hydrogel IIIn on initial metal ions concentration (pH 7, and 25 °C)

3.4.2. Biological activities

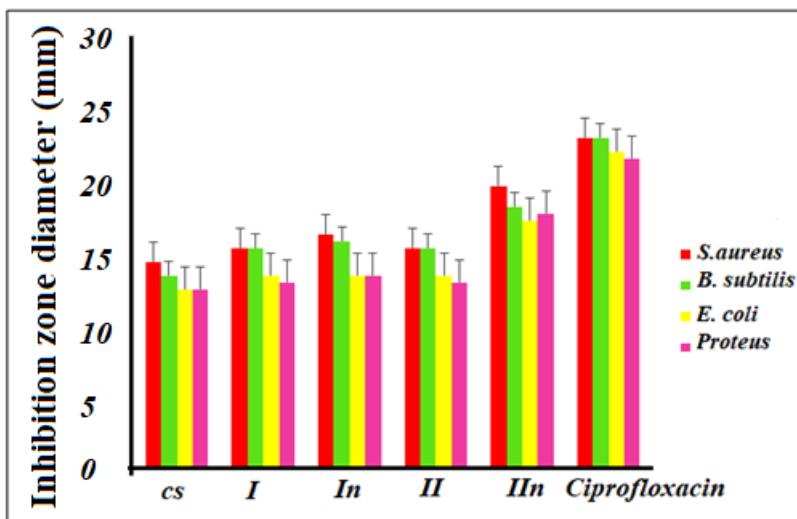
3.4.2.1. Bacterial Inhibition Zone Activity, Minimum Inhibition Concentration (MIC) and Minimum Bactericidal Concentrations (MBC)

The values of IZ, MIC and MBC of chitosan, and hydrogels I, In, II and IIIn against the growth of tested bacteria *S. aureus*, *B. subtilis*, *E. coli* and *proteus*, were investigated to study the effect of the hydrogels on the bacterial strains, Ciprofloxacin was used as standard drug, as shown in Table 2. and Fig. 9. Et al reported

Bacterial inhibition zone for *S. aureus*, *B. subtilis*, *E. coli* and *proteus* were more sensitive to hydrogel IIIn than hydrogels I, In, and II, reached (20.5 mm, 19 mm) and (18mm, 18.5 mm) respectively [56]. MIC for hydrogels In, and IIIn revealed the same value in Gram-positive (*S. aureus* & *B. subtilis*) equal to 19.5 ppm. And the highest value of MBC for hydrogel In, revealed the same value in Gram-positive (*S. aureus* & *B. subtilis*) equal 38 ppm and for hydrogel IIIn the same value in Gram-positive (*B. subtilis*) equal 38 ppm to antibiotic Ciprofloxacin. This indicated that hydrogels In, and IIIn represented the highest inhibitory effect and the ability to prevent the growth of organisms.

Table 2. MIC and [MBC] of Cs and hydrogels I, In, II and IIIn

Sample	<u>Gram-positive</u>		<u>Gram-negative</u>	
	<i>S. aureus</i>	<i>B. subtilis</i>	<i>E. coli</i>	<i>Proteus</i>
Cs	78 [156]	117 [234]	625 [2500]	468.5 [1875]
I	29.25 [117]	58.5 [117]	175.5 [351]	250 [950]
In	19.5 [38]	19.5 [38]	58.5 [117]	78 [152]
II	31.2 [62.4]	46.8 [93.6]	170.8 [1000]	128.1 [750]
IIIn	19.5 [78]	19.5 [38]	78 [152]	58.5 [117]
Ciprofloxacin	12.5 [25]	19 [38]	31 [50]	38 [72]

**Fig. 9. Bacterial Inhibition Zone of Cs, hydrogels I, In, II, IIIn and Ciprofloxacin**

4. Conclusions

New composite and nanocomposite hydrogels were prepared by modification of chitosan with bentonite, nano bentonite and isonicotinic aldehyde under different reaction conditions. Chitosan was modified with bentonite or nanobentonite to give the composite and nanocomposite hydrogels I and II respectively. However, chemical modification of chitosan with isonicotinic aldehyde via Schiff base formation from the reaction of chitosan amine groups with the aldehydic groups of isonicotinic aldehyde

in presence of bentonite or nanobentonite to yield chitosan composite and nanocomposite derivative hydrogels I and IIIn respectively.

The new hydrogels I, In, II, and IIIn were characterized by various tools. The crystallinity of the new modified hydrogels showed reflections at different angles differ than crystallinity of native chitosan. All the prepared hydrogels improved the thermal stability of chitosan. The swelling behavior results showed high swelling ratios at different solvents (acetic acid (99.85%), dimethyl sulphoxide, dimethyl formamide, and water). The surface morphology of the hydrogels showed morphological changes than chitosan due to the formation of composite and nanocomposite hydrogels. Efficiency of new hydrogels for removal of cobalt and mercuric ions revealed that the adsorption capacity increased as the time of immersion of Cs and hydrogels increased, and the highest efficiency for adsorption of cobalt and mercuric ions was observed for composite hydrogels In, and IIIn at 10 h reached (92%, 93.2%) and (96%, 97.8%) respectively. Adsorption capacity increased with the increase of the initial concentration of heavy metals, and the highest adsorption capacity of hydrogel IIIn using 1 g/l of metal ions due to the presence of heterocyclic moiety in isonicotinic aldehyde which have nitrogen atom carrying free lone pair of electrons thus increase the chelation of metal ions. The results of evaluation of biological activity of the new chitosan composite and chitosan nanocomposite hydrogels showed higher biological activity compared to native chitosan toward the tested bacteria, also hydrogels In, and IIIn represented the highest inhibitory effect and the ability to prevent the growth of organisms.

Declaration of Competing Interest

Authors have declared no conflict of interest for the publication of this paper.

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References

- [1] A. L. Cukierman, P. R. Bonelli, Nanotechnology for Sustainable Water Resources, Wiley. ch. 8: (2018) 227-276.
- [2] D. Liu, C. Ding, F. Chi, N. Pan, J. Wen, J. Xiong, S. Hu, Polymer brushes on graphene oxide for efficient adsorption of heavy metal ions from water, *J. Appl. Polym. Sci.* 136(43): (2019) 48156.

- [3] L. A. Malik, A. Bashir, A. Qureashi, A. H. Pandith, Detection and removal of heavy metal ions: a review. Environ. Chem. Lett. 17(4): (2019) 1495-1521.
- [4] G. Sharma, B. Kandasubramanian, Molecularly imprinted polymers for selective recognition and extraction of heavy metal ions and toxic dyes, J. Chem. Eng. Data. 65(2): (2020) 396-418.
- [5] H. Shayegan, G. A. Ali, V. Safarifard, Recent Progress in the Removal of Heavy Metal Ions from Water Using Metal-Organic Frameworks, Chemistry Select 5(1): (2020) 124-146.
- [6] L. Liu, X. B. Luo, L. Ding, S. L. Luo, Application of nanotechnology in the removal of heavy metal from water, (2019) In Nanomaterials for the removal of pollutants and resource reutilization (pp. 83-147). Elsevier.
- [7] G. Crini, E. Lichtfouse, L. D. Wilson, N. Morin-Crini, Conventional and non-conventional adsorbents for wastewater treatment, Environ. Chem. Lett. 17(1): (2019) 195-213.
- [8] M. Yao, Z. Wang, Y. Liu, G. Yang, J. Chen, Preparation of dialdehyde cellulose grafted graphene oxide composite and its adsorption behavior for heavy metals from aqueous solution, Carbohydr. Polym. 212: (2019) 345-351.
- [9] A. Maleki, Z. Hajizadeh, V. Sharifi, Z. Emdadi, A green, porous and eco-friendly magnetic geopolymer adsorbent for heavy metals removal from aqueous solutions, J. Clean. Prod. 215: (2019) 1233– 1245.
- [10] A. Maleki, M. Mohammad, Z. mdadi, N. Asim, M. Azizi, J. Safaei, Adsorbent materials based on a geopolymer paste for dye removal from aqueous solutions, Arab. J. Chem. 13: (2020) 3017–3025.
- [11] Z. Hajizadeh, K. Valadi, R. Taheri-Ledari, A. Maleki, Convenient Cr (VI) Removal from Aqueous Samples: Executed by a Promising Clay-Based Catalytic System, Magnetized by Fe₃O₄ Nanoparticles and Functionalized with Humic Acid Chemistry Select 5: (2020) 2441–2448.
- [12] K.Z. Elwakeel, S.M. El-kousy, H.G. El-Shorbagy, M.A. Abd El-Ghaffar, Comparison between the removal of Reactive Black 5 from aqueous solutions by 3-amino-1, 2, 4 triazole, 5-thiol and melamine grafted chitosan prepared through four different routes, J. Environ. Chem. Eng. 4: (2016) 733–745.
- [13] A. Maleki, R. Firouzi-Haji, Z. Hajizadeh, Magnetic guanidinylated chitosan nanobiocomposite: A green catalyst for the synthesis of 1,4-dihydropyridines, Int. J. Biol. Macromol. 116: (2018) 320– 326.
- [14] M. Rouhi, M. Babamoradi, Z. Hajizadeh, A. Maleki, S.T. Maleki, Design and performance of polypyrrole/halloysite nanotubes/Fe₃O₄/Ag/Co nanocomposite for photocatalytic degradation of methylene blue under visible light irradiation, Optik. 212: (2020) 164721–164732.
- [15] A. Maleki, R. Rahimi, S. Maleki, Efficient oxidation and epoxidation using a chromium (VI)-based magnetic nanocomposite, Environ. Chem. lett. 14 (2): (2016) 195–199.

- [16] N. M. Abdelazeem, E. M. El-Sayed, Sh. M. Abo-Naf, H. M. Abu- Zeid, G. A. Meligi, Preparation and characterization of silica hydrogel nanocomposites as a drug delivery system, *J. Sci. Res. Sci.*, 37: (2020) 44-60.
- [17] E. Etebu, I. Arikekpar, Antibiotics: Classification and mechanisms of action with emphasis on molecular perspectives, *Int. J. Appl. Microbiol. Biotechnol. Res.* 4(2016): (2016) 90-101.
- [18] J. V. Pham, M. A. Yilma, A. Feliz, M. T. Majid, N. Maffetone, J. R. Walker, Y. J. Yoon, A review of the microbial production of bioactive natural products and biologics, *Front. Microbiol.* 10: (2019) 1404.
- [19] M. M. A. Elsoud, E. M. El Kady, Current trends in fungal biosynthesis of chitin and chitosan, *Bull. Natl. Res. Cent.* 43(1): (2019) 59.
- [20] K. Moreno-Sader, S. I. Meramo-Hurtado, A. D. González-Delgado, Environmental sustainability analysis of chitosan microbeads production for pharmaceutical applications via computer-aided simulation, *WAR and TRACI assessments, Sustain. Chem. Pharm.* 15: (2020) 100212.
- [21] H. Oudadesse, S. Najem, S. Mosbahi, N. Rocton, J. Refifi, H. El Feki, B. Lefevre, Development of hybrid scaffold: Bioactive glass nanoparticles/chitosan for tissue engineering applications, *J Biomed Mater Res A*. (2020).
- [22] P. Nezhad-Mokhtari, M. Akrami-Hasan-Kohal, M. Ghorbani, An injectable chitosan-based hydrogel scaffold containing gold nanoparticles for tissue engineering applications, *Int. J. Biol. Macromol.* 154: (2020) 198-205.
- [23] B. Qu, Y. Luo, Chitosan-based hydrogel beads: Preparations, modifications and applications in food and agriculture sectors—A review, *Int. J. Biol. Macromol.* 152: (2020) 437-448.
- [24] P. S. Bakshi, D. Selvakumar, K. Kadirvelu, N. S. Kumar, Chitosan as an environment friendly biomaterial—a review on recent modifications and applications, *Int. J. Biol. Macromol.* 150: (2020) 1072-1083.
- [25] H. G. El-Shorbagy, S. M. El-Kousy, K. Z. Elwakeel, M.A. Abd El-Ghaffar, Eco-friendly Chitosan Condensation Adduct Resins for Removal of Toxic Silver Ions from Aqueous Medium, *J. Ind. Eng. Chem.* 100: (2021) 410–421
- [26] K. Z. Elwakeel, M. F. Hamza, E. Guibal, Effect of agitation mode (mechanical, ultrasound and microwave) on uranium sorption using amine- and dithizone-functionalized magnetic chitosan hybrid materials, *Chem. Eng. J.* 411: (2021) 128553.
- [27] K. Z. Elwakeel, A. S. Al-Bogami, E. Guibal, 2-Mercaptobenzimidazole derivative of chitosan for silver sorption –Contribution of magnetite incorporation and sonication effects on enhanced metal recovery, *Chem. Eng. J.* 403: (2021) 126265.
- [28] M. S. Almughamisi, Z. A. Khan, W. Alshitari, Kh. Z. Elwakeel, Recovery of Chromium (VI) Oxyanions from Aqueous Solution Using Cu (OH)₂ and CuO Embedded Chitosan Adsorbents, *J. Polym. Environ.* 28: (2020) 47–60.

- [29] N. El-Tohamy, M. Attia, S. M. Easa, N. M. Awad, Characterization and evaluation of nanocomposites chitosan-multiwalled carbon nanotubes as broad-spectrum antibacterial agent, *J. Sci. Res. Sci.* 35: (2018) 16-27.
- [30] G. A. Seif, R. F. M. Elshaarawy, M. E. El-Naggar, T. B. Mostafa, E. A. El- Sawi, Tetrabutylphosphonium-salicyl-imine-chitosan metallo-Schiff bases: Supramolecular architectures as multifunctional pharmacological materials, *J. Sci. Res. Sci.* 36: (2019) 526-538.
- [31] E. Srasra, I. Bekri-Abbes, Bentonite clays for therapeutic purposes and biomaterial design, *Curr. Pharm. Des.* 26(6): (2020) 642-649.
- [32] L. Laysandra, I. J. Ondang, Y. H. Ju, B. H. Ariandini, A. Mariska, F. E. Soetaredjo, S. Ismadji, Highly adsorptive chitosan/saponin-bentonite composite film for removal of methyl orange and Cr (VI), *Environ Sci Pollut R.* 26(5): (2019) 5020-5037.
- [33] G. Feng, J. Ma, X. Zhang, Q. Zhang, Y. Xiao, Q. Ma, S. Wang, Magnetic natural composite Fe_3O_4 -chitosan-bentonite for removal of heavy metals from acid mine drainage, *J. Colloid Interface Sci.* 538: (2019) 132-141.
- [34] J. Kaushal, G. Singh, S. K. Arya, Immobilization of catalase onto chitosan and chitosan–bentonite complex: a comparative study, *Biotechnol. Rep.* 18: (2018) e00258.
- [35] S. D. Chaudhuri, A. Mandal, A. Dey, D. Chakrabarty, Tuning the swelling and rheological attributes of bentonite clay modified starch grafted polyacrylic acid-based hydrogel, *Appl. Clay Sci.* 185: (2020) 105405.
- [36] Y. S. Chang, P. I. Au, N. M. Mubarak, M. Khalid, P. Jagadish, R. Walvekar, E. C. Abdullah, Adsorption of Cu (II) and Ni (II) ions from wastewater onto bentonite and bentonite/GO composite, *Environ. Sci. & Pollut. Res.* 27(26): (2020) 33270-33296.
- [37] G. Cheng, H. H. Zhu, Y. N. Wen, B. Shi, L. Gao, Experimental investigation of consolidation properties of nano-bentonite mixed clayey soil, *sustain.* 12(2): (2020) 459.
- [38] S. A. El-Enein, M. A. Okbah, S. G. Hussain, N. F. Soliman, H. H. Ghounam, Adsorption of Selected Metals Ions in Solution Using Nano-Bentonite Particles: Isotherms and Kinetics, *Environ. Process.* 7(2): (2020) 463-477.
- [39] D. A. El-Nagar, D. H. Sary, Synthesis and characterization of nano bentonite and its effect on some properties of sandy soils, *Soil Tillage Res.* 208: (2021) 104872.
- [40] D. N. Lukmanova, S. Y. Balandina, R. R. Makhmudov, I. V. Mashevskaya, Antinociceptive and Antimicrobial Activity of Products from Reactions of Pyrrolobenzoxazinetriones with Thiosemicarbazones of Aromatic and Heteroaromatic Aldehydes, *Pharm. Chem. J.* 54(3): (2020) 236-240.
- [41] L. Gao, G. Wang, H. Chen, J. Cao, X. Su, X. Liu, S. Li, Metal-free reductive coupling of aliphatic aldehydes/ketones with 4-cyanopyridines: expanded scope and mechanistic studies, *Org. Chem. Front.* 7(18): (2020) 2744-2751.

- [42] Y. Jiao, A. Chen, B. Yu, H. Huang, Brønsted Acid Catalyzed Cyclization of Aminodiazooesters with Aldehydes to 3-Carboxylate-N-Heterocycles, *Org. Lett.* 22(15): (2020) 6031-6034.
- [43] S. G. Abd Alla, H. M. N. El-Din, A. W. M. El-Naggar, Structure and swelling-release behaviour of poly (vinyl pyrrolidone) (PVP) and acrylic acid (AAc) copolymer hydrogels prepared by gamma irradiation, *Eur. Polym. J.* 43(7): (2007) 2987-2998.
- [44] M. M. Eldin, A. M. Omer, M. A. Wassel, T. M. Tamer, M. S. Abd-Elmonem, S. A. Ibrahim, Novel smart pH sensitive chitosan grafted alginate hydrogel microcapsules for oral protein delivery: I. preparation and characterization, *Int J Pharm Pharm Sci.* 7(10): (2015) 320-326.
- [45] E. A. Azmy, H. E. Hashem, E. A. Mohamed, N. A. Negm, Synthesis, characterization, swelling and antimicrobial efficacies of chemically modified chitosan biopolymer, *J. Mol. Liq.* 284: (2019) 748-754.
- [46] N. G. Kandile, A. S. Nasr, New hydrogels based on modified chitosan as metal biosorbent agents, *Int. J. Biol. Macromol.* 64: (2014) 328-333.
- [47] N. Y. Abou-Zeid, A. I. Waly, N. G. Kandile, A. A. Rushdy, M. A. El-Sheikh, H. M. Ibrahim, Preparation, characterization and antibacterial properties of cyanoethylchitosan/cellulose acetate polymer blended films, *Carbohydr. Polym.* 84(1): (2011) 223-230.
- [48] M. R. Kasaai, J. Arul, G. Charlet, Intrinsic viscosity–molecular weight relationship for chitosan, *J Polym Sci B Polym Phys.* 38(19): (2000) 2591-2598.
- [49] K. Kabiri, H. Mirzadeh, M. J. Zohuriaan-Mehr, M. Daliri, Chitosan-modified nanoclay–poly (AMPS) nanocomposite hydrogels with improved gel strength, *Polym. Int.* 58(11): (2009) 1252-1259.
- [50] H. Moussout, H. Ahlafi, M. Aazza, C. El Akili, Performances of local chitosan and its nanocomposite 5% Bentonite/Chitosan in the removal of chromium ions (Cr (VI)) from wastewater, *Int. J. Biol. Macromol.* 108: (2018) 1063-1073.
- [51] Q. Liu, B. Yang, L. Zhang, R. Huang, Adsorption of an anionic azo dye by cross-linked chitosan/bentonite composite, *Int. J. Biol. Macromol.* 72: (2015) 1129-1135.
- [52] D. S. Olivera, M. T. Morgan, S. N. Tewolde, E. C. Botts, F. P. Horvath, N. J. Hamlin, Clinical Evaluation of a Chairside Amalgam Separator to Meet Environmental Protection Agency Dental Wastewater Regulatory Compliance, *Oper. Dent.* 45(2): (2020) 151-162.
- [53] P. Negrea, A. Caunii, I. Sarac, M. Butnariu, The study of infrared spectrum of chitin and chitosan extract as potential sources of biomass, *Dig. J. Nanomater. Biostructures* 10(4): (2015).
- [54] X. Xu, W. Lu, J. Zhu, X. Pan, X. Zhu, An On-Demand Dissoluble Chitosan Hydrogel Containing Dynamic Diselenide Bond, *Gels* 7(1): (2021) 21.
- [55] G. M. Vlasceanu, L. E. Crica, A. M. Pandele, M. Ionita, Graphene oxide reinforcing genipin crosslinked chitosan-gelatin blend films, *coat.* 10(2): (2020) 189.

- [56] S. Abdelkrim, A. Mokhtar, A Djelad, F. Bennabi, A. Souna, A. Bengueddach, M. Sassi, Chitosan/Ag-Bentonite Nanocomposites: Preparation, Characterization, Swelling and Biological Properties, *J. Inorg. Organomet. Polym. Mater.* 30: (2020) 831–840.
- [57] J. Liang, R. Wang, R. Chen, The impact of cross-linking mode on the physical and antimicrobial properties of a chitosan/bacterial cellulose composite, *Polymers* 11(3): (2019) 491.
- [58] Z. Lin, Y. Yang, Z. Liang, L. Zeng, A. Zhang, Preparation of Chitosan/Calcium Alginate/Bentonite Composite Hydrogel and Its Heavy Metal Ions Adsorption Properties, *Polymers* 13: (2021)1891.
- [59] Y. Gutha, V. S. Munagapati, Removal of Pb (II) ions by using magnetic chitosan-4-((pyridin-2-ylimino) methyl) benzaldehyde Schiff's base, *Int. J. Biol. Macromol.* 93: (2016) 408-417.

الملخص باللغة العربية

كيتوزان كمبوزيت وكمبوزيت النانوية المعدلة الجديدة لتطبيقات مختلفة

تغريد حسن عبد اللا¹ - عبير صلاح نصر¹ - غادة بسيونى² - دافيد ر.هاردينج³ - نادية غريب قديل¹

1. قسم الكيمياء - كلية البنات للأداب والعلوم والتربية - جامعة عين شمس - القاهرة - جمهورية مصر العربية.

2. قسم الكيمياء - كلية الهندسة - جامعة عين شمس - القاهرة - جمهورية مصر العربية.

2. معهد الكيمياء للعلوم الأساسية - الكيمياء - جامعة ماسى - نيوزيلاندا

يركز العمل الحالي على تحضير مشتقات الكيتوزان كمبوزيت ومشتقات الكيتوزان كومبوزيت النانوية لتطبيقات مختلفة. تم تعديل الكيتوزان مع البنتونيت أو البنتونيت النانوي لإعطاء هيدروجيلاط مركب الكيتوزان ومشتقات المركبات النانوية المقابلة I و II على التوالي ومع ذلك فإن التعديل الكيميائي للكيتوزان مع ايزونيكوتينيك ألدヒيد يتم عن طريق تكوين قاعدة شيف في وجود البنتونيت أو البنتونيت النانوي لينتج هيدروجيلاط الكيتوزان المعدلة In , IIIn التوالي. تميزت الهلاميات المائية المحضررة بسلوك الأنفاس و FT-IR و X-Ray و DSC و SEM. تمت دراسة دراسات الامتراز لإزالة أيونات المعادن الثقيلة من الوسط المائي والنشاط البيولوجي للهلاميات المائية الجديدة. وأظهرت النتائج أن الهلاميات المائية In , IIIn لها أعلى كفاءة لامتصاص أيونات الكوبالت والزنبق (93.2٪) و (97.8٪) على التوالي كما أظهرت أيضا نتائج MIC و MBC ملحوظة ومميزة تجاه بكتيريا موجبة الجرام (*B. subtilis*) (19.5 ، 38) ميكروغرام. / مل مقارنة بالمضاد الحيوي القياسي سيبروفلووكساسين (19 ، 38) ميكروغرام / مل على التوالي.