



Novel nanocomposite synthesis of carboxymethyl cellulose coated to zero-valent iron supported on chitosan for simultaneous removal of heavy metals and pesticides in water: Performance and mechanism

Ahmad Abo Markeb^{a,b,*}, Javier Moral-Vico^a, Antoni Sánchez^a, Xavier Font^a

^a Department of Chemical, Biological and Environmental Engineering, Escola d'Enginyeria, Universitat Autònoma de Barcelona 08193 Bellaterra, Spain

^b Chemistry Department, Faculty of Science, Assiut University 71516 Assiut, Egypt

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ABSTRACT

This study reports the synthesis and performance of a novel nanocomposite, CS@nZVI-CMC NC, consisting of zero-valent iron nanoparticles cross-linked to chitosan and coated to carboxymethyl cellulose. Also, the novelty of this work has been proven by eliminating several heavy metals and pesticides from aqueous solutions and drinking water simultaneously. The NC structure, morphology, size, and functional groups were investigated using advanced techniques such as TEM, SEM, XRD, FTIR, and BET. It showed that the surface area of the NC is found to be 127.95 m²/g and a pore volume of 0.659 cm³/g. A spherical shape of the nanoparticles with an average size of 8 ± 2 nm was obtained. The functional groups of the NC such as the —NH, —OH, —C=O, and —CN were demonstrated using the FTIR analysis. The NC shows 96.91 %, 90.00 %, 60.61 %, 52.73 %, and 40.43 % simultaneous removal of Cr(VI), As(V), Cd(II), Pb(II) and Mn(II), respectively. Also, it demonstrates a significant simultaneous elimination of organochlorine pesticides: DDE, heptachlor, endrin aldehyde, endosulfan, and heptachlor epoxide, being 98.52 %, 94.01 %, 70.98 %, 65.39 %, and 63.02 % the elimination percentage, respectively. In addition, the NC exhibited the highest removal (77.09 %) of parathion methyl when simultaneously removing several organophosphorus pesticides. Adsorption mechanisms for the targeted pollutants were also studied, and adsorption and electron transfer were the predominant mechanisms. Therefore, this novel NC could be a promising water and wastewater treatment adsorbent.

1. Introduction

In the last decade, there has been an increasing amount of emerging contaminants in the environment due to industrialization outcomes and human activities [1]. So, water quality degradation and scarcity are global issues [2]. Therefore, several studies for large-scale water purification have been proposed, and no final solution has yet been suggested, in consequence, emerging contaminants continue to adversely affect public health, plants, aquatic systems, and soils [3]. A promising solution for operational cost reduction is water regeneration, which has been studied recently and applied to water systems [4].

Heavy metals, pesticides, dyes, and pharmaceuticals are among the diverse emerging contaminants considered major concerns in different areas worldwide that prevent water reuse [5]. For instance, the hazardous effects of pesticides on humans and the environment have been

reported in many studies due to the threat they pose to human health, as well as their extended persistence in aqueous media [6]. For example, pesticides, such as organochlorine pesticides (OCPs) and organophosphorus pesticides (OPPs), show endocrine-disrupting effects, neurotoxicity, carcinogenicity, and immunotoxicity [7,8]. These contaminants can enter the human body through drinking water or food [9]. Moreover, the toxicity of the products obtained by pesticides' abiotic and biotic degradation processes can be higher than that of their parent compounds [10]. OCPs and OPPs can be used in industrial sectors such as herbicides, insecticides, flame stabilizers, and coatings, as well as in household and agricultural uses [11,12]. In addition, the United States Environmental Protection Agency (USEPA) states that the maximum contaminant level (MCL) of pesticides is in the range of 0.2 to 700.0 µg/L [13].

Besides pesticides, the expansion of heavy metals in water bodies has

* Corresponding author at: Department of Chemical, Biological and Environmental Engineering, Escola d'Enginyeria, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain.

E-mail addresses: a_markeb@aun.edu.eg, AhmadMohamed.AhmadAbomarked@uab.cat (A.A. Markeb).

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become an emergent issue of environmental concern due to their toxicity [14,15]. Also, heavy metals' biological accumulation, non-biodegradability, and carcinogenic effects threaten both human health and aquatic ecosystems [16]. The major sources of heavy metal contamination are metal industries, the manufacturing of nickel–cadmium batteries, landfill leachates, pesticide development, and electroplating, among others [17]. Therefore, prospective risks to aquatic and human health were found to be due to heavy metal non-biodegradability properties, and their removal is crucial to mitigate their detrimental impacts on the environment [18]. Thus, the USEPA stipulates that the maximum permissible concentration of heavy metals in drinking water such as lead, cadmium, arsenic, and chromium be 0.006 mg/L, 0.005 mg/L, 0.010 mg/L, and 0.010 mg/L, respectively [19].

Several methods have been used to eliminate pollutants from water and aqueous solutions, such as filtration, reverse osmosis, electrolysis, chemical disinfectants, and ion exchange [20]. The high-cost and hazardous effects of the chemicals on the environment are examples of the disadvantages of the typical purification methods [21]. However, adsorption does not imply the removal of the pollutant, but its transfer to a solid phase, which can be more easily managed and permits the reuse of water sources [22–24]. Among several biosorbents, chitosan (CS) is a naturally abundant and multilateral biopolymer, playing an important role in gas and water treatments [25]. It contains many significant functional groups, such as amino and hydroxyl groups, which provide active sites for efficient adsorption [26]. The combination with nanomaterials reported an enhancement of the properties of some biosorbents as chitosan. The main distinctive features of nanomaterials are high surface area, pore size, and high affinity to pollutants [27].

Several adsorbent nanomaterials have been reported for pollutant removal from aqueous solutions, water, and wastewater [27–29]. However, no study was found to have an adsorbent that can eliminate different types of contaminants and several pollutants simultaneously. One of the most extensively used in environmental pollution reduction is zero-valent iron nanoparticles (nZVI) because they have low toxicity and comparative abundance in nature [30]. Therefore, this work aims to: (1) synthesize a novel nanocomposite (NC) based on nZVI with higher stability and functional groups by its immobilization and coating with two natural biopolymers of CS and carboxymethyl cellulose (CMC), (2) apply this novel NC to eliminate heavy metals from aqueous solutions, (3) evaluate its efficiency towards the removal of organochlorine and organophosphorus pesticides from aqueous solutions and drinking water, and (4) compare the performance of this new NC with other previous works, although most of them are focused on a unique pollutant. It is also important to note that the NC magnetic properties make its separation from the water media very easy.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals and reagents used are described in detail in [Supplementary Information \(S1.1\)](#).

2.2. Synthesis of CS@nZVI-CMC NC

The CS@nZVI-CMC NC was prepared based on the reduction method and modification of the reported one [28], as illustrated in [Fig. 1](#). Typically, chitosan solution (0.1 %, wt/vol) was prepared by dissolving the appropriate amount of chitosan (low molecular weight) in a defined volume of Milli-Q water containing acetic acid (1 %) under a magnetic stirrer at room temperature for 24 h. Next, ferric chloride hexahydrate (0.93 M) was dispersed in the CS solution after purging with nitrogen for 1 h to obtain the CS/Fe solution. Later, 100 mL of sodium borohydride solution (1M) was purged with nitrogen for 1 h and added dropwise to CS/Fe solution until the formation of a black precipitate confirmed the formation of CS/nZVI. Then, the mixture solution was continuously stirred at room temperature under a nitrogen atmosphere for 2 h. After that, 0.1 g of CMC was added dropwise to CS@nZVI suspension and left for continuous stirring for 4 h at room temperature. Finally, the CS@nZVI-CMC NC was freeze-dried for 24 h after washing using magnetic decantation with Milli-Q water and ethanol. This method can be easily scaled up to obtain large amounts of NC.

2.3. Characterization of CS@nZVI-CMC NC

The morphology of the surface and composition of the synthesized NC were investigated using a Scanning Electron Microscope (SEM) (Merlin FE-SEM, USA) equipped with an Energy Dispersive Spectroscopy (EDS) detector (EDS Oxford LINCA X-Max). The size and morphology of the NC were determined using Transmission Electron Microscopy (TEM) (Hitachi H-7000, USA). Crystallinity and crystal structure were determined using X-ray Diffraction (XRD) (Panalytical X'Pert, Malvern, UK) with Cu-K α radiation. The measurements ranged from 10° – 80° on 2 θ with a step size of 0.026°, and the results were analyzed using HighScore Plus software. The specific surface area of the CS@nZVI-CMC NC was determined using the Brunauer–Emmett–Teller (BET) with a sorption analyzer (ASAP 2000, Micromeritics, Co., USA). Before analysis, the NC was degassed at 196 °C with nitrogen gas as adsorbate. The functional groups of the synthesized NC were determined using Fourier-Transform Infrared Red (FTIR) spectroscopy (Bruker Tensor 27, USA).

2.4. Adsorption studies in pure water solutions

The adsorption experiments were conducted in batch mode. First, stock solutions (1000 mg/L) for each heavy metal were prepared by dissolving the appropriate amount of each precursor salt in 50 mL of Milli-Q water containing nitric acid (1%). For working solutions of

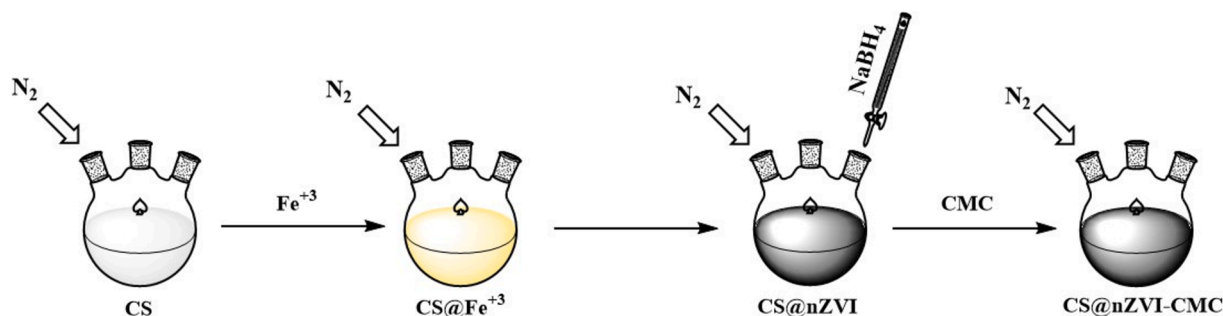


Fig. 1. Schematic illustration of the synthesis of CS@nZVI-CMC NC.

pesticides (10 mg/L), each pesticide stock solution was diluted in methanol. Then, 10 mg of the synthesized CS@nZVI-CMC NC was added to 100 mL of each heavy metal standard solution (10 mg/L as initial concentration, C_0) and pesticide standard solution (100 $\mu\text{g/L}$ as initial concentration, C_0) and mixed for 24 h in an incubating shaker at 180 rpm, and 25 °C. After that, the residual concentrations (C_e) of heavy metals and pesticides after magnetic separation of the NC were determined using Inductively Coupled Plasma with Optical Emission Spectrometry (ICP-OES), Agilent 5900 (Germany), and Gas Chromatography coupled to Mass Spectrometry (GC/MS), Agilent 7820A/5975B (Germany), respectively. The detailed extraction and treatment procedures for pesticides and heavy metals are shown in the [Supplementary Information](#) (S1.2.). Each pollutant removal efficiency and adsorption capacity were calculated using the equations explained in the [Supplementary Information](#) (S1.3.).

2.5. Application to real drinking water

The efficiency of the CS@nZVI-CMC NC was evaluated through the treatment of drinking water obtained from the Department of Chemical, Biological and Environmental Engineering, Universitat Autònoma de Barcelona (Spain). The sample was collected after opening the tap water for 10 min to allow the system to flush until the water temperature had stabilized; then, two liters were collected. Next, the water sample was divided into four parts: unspiked drinking tap water, spiked with a mixture of heavy metals (each heavy metal concentration is 10 mg/L), OCPs (each OCP concentration is 100 $\mu\text{g/L}$), and the last part is OPPs spiked water (each OPP concentration is 100 $\mu\text{g/L}$). Later, the spiked samples were exposed to a dose of the NC (0.1 g/L) and left for 24 h under an incubating shaker at 25 °C and 180 rpm. After that, the residual concentration of each contaminant was determined, as explained before.

3. Results and discussion

3.1. Characterization of the synthesized nanocomposite

The morphology of the CS@nZVI-CMC NC is presented in [Fig. 2](#). First, the TEM images offer a spherical shape of nZVI with an average particle size of 8 ± 2 nm in the synthesized NC. The smaller particle size

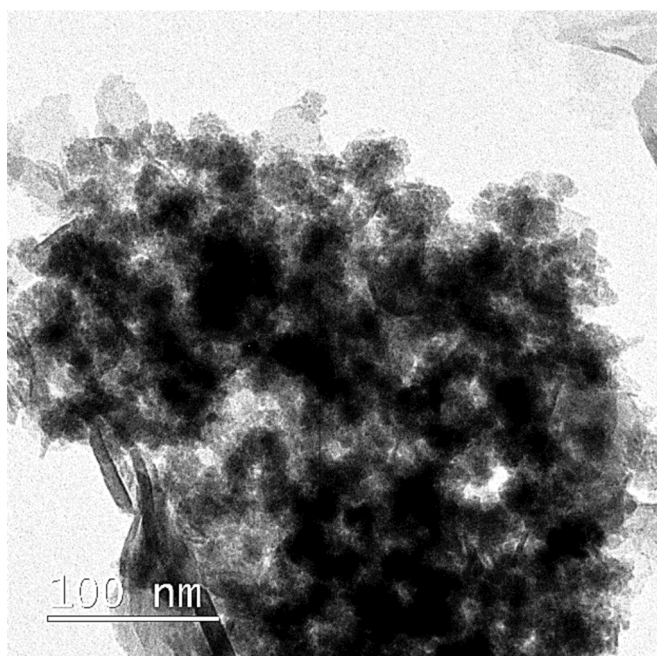


Fig. 2. TEM image of CS@nZVI-CMC NC.

of the CS@nZVI-CMC NC in comparison to the reported ones [\[31,32\]](#) could be attributed to two main factors: (1) the addition of the iron to the chitosan as a crosslinker led to the dispersion of the ZVI nanoparticles and decreased their aggregation, which is a typical drawback of the metal nanoparticles without supporting agent or (2) the increase of the electrostatic repulsion forces due to the increase of the negatively charged nZVI and due to the addition of CMC. In addition to these factors, the dispersion of the nZVI compared to the reported results could arise from the repulsion of the negatively charged nZVI nanoparticles and the carbonyl functional group in the CMC structure [\[32\]](#).

Also, the structural heterogeneity and surface morphology analysis of CS@nZVI-CMC NC were determined using SEM. [Fig. 3a](#) shows the spherical shape of ZVI nanoparticles. Also, it confirms that iron is attached to the surface of chitosan and coated with carboxymethyl cellulose, and the surface is found to be heterogeneous, which is preferable for adsorption. The results agreed with the CS-nZVI by Jin et. al. where they found that chitosan enhances the dispersion of the ZVI nanoparticles [\[33\]](#). Moreover, the elemental distribution between the iron and the elemental composition of chitosan was confirmed using EDS. [Fig. 3b](#) shows the EDS mappings, where yellow corresponds to iron,

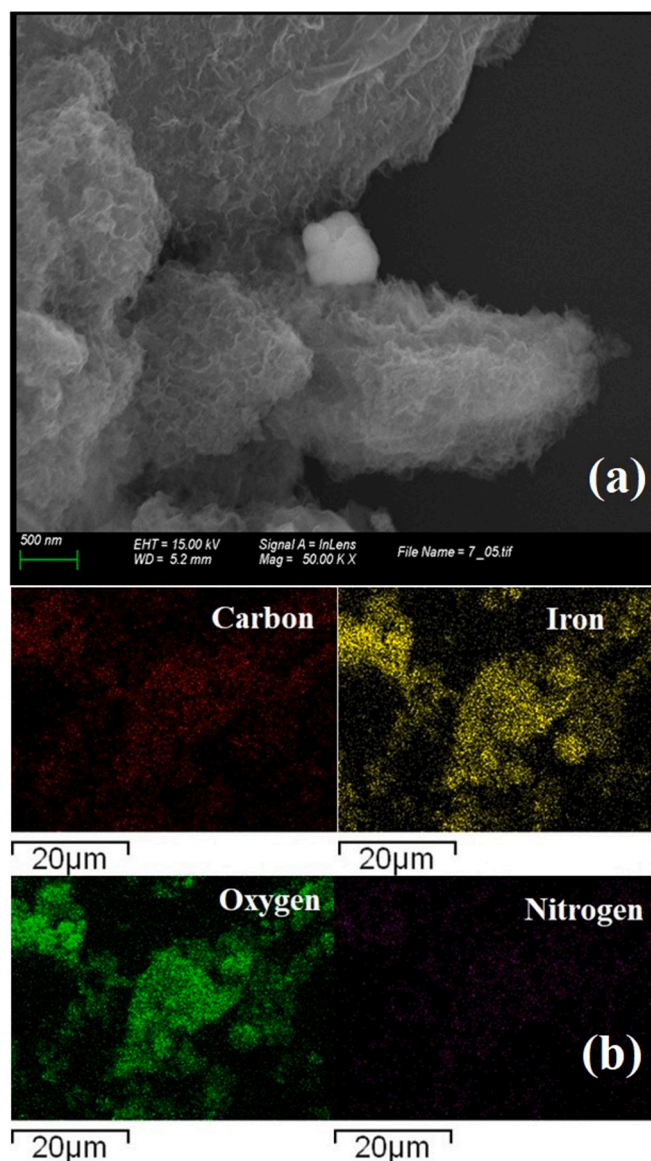


Fig. 3. SEM image of CS@nZVI-CMC NC (a) and elemental mapping profile of CS@nZVI-CMC NC (b).

while red, green, and purple represent carbon, oxygen, and nitrogen, respectively. The elemental distribution mapping of the NC was used to enhance the incorporation of the zero-valent iron into the structures of CS and CMC. As a result of the different colors obtained from the EDS analysis, the immobilization and coating of iron could be observed. Thus, confirmation of the main elements in the CS@nZVI-CMC NC by the EDS analysis agreed with the reported nZVI@nbcnt-CMC composite by Eltaweil et. al. [34].

Furthermore, the elemental mapping via the FE-SEM of the CS@nZVI-CMC NC revealed that the iron atoms were homogenously immobilized on the surface of chitosan. In addition, the weak color intensity of nitrogen atoms indicates the interaction of the amino groups in chitosan support with iron atoms and carboxylic groups of carboxymethyl cellulose. A tabulation of the weight and atomic percentages of each atom illustrated in the elemental mapping is presented in Table 1. These results demonstrate that the weight percentage of iron was 25.28 %, which was matched with the experimental weight percentage of iron added into the CS solution (25.14 %, wt/ vol.). Therefore, complete immobilization of iron into chitosan support was proved.

The XRD pattern of CS-ZVI@CMC is shown in Fig. 4 for further analysis of structural properties. It was found that the peaks of 2θ at 45° and 65° corresponded to the (110) and (200) crystal planes of αFe^0 (JCPDS 06–0696), respectively. Moreover, the small peak at 2θ of 20° is attributed to the amorphous nature of the chitosan and carboxymethyl cellulose biopolymers. Also, the small peak at 2θ of 32° is attributed to the CMC structure [35]. These results agree with those reported in the literature related to CS-nZVI and nZVI-CMC [18,32].

The functional groups of CS@nZVI-CMC NC were determined using FTIR spectroscopy, as shown in Fig. 5. In the FTIR of the synthesized CS@nZVI-CMC NC, the characteristic peaks were displayed, such as the absorption band at 3326 cm^{-1} (the stretching vibration of $-\text{OH}$ and $-\text{NH}$), the peak at 1654 cm^{-1} (asymmetric stretching vibration of $-\text{C}=\text{O}$ stretching), the peak at 1331 cm^{-1} (stretching vibration of $\text{C}-\text{O}-\text{C}$ and $-\text{CN}$), the peak at 1040 cm^{-1} (stretching vibration of $\text{C}-\text{O}$), the peak at 907 cm^{-1} (the bending vibration of $-\text{NH}$), the peak at 693 cm^{-1} ($-\text{OH}$ bond plane bending vibration), and the peak at 564 cm^{-1} (the $\text{Fe}-\text{O}$ group). A comparison of the obtained functional groups of the synthesized NC agreed with the reported ones in the literature related to chitosan, CMC, nZVI, chitosan-nZVI, and nZVI-CMC [36–38]. For instance, the absorption bands of chitosan at 3440 cm^{-1} , 897 cm^{-1} , 1656 cm^{-1} , and 1323 cm^{-1} corresponded to the superimposed stretching vibration of $-\text{OH}$ and $-\text{NH}$ on chitosan, the bending vibration of $-\text{NH}$, the stretching vibration of $\text{C}=\text{O}$ and the $-\text{CN}$ functional group. Moreover, the absorption bands were determined at 3437 cm^{-1} (the stretching vibration of $-\text{OH}$), 1629 cm^{-1} (the asymmetric stretching vibration of $-\text{COO}$), 1337 cm^{-1} (the stretching vibration of $-\text{C}-\text{O}-\text{C}-$), and 1049 cm^{-1} (the stretching vibration of $-\text{CO}-$) for the CMC identification structure. Besides, the characteristic peaks of nZVI were assigned to be at 596 cm^{-1} (the stretching vibration of $-\text{Fe}-\text{O}$) and 3426 cm^{-1} (the stretching vibration of $-\text{OH}$ resulting from the residual moisture on the surface of nZVI). Also, when combining ZVI with chitosan or CMC, the characteristic absorption bands were shifted to lower or longer wavenumbers. As observed, the involvement of $-\text{NH}_2$ and $-\text{OH}$ groups in the CS@nZVI-CMC NC was demonstrated due to the shift from 3440 cm^{-1} of chitosan and 3437 cm^{-1} of CMC to 3326 cm^{-1} . Furthermore, the coordination between the carboxylate group and the iron metal could be formed in one of three

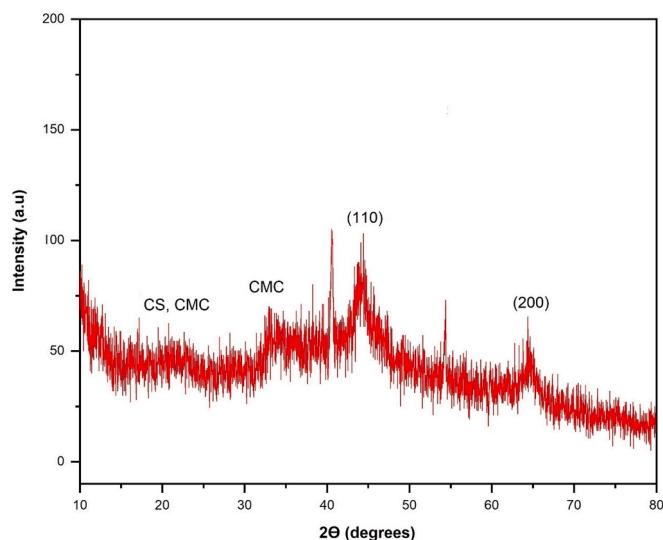


Fig. 4. XRD pattern of CS@nZVI-CMC NC.

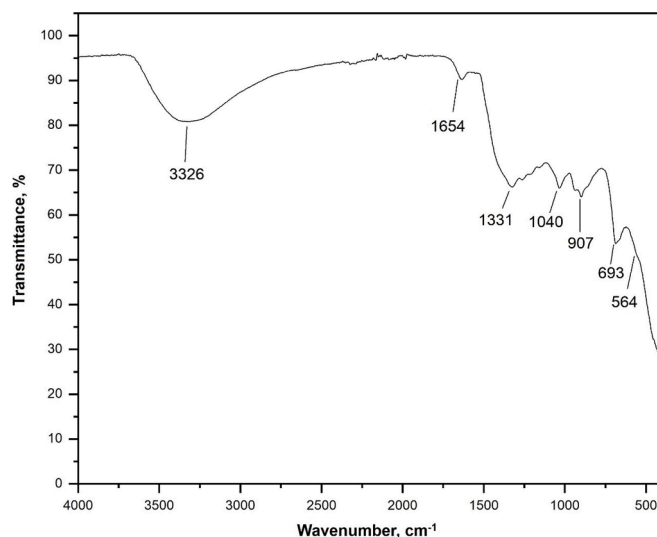


Fig. 5. FTIR analysis of CS@nZVI-CMC NC.

different types of interactions: monodentate, bidentate chelating, or bidentate bridging [39]. Thus, the change and decrease in the intensity of the peak from 1629 cm^{-1} of CMC to 1654 cm^{-1} of the CS@nZVI-CMC NC illustrate the bridging between the iron and carboxylate group. Hence, the FTIR spectrum shows that the nZVI were coated to CMC and cross-linked to the chitosan due to the evidence of the interaction between the iron, chitosan, and CMC that was proved based on the results of the synthesized CS@nZVI-CMC NC. Therefore, all the functional groups present in this NC could be a promising adsorbent for removing contaminants.

The CS-ZVI@CMC adsorbent exhibited a surface area of $127.95\text{ m}^2/\text{g}$. The nitrogen sorption isotherms of the adsorbent are shown in Fig. 6 (6a). It can be observed that the adsorbent shows a microporous structure due to the appearance of the type-I sorption isotherms [40]. This result is in agreement with SEM analysis. In addition, the pore size distribution of the adsorbent (Fig. 6b) presents a pore volume of $0.659\text{ cm}^3/\text{g}$. Also, the average pore diameter was found to be 20.60 nm .

Table 1
EDS analysis of CS@nZVI-CMC nanocomposite.

Element	Weight (%)	Atomic (%)
Carbon	18.06	27.32
Nitrogen	0.70	0.91
Oxygen	55.97	63.55
Iron	25.28	8.22

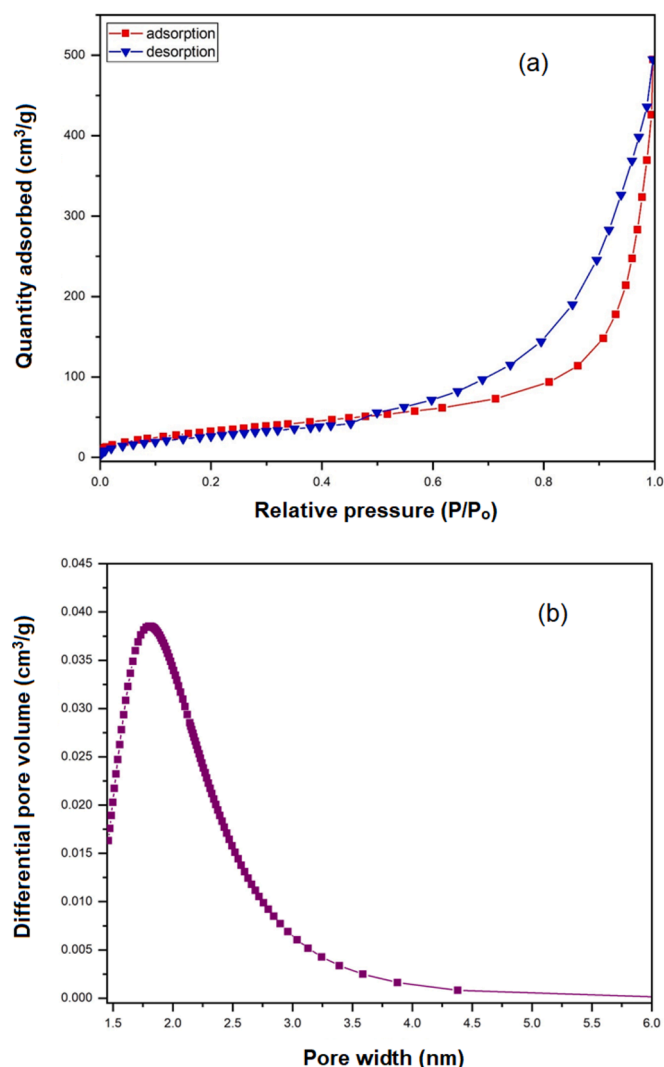


Fig. 6. BET analysis of CS@nZVI-CMC adsorbent: (a) nitrogen sorption isotherm plot and (b) pore size distribution plot.

3.2. Performance of this NC as adsorbent of water pollutants

3.2.1. Heavy metals removal from pure aqueous solutions

Two of the most important factors that could affect the removal process of heavy metals such as lead (II), cadmium(II), manganese(II), arsenic(V), and chromium(VI) are the solution pH and contact time. Thus, the adsorption tests were performed at pH 6 and 24 h as the optimum pH value for heavy metals removal based on the literature [41,42] and to ensure that the equilibrium state of the adsorption studies was achieved [43]. It must be taken into account that the nanocomposite under investigation was protonated at a pH lower than 6, an acidic pH. Thus, the interaction between the heavy metal and the adsorbent will decrease. When pH exceeds 6, heavy metals could be precipitated in the hydroxide form [44]. As shown in Fig. 7, the highest efficiency was observed in the case of Cr(VI) and As(V) at 99.36 % and 95.42 %, respectively. At the same time, moderate removal efficiencies were found to be 69.97 % (Cd(II)), 57.11 % (Pb(II)), and Mn(II) shows lower removal efficiency (42.64 %).

Interestingly, these results showed the highest efficiency in removing heavy metals in anionic forms rather than cationic forms, which could also open the door for removing inorganic anions, such as nitrate and phosphate, from aqueous solutions [45,46]. This observation could be attributed to the surface of the synthesized nanocomposites being positively charged; hence, electrostatic attraction could occur. For

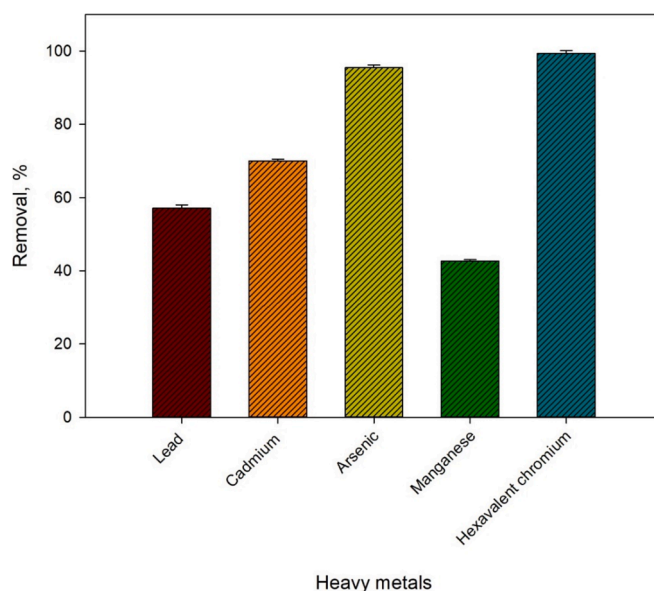


Fig. 7. Individual heavy metals removal using CS@nZVI-CMC NC.

example, the hexavalent chromium as heavy metal is present in anionic form, $\text{Cr}_2\text{O}_7^{2-}$, and it was first adsorbed on the surface of the nanocomposite by the electrostatic attraction of the protonated amine group of the chitosan or by the coordination bond [36]. Then, partial reduction of the Cr(VI) by the effect of Fe(0) and the hydroxyl group could occur. So, the unreduced and reduced forms were adsorbed on the surface of the synthesized nanocomposite. Also, the hydroxyl group was oxidized to the carbonyl group, and our results agree with the reported one [36].

Additionally, the synthesized nanocomposite shows the removal of not only anionic forms of heavy metals, as explained before, but also of the cationic forms. Hence, the efficiency of removing the cationic forms of heavy metals could be due to the coordination between the heavy metal and the donor atoms with a lone pair of electrons, such as nitrogen or oxygen [9]. Thus, the prepared novel CS@nZVI-CMC NC could adsorb cationic and anionic forms of heavy metals because it has more active sites. Moreover, the selectivity tests were evaluated by determining each heavy metal removal efficiency under the same adsorption conditions as in industrial or real wastewater, which consists of a mixture of heavy metals and rarely contains a single heavy metal. For instance, the efficacy of the CS@nZVI-CMC adsorbent shows the removal of 96.91 %, 90.00 %, 60.61 %, 52.37 %, and 40.43 % for Cr(VI), As(V), Cd(II), Pb(II) and Mn(II), respectively. It can be observed that there is a slight decrease in the removal capacity for each heavy metal in the case of a mixture of heavy metal contaminants. For instance, Cr(VI) and Mn(II) show a decrease of 2.45 % and 2.21 %, respectively. Moreover, a little bit higher in the decrease of the efficacy in the case of Pb(II) being 4.74 % and As (V) being 5.42 %. The maximum value of the decrease in removing Cd (II) is 9.36 %. The decrease in the removal efficiencies could be attributed to the heavy metal ions interfering with one another, influencing the adsorption of other heavy metal ions [42,47]. Therefore, the synthesized CS@nZVI-CMC NC successfully eliminates the heavy metals simultaneously, and the affinity order was $\text{Cr(VI)} > \text{As(V)} > \text{Cd(II)} > \text{Pb(II)} > \text{Mn(II)}$. Thus, the synthesized NC proved to be a new route to eliminate more than four heavy metals simultaneously, which differs from the reported studies [42].

3.3.2. Pesticide removal from aqueous solution

Residues of pesticides are extensively dispersed in drinking water, groundwater, and soils because they are widely used in agricultural production. Research studies are focused on removing one type or analyte of pesticide from water. Hence, the challenge of this part of the work is to remove several pesticides simultaneously from aqueous

solutions and drinking tap water. Based on the literature studies, the removal of pesticides is increased from low pH values to neutral pH (3 to 7), and the efficiency at pH 7 is not very different when compared to pH 6 [48]; thus, the adsorption experiments were kept at fixed pH of 6 as the adsorption process of heavy metals. Fig. 8 shows the removal efficiencies of organochlorine and organophosphorus pesticides using CS@nZVI-CMC NC. The highest removal efficiencies of organochlorine pesticides were demonstrated in the case of DDE, heptachlor, endrin aldehyde,

endosulfan, and heptachlor epoxide, being 96.52 %, 94.01 %, 70.98 %, 65.39 %, and 63.02 %, respectively, as shown in Fig. 8a. In addition, moderate efficiencies were observed in the case of DDT (22.59 %) and α -BHC (16.09 %). Low efficiency was observed (6.79 %, 5.26 %, 4.69 %, 2.61 %, 2.15 %, and 1.09 %) for DDD, lindane, β -BHC, δ -BHC, aldrin, and dieldrin. The highest removal efficiency of DDE could be attributed to the lowest number of electron withdrawal groups (chloride) compared to DDD. To explain the lowest affinity of dieldrin towards the

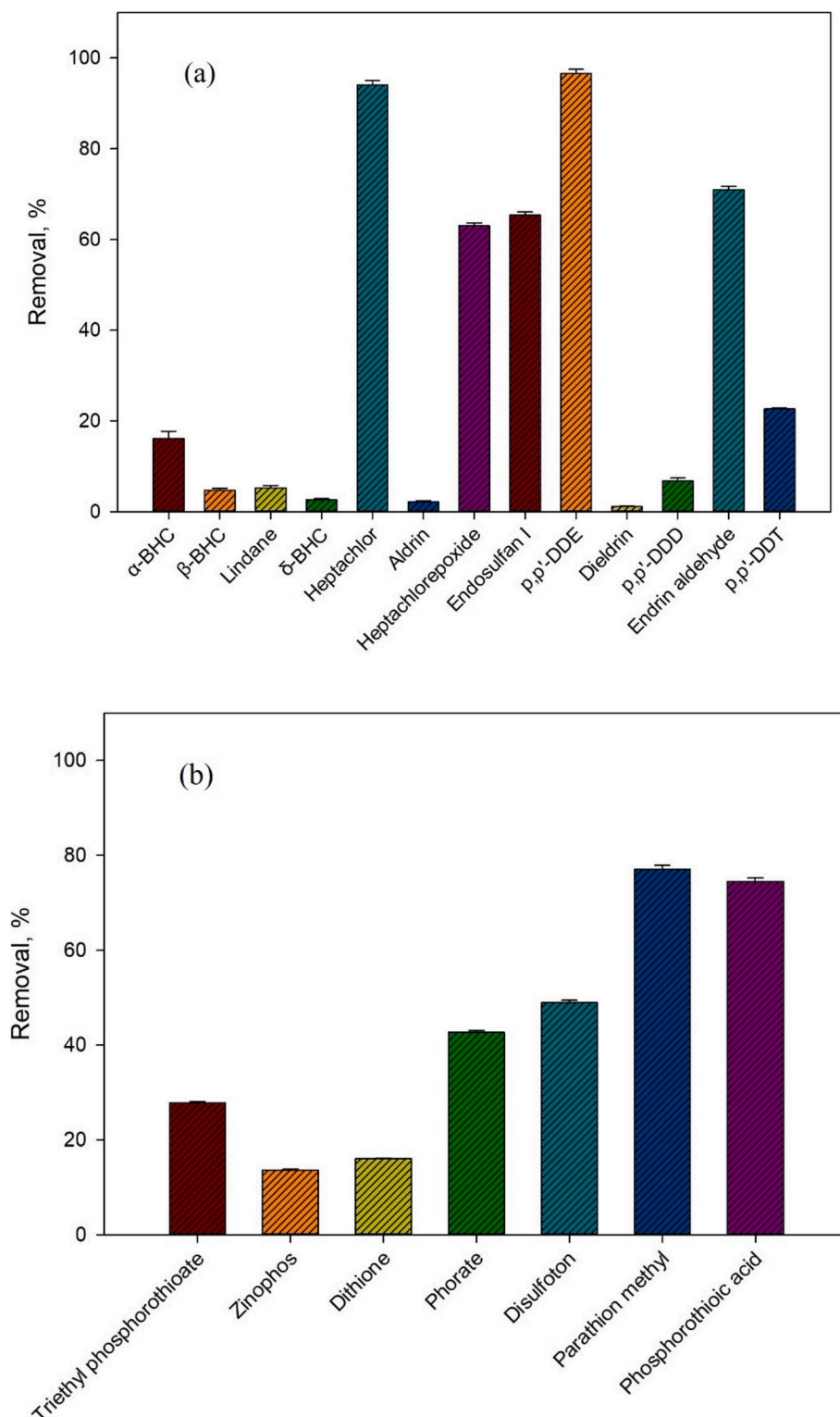


Fig. 8. Pesticides removal using CS@nZVI-CMC NC; (a) Organochlorine pesticides, and (b) Organophosphorus pesticides.

synthesized NC, the presence of a high electronegativity group (oxygen) and withdrawing chloride groups can be important [49]. Fig. 8b shows the adsorption of organophosphorus pesticides using the CS@nZVI-CMC NC. For instance, the removal efficiency was found to be in the following order: parathion methyl (77.09 %) > Phosphorothioic acid (74.49 %) > Disulfoton (48.96 %) > Phorate (42.62 %) > Triethyl phosphorothioate (27.78 %) > Dithione (15.97 %) > Zinophos (13.67 %). The highest removal efficiency of parathion methyl could be attributed to electron transfer between the CS@nZVI-CMC NC and organophosphorus pesticides, hydrogen bonding, or hydrolysis, as shown in the Supplementary Information (Fig. S1) [50].

3.3. Comparison with literature results

The adsorption capacities and removal efficiencies of pesticides and heavy metals using CS@nZVI-CMC NC were compared with other reported adsorbents and summarized in Table 2. The variation in the adsorption capacities of the adsorbents could be attributed to their surface structure and the associated functional groups.

It can be observed that a large number of adsorbents have been used

for the removal of heavy metals and pesticides. Unfortunately, no adsorbents were shown to eliminate more than three heavy metals with high adsorption capacity compared to the NC synthesized in this work. Although Du *et al.* reported a high value of adsorption capacity of the hexavalent chromium (100 mg.g⁻¹) using g-ZVI nanoparticles, the CS@nZVI-CMC NC in this work shows a closer value of removal percentage and adsorption capacity with a lower dosage of adsorbent.

Few studies have reported the efficacy of pesticide removal using nanoparticles, as shown in Table 2 [49,51–53]. The great advantage of the synthesized NC compared to other adsorbents illustrated in Table 2 is the highest adsorption capacity of the pesticides. Thus, the CS@nZVI-CMC NC is a promising adsorbent for water remediation in this pollution scenario.

3.4. Application for drinking water

According to the good results of removing heavy metals and pesticides from aqueous solutions, applications to real water matrices, such as drinking water, are very important. It is well-known that drinking water contains other coexisting ions in the form of cations and anions.

Table 2

Comparison of adsorption capacity and removal of the contaminants with adsorbents reported in the literature.

Adsorbent	Type of Contaminants	Contaminant	Experimental conditions	Removal, %	Q _e , mg ⁻¹ .g ⁻¹ * or μg ⁻¹ .g ⁻¹ **	Reference
Activated carbon	Heavy metals	Cadmium	1 g/L NC, 25 °C, 10 mg/L	33.70	3.37	[54]
FeOOH			2 g/L NC, 35 °C, 100 mg/L	9.88	4.94	[55]
nZVI			0.5 g/L NC, 24 °C, 10 mg/L	60.70	12.14	[56]
Chitin		Lead	2 g/L NC, 25 °C, 100 mg/L	29.40	14.70	[57]
CS@nZVI-CMC			0.1 g/L NC, 25 °C, 10 mg/L	60.61	60.61	This work
CS-Fe/Ag			1.0 g/L NC, 25 °C, 10 mg/L	14.00	1.40	[18]
nZVI		Lead	N.A g/L NC, 25 °C, 200 mg/L	N.A	50.32	[58]
CS@nZVI-CMC			0.1 g/L NC, 25 °C, 10 mg/L	52.73	52.73	This work
CMC-nZVI			1.0 g/L NC, 25 °C, 100 mg/L	80.00	80.00	[32]
nZVI		Arsenic	1.0 g/L NC, 25 °C, 10 mg/L	35.00	3.50	[59]
CV/nZVI			1.5 g/L NC, 25 °C, 100 mg/L	10.14	6.76	[60]
nZVI/AC			1.0 g/L NC, 25 °C, 100 mg/L	12.00	12.00	[61]
CMC-nZVI		Manganese	0.3 g/L NC, 25 °C, 10 mg/L	42.00	14.00	[62]
Mn/SA-BC@nZVI			0.5 g/L NC, 25 °C, 10 mg/L	90.17	18.03	[63]
Fe ₃ O ₄			0.5 g/L NC, 25 °C, 100 mg/L	29.10	58.20	[64]
CS@nZVI-CMC	Heavy metals	Manganese	0.1 g/L NC, 25 °C, 10 mg/L	90.00	90.00	This work
nZVI			0.1 g/L NC, 25 °C, 2 mg/L	38.55	7.71	[65]
nZVI/RSBC			0.5 g/L NC, 25 °C, 40 mg/L	14.79	11.83	[66]
Phosphate coated nZVI		Hexavalent chromium	0.1 g/L NC, 25 °C, 2 mg/L	82.60	16.52	[65]
CA/nZVI/RSBC			0.5 g/L NC, 25 °C, 40 mg/L	26.90	21.52	[66]
CS@nZVI-CMC			0.1 g/L NC, 25 °C, 10 mg/L	40.43	40.43	This work
FP-nZVI		Hexavalent chromium	0.8 g/L NC, 25 °C, 20 mg/L	48.64	12.16	[67]
nZVI			0.1 g/L NC, 25 °C, 10 mg/L	18.73	18.73	[68]
nZVI@SBC-KOH			1.0 g/L NC, 25 °C, 50 mg/L	99.36	49.68	[69]
PEG-nZVI/D201		Hexavalent chromium	1.0 g/L NC, 25 °C, 100 mg/L	76.22	76.22	[70]
nZVI/ZIF-8			0.5 g/L NC, 25 °C, 50 mg/L	80.35	80.35	[71]
CMC-nZVI@BC			0.1 g/L NC, 25 °C, 10 mg/L	80.71	80.71	[68]
CS@nZVI-CMC		Hexavalent chromium	0.1 g/L NC, 25 °C, 10 mg/L	96.91	96.91	This work
g-nZVI			0.5 g/L NC, 25 °C, 50 mg/L	100.00	100.00	[72]
Fe ₃ O ₄ @UiO-6@UiO-67/CTAB			1.0 g/L NC, 25 °C, 50 mg/L	90.14	112.68	[73]
S-nZVI	Pesticides	Heptachlor	50.0 g/L NC, 25 °C, 550 μg/L	88.18	9.70	[51]
CS@nZVI-CMC			0.1 g/L NC, 25 °C, 100 μg/L	94.01	940.10	This work
nZVI			1.0 g/L NC, 25 °C, 2.9 μg/L	91.00	2.64	[52]
CS@nZVI-CMC		Dieldrin	0.1 g/L NC, 25 °C, 100 μg/L	5.26	52.60	This work
nZVI			1.0 g/L NC, 25 °C, 2.2 μg/L	93.00	2.05	[52]
CS@nZVI-CMC			0.1 g/L NC, 25 °C, 100 μg/L	1.09	10.90	This work
Fe/Pd		DDE	1.0 g/L NC, 25 °C, 2.2 μg/L	99.54	235.27	[53]
CS@nZVI-CMC			0.1 g/L NC, 25 °C, 100 μg/L	96.52	965.20	This work
CS@nZVI-CMC		DDT	0.1 g/L NC, 25 °C, 100 μg/L	22.59	225.90	This work
nZVI			0.55 g/L NC, 25 °C, 250 μg/L	85.00	386.36	[53]
Fe/Pd			0.55 g/L NC, 25 °C, 250 μg/L	90.00	409.09	[53]

* Q_e (mg⁻¹ g⁻¹) corresponds to the equilibrium adsorption capacity of heavy metals.

** Q_e (μg⁻¹ g⁻¹) corresponds to the equilibrium adsorption capacity of pesticides.

For instance, the main characteristics of the drinking tap water were found to be: pH 7.44, chloride (67.39 mg/L), nitrate (2.17 mg/L), sulfate (30.96 mg/L), sodium (39.32 mg/L), and magnesium (23.10 mg/L). In addition, the heavy metals and pesticides under investigation were not detected in the drinking water matrix. So, the efficiency of the CS@nZVI-CMC NC was evaluated through the treatment of drinking water spiked with the contaminants under investigation. The unspiked tap water sample showed no contaminants (below the detection limit). Moreover, the NC in this study shows a similar tendency to that found with simultaneous heavy metal and pesticide removal from aqueous solutions. For instance, the removal efficiency of heavy metals was found to be 91.63 %, 85.24 %, 59.19 %, 50.46 %, and 39.24 % for Cr (VI), As(V), Cd(II), Pb(II), and Mn(II), respectively. A slight decrease in the removal efficiencies could be observed in the case of the cationic forms of heavy metals compared to the anionic forms. The reduction of efficiency could be attributed to the competitive adsorption of the anions in the drinking tap water [72]. In addition, a decrease in removing both organochlorine and organophosphorus pesticides was found, which could be attributed to the presence of other elements in the water matrix. For instance, the order of the OCP elimination was found to be DDE (94.15 %) > heptachlor (93.23 %) > endrin aldehyde (70.98 %) > endosulfan (69.05 %) > heptachlor epoxide (61.13 %) > DDT (22.21 %) > α -BHC (15.24 %) > DDD (5.16 %) > lindane (4.02 %) > β -BHC (3.56 %) > δ -BHC (2.13 %) > aldrin (1.61 %) > dieldrin (0.74 %). Also, the CS@nZVI-CMC NC exhibited 72.16 %, 70.69 %, 47.34 %, 40.09 %, 24.13 %, 13.52 %, and 11.97 % removal of Parathion methyl, Phosphorothioic acid, Disulfoton, Phorate, Triethyl phosphorothioate, Dithione, and Zinophos, respectively. Therefore, it can be concluded that the CS@nZVI-CMC NC could be successfully applied to a real water matrix.

3.5. Proposed adsorption mechanism for heavy metals and pesticides

The availability of functional groups and active sites of zero-valent iron nanoparticles has been previously reported [9]. Besides, the synthesized CS@nZVI-CMC NC shows several functional groups, as previously explained in detail. The nZVI in the synthesized NC also has core-shell properties in aqueous solutions. For this reason, it is essential to propose an adsorption mechanism based on the NC characterization. In the case of this NC, the core consists of metallic iron, and the shell is an oxide layer of Fe^{2+} and Fe^{3+} due to the quick oxidation of iron in the environment where the ZVI reacts with water and oxygen to form an iron hydroxide layer [9]. Metallic iron could enhance the reduction of

several contaminants in the environment due to its reducing properties, and it acts as an electron donor. In addition, the iron hydroxide layer (shell) acts as an efficient adsorbent for pollutants such as heavy metals [9]. Therefore, the CS@nZVI-CMC NC in water can form a coordination bond between the metal and ligand depending on the pH of the aqueous solution. Heavy metal removal, cationic forms such as Pb(II), Cd(II), and Mn(II), can be explained in two main steps: the heavy metal is first reduced by the effect of ZVI in an aqueous solution as a result of the pH of the aqueous solution (6). Then, the heavy metal is adsorbed onto the core-shell structure of the synthesized nanocomposite [9]. For instance, the FTIR of the CS@nZVI-CMC NC before and after the adsorption of Pb^{2+} , as a selected example of heavy metal in this study, is shown in [Supplementary Information \(Fig. S1\)](#). It can be observed that there is a decrease and a slight shift in the peak at 3267 cm^{-1} , which corresponds to $-\text{NH}_2$, $-\text{OH}$, and the band at 1311 cm^{-1} , which corresponds to $-\text{CN}$ and $-\text{C}-\text{O}-\text{C}$ compared to the adsorbent before Pb^{2+} treatment. More evidence of the Pb^{2+} adsorption onto the synthesized NC is illustrated in the [Supplementary Information \(Fig. S2\)](#). The surface of the CS@nZVI-CMC NC was covered by the Pb^{2+} , as shown in the SEM image ([Fig. 9](#)), and its demonstration was presented in the elemental mapping after adsorption by the appearance of the Pb^{2+} profile using the EDS technique ([Fig. 9](#)). Therefore, the adsorption mechanism of heavy metal is mainly controlled by adsorption and other processes such as electron transfer and reduction. Our results agree with reported studies in which heavy metal removal in solutions could undergo one or more routes, such as physisorption, reduction, complexation and/ or precipitation [29,74].

One of the adsorption mechanisms for the degradation of the pesticides on the surface of the nanomaterial could be explained by the effect of surface hydroxyl groups on the surface of the NC, where it could hydrolyze the pesticides via the polarization of the oxygen-hydrogen bonds of the water molecule (indirect way) or the nucleophilic substitution at the phosphorus or chloride atoms (direct route) [75]. The other possible mechanism of pesticide removal is the electrostatic interaction of the positively charged amine group at pH 6 and the anion form of the pesticides [76] or the formation of hydrogen bonds between the hydroxyl group of the nanomaterial and the phosphorus, oxygen, or other electron donor group. Some possible evidence of the adsorption of organochlorine and organophosphorus pesticides is shown in the [Supplementary Information \(Fig. S3\)](#). It can be observed that after adsorption of the organophosphorus pesticides, the intensity of the absorption band of $-\text{NH}_2$ and $-\text{OH}$ groups at 3277 cm^{-1} was decreased and shifted when compared to those of NC before adsorption. This confirms an

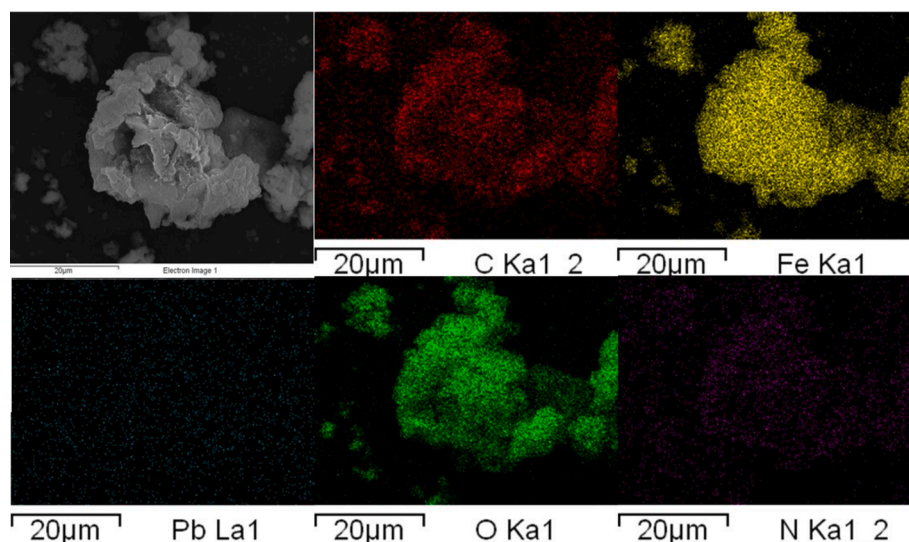


Fig. 9. SEM image and elemental mapping profile of CS@nZVI-CMC NC after Pb^{2+} adsorption.

interaction of the electron donor atom of pesticides with the hydroxyl group of the CS@nZVI-CMC NC by forming a hydrogen bond [77]. Additionally, the absorption bands were found at 3191 cm^{-1} (—CH stretching), 1645 cm^{-1} (C=N stretching), 1418 cm^{-1} (S=O stretching), 1305 cm^{-1} (C—O aromatic ester), and 687 cm^{-1} (benzene derivatives) [28]. Furthermore, in the case of organochlorine pesticide adsorption, a confirmation of the adsorption was observed by the distinct peaks at 3180 cm^{-1} (—CH stretching), 1625 cm^{-1} (C=C stretching for disubstituted in cis position), 1385 cm^{-1} (—CH bending), and 685 cm^{-1} (C—Cl stretching and benzene derivatives). Unfortunately, practically no studies report detailed adsorption mechanisms of several pesticides with complex high-efficiency adsorbents. In any case, this can be considered the first approach to the explanation of this phenomenon.

4. Conclusions

In this work, we successfully synthesized a novel CS@nZVI-CMC NC using a simple and easy-to-scale method. We used it as an adsorbent for heavy metals and pesticide removal simultaneously from pure aqueous solutions and drinking water. TEM and SEM techniques show a spherical nanoparticle with an average size of $7.56 \pm 1.86\text{ nm}$. Moreover, the CS@nZVI-CMC NC exhibited a surface area of $127.95\text{ m}^2/\text{g}$. The CS@nZVI-CMC NC demonstrated the removal of heavy metals in the following order: $\text{Cr(VI)} > \text{As(V)} > \text{Cd(II)} > \text{Pb(II)} > \text{Mn(II)}$. Also, it presents high efficiency in removing organochlorine pesticides, for example, DDE (98.52 %) and heptachlor (94.01 %). In addition, the synthesized NC proved the removal of organophosphate pesticides, parathion methyl (77.09 %), and phosphorothioic acid (74.49 %), among other pesticides. Moreover, high removal efficiencies were found in the case of spiking drinking tap water with heavy metals, organochlorine, and organophosphorus pesticides. According to adsorbent observations after treatment, the main adsorption mechanism of pesticide and heavy metal removal was based on adsorption and electron transfer processes. Based on these results, future research will be focused on (1) optimizing the adsorption process for both heavy metals and pesticides and determining the optimum time for contaminants removal under investigation through kinetic study as well as the estimation of the maximum adsorption capacities of each contaminant via the isotherms tests, (2) extending the efficiency of the synthesized nanomaterial in wastewater treatment, (3) evaluating its performance via NC recovery and reusability, and (4) studying the effect of interferences between heavy metals, pesticides, and a mixture of both types of contaminants. Anyway, the CS@nZVI-CMC NC can be a promising water and wastewater treatment adsorbent.

CRediT authorship contribution statement

Ahmad Abo Markeb: Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Javier Moral-Vico:** Writing – review & editing, Validation. **Antoni Sánchez:** Writing – review & editing, Resources, Funding acquisition. **Xavier Font:** Writing – review & editing, Validation, Supervision, Resources, Funding acquisition.

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Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rechem.2025.102041>.

Data availability

Data will be made available on request.

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