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## **Applications of Chitosan in Wastewater Treatment**

Petronela Nechita

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#### **Abstract**

In the last time, the use of natural additives that are biocompatible, are biodegradable, have low toxicity and are from renewable resources attracted attention of many researchers due to their high ability to retain different pollutants from wastewaters. In this context, there are many research studies that highlight the biosorbent ability of chitosan and their composites for the pollutants from wastewaters such as heavy metal ions, organochloride pesticides, suspended solids, turbidity, organic oxidised substances, fatty and oil impurities or textile wastewater dyes. Furthermore, the increase of adsorption ability of chitosan by chemical modifications leading to the formation of chitosan derivatives, grafting chitosan and chitosan composites gained much attention, being extensively studied and widely reported in the literature. In this chapter the research studies regarding the chitosan application in wastewater treatments as well as the preliminary results on its chemical modification to obtain and utilisation of zeolitechitosan composites in adsorption of organic pollutants from industrial wastewaters are presented.

**Keywords:** Chitosan, Chitosan composites, Wastewaters, Chitosan-magnetite, Chitosan-zeolites, Adsorption isotherm, Adsorption kinetics, Pollutants, Total suspended solids, Chemical oxygen demand, Heavy metal ions, Removal efficiency

#### 1. Introduction

In the last time, different wastewater decontamination methods that include chemical precipitation, nanofiltration, solvent extraction, ion exchange, reverse osmosis and adsorption have been extensively studied. Out of these methods, adsorption is particularly attracting scientific focus mainly because of its high efficiency, low cost and easy handling and high availability of different adsorbents [1].



Chitosan is a versatile polysaccharide widely distributed in nature (second most abundant biopolymers after cellulose) produced by alkaline N-deacetylation of chitin. Many application fields are described in scientific publications regarding the use of chitin, chitosan and their derivatives. Wastewater treatment using chitin or chitosan is an important application. According to this, there are many research studies that highlight the biosorbent ability of chitosan and their composites to remove the pollutants from wastewater. They could be used as coagulating/flocculating agents for polluted wastewaters [2, 3], in heavy metal or metalloid adsorption (Cu(II), Cd(II), Pb(II), Fe(III), Zn(II), Cr(III), etc.) [4, 7, 8] for the removal of dyes from industrial wastewater (i.e. textile wastewaters) [6], as well as for the removal of other organic pollutants such as organochloride pesticides, organic oxidised or fatty and oil impurities.

Due to the high performances, chitosan derivatives are used as adsorption additives [5] in many research investigations. Some examples are derivatives that contain heteroatoms based on nitrogen, phosphorous and sulphur or complex combinations of chitosan with ethylene-diaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA).

In the last time, the chitosan composites have been tested in wastewater treatments for adsorption of dyes [6] and heavy metals [7–9]. To form composites with chitosan, different substances have been used, such as montmorillonite, polyurethane, activated clay, bentonite, zeolites, oil palm ash, calcium alginate, polyvinyl alcohol, cellulose, magnetite, sand, cotton fibres, perlite and ceramic alumina [10–14].

This chapter highlights the application of chitosan and their composites (zeolite-chitosan composites) as adsorbents and flocculants in wastewater treatments including the method of preparation, mechanisms/kinetics and factors that can affect their efficiency in the pollutant adsorption capacity (pH, biosorbent dosage, contact time). Some experimental results obtained on static adsorption methods applied on industrial and municipal wastewaters are presented.

#### 2. Chitosan in wastewater treatments

#### 2.1. Chitosan structure and properties

Chitosan is a partially deacetylated polymer obtained by the alkaline deacetylation of chitin, a biopolymer extracted from shellfish sources. It is a linear hydrophilic amino polysaccharide with a rigid structure containing both glucosamine and acetylglucosamine (poly- $\beta$ -(1  $\rightarrow$  4)-2-amino-2-deoxy-p-glucose) units (**Figure 1a**). Chitin (poly- $\beta$ -(1  $\rightarrow$  4)-*N*-acetyl-p-glucosamine) can be characterised as one of the most abundant natural biopolymers (**Figure 1b**) [15].

Native chitosan is insoluble in water or organic solvents, but at acidic pH (below pH 5), when the free amino groups are protonated, chitosan becomes a soluble cationic polymer with high charge density [16–18].

The infrared (IR) absorption spectra of chitosan and chitin are presented in **Figure 2**. It can be observed that three types of absorption bands exist: the amide I bands of chitosan characterised

by absorption at approximately 1655 and 1630 cm<sup>-1</sup>, the amide II bands of chitin at approximately 1560 cm<sup>-1</sup> and the absorption bands for –OH groups at 3450 cm<sup>-1</sup> [19].

Figure 1. Chemical structural representation of chitin (a) and chitosan (b).

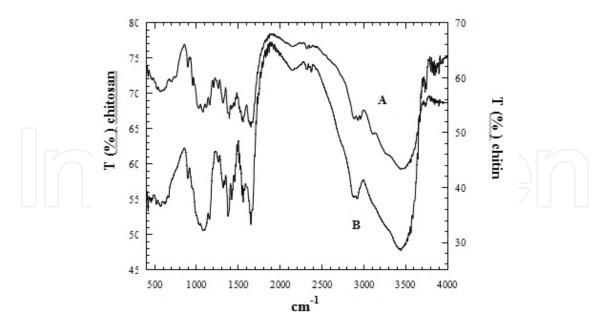


Figure 2. Infrared spectra of chitin (A) and chitosan (B) [19].

Chitosan has many attractive properties such as hydrophobicity, biocompatibility, biodegradability, non-toxicity and the presence of very reactive amino (–NH<sub>2</sub>) and hydroxyl (–OH)

groups in its backbone, which makes chitosan to be used as an effective adsorbent material for the removal of wastewater pollutants.

The main advantage of chitosan over other polysaccharides (cellulose or starch) is their chemical structure that allows specific modifications to design polymers for selected applications. On the one hand, their *reactive groups* are able to develop composites with different compounds that have proven to have better capacity to adsorb the wastewater pollutants and to resist in acidic environment. Some examples include bentonite, kaolinite, oil palm ash, montmorillonite, polyurethane, zeolites, magnetite, etc. On the other hand, their *cationic charge* (chitosan is single cationic biopolymer) is able to neutralise and successfully flocculate the anionic suspended colloidal particles and reduce the levels of chemical oxygen demand, chlorides and turbidity in wastewaters [2, 3].

#### 2.2. Chitosan as flocculant/coagulant of pollution colloid impurities

Flocculation is an essential phenomenon in industrial wastewater treatment. Organic polymeric flocculants are widely used nowadays due to its remarkable ability to flocculate efficiently with low dosage compared with inorganic coagulants (salts of multivalent metals) that are being commonly used (due to its low cost and ease of use) but have low flocculating efficiency and present the residual concentration of metal in the treated water. In this context, the coagulation and flocculation properties of chitosan (given by their cationic charge) can be exploited to remove the negative-charged colloidal organic or inorganic impurities from wastewaters [16].

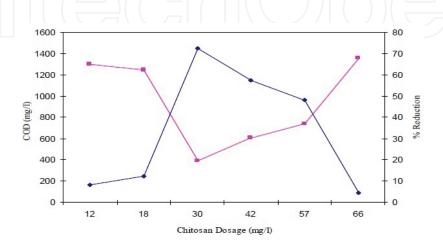
Since most pollution colloids are negatively charged, cationic polymers or polyelectrolytes are of particular interest as potential coagulants/flocculants. Due to its cationic unique feature, chitosan is one of the most promising biopolymers for extensive application in wastewater treatment, and its coagulative action is very effective compared with the mineral coagulants such as aluminium sulphate, polyethyleneimine and polyacrylamide in removing different pollutants from aqueous solution [20, 21].

The protonated amine groups along the chain obtained by dissolving of chitosan in acids facilitate electrostatic interactions between polymer chains and the negatively charged contaminants (metal anions, dyes, organic compounds, etc.) [16]. Due to the presence of primary amino groups, the biopolymer has a high cationic charge density [22] and long chains with high molecular weight, being an effective coagulant and/or flocculant for the removal of contaminants in the suspended and dissolved state [16, 23,24]. The active amino groups (NH<sub>2</sub>) in the chitosan molecule can be protonated with H+ in water into a cationic polyelectrolyte [25] such that the molecule has characteristics of static attraction and adsorption. Chitosan coagulation produces better quality floaters, namely, larger floaters with faster settling velocity. The effectiveness of chitosan for coagulating mineral suspensions can be improved due to the presence of inorganic solutes or due to the addition of materials extracted from soils at high pH [26].

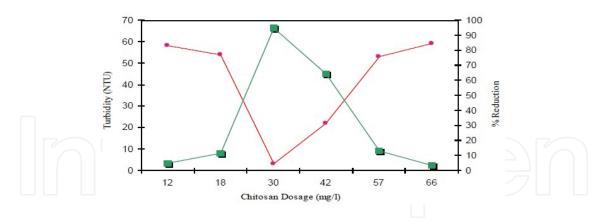
Based on the high affinity of chitosan for different contaminants, there are many studies where these properties of chitosan for removing of dyes from solution [22] or textile waste-

water [27, 28], organic matter (e.g. lignin and chlorinated compounds) in pulp and paper mill wastewater [29], heavy metals and phenolic compounds in cardboard-mill wastewater [30, 31] and inorganic suspensions in kaolinite suspension are demonstrated [32].

In this context, Abu Hassan et al. in their research, have emphasised that a chitosan dosage between 12 mg/l and 30 mg/l lead to an important decreasing of chemical oxygen demand and turbidity (**Figures 3** and **4**) as result of high charge density of chitosan that has effect to quickly destabilisation of colloidal equilibrium [33].



**Figure 3.** Effects of chitosan dosage on COD level and the percentage of COD level reduction: ¬■¬, COD level and ¬◆¬, % COD level reduction [33].



**Figure 4.** Effects of chitosan dosage on turbidity level and the percentage of turbidity level reduction by using chitosan, ● -, turbidity level and - ■ -, % turbidity level reduction [33].

Zeenat et al. [3] have extracted the chitosan from Indian prawn and used it in treatment of wastewaters from ghee industry. They examined the flocculation process regarding the influence parameters such as chitosan dosage, optimum pH and mixing times. The chitosan showed significant difference by successfully flocculating the negatively charged suspended particles, thereby reducing chemical oxygen demand with 80.1 %, turbidity with 91.8 %, total dissolved solids with 72.5 % and conductivity of analysed wastewaters with 73.7 % (**Table 1**).

Parameters	Wastewater from ghee industry	Chitosan-treated wastewater	Reduction, %
COD, mg/l	1934	383	80.1
TDS, mg/l	3108	852	72.5
Conductivity, µS/cm	1987	521	73.7
Turbidity, NTU	69	5.6	91.8

Table 1. Effect of chitosan treatment on the ghee wastewater quality [3].

In our studies [34, 35] we have been using the chitosan (with high molecular mass and 20.8 % acetylation degree) to remove the pollutants from textile wastewaters. The obtained results highlighted a high efficiency for suspended solid removal (99.65%), for chemical oxygen demand (70.5%) and about 79.57% for grease impurity removal (**Table 2**).

Pollution indicator	Before the treatment	After the treatment	The wastewater pollutant
	with chitosan	with chitosan	removal efficiency, %
Total suspended solids, mg/l	5798	20.0	99.65
COD, mg/l	51.5	15.17	70.5
Sulphides, mgH <sub>2</sub> S/l	5.64	4.2	25.53
Greases and oil content (extractives in organic solvents), mg/l	1351	276	79.57

**Table 2.** The wastewater pollutant removal efficiency after chitosan treatment.

For a dosage of about 1 g chitosan/100 ml wastewater and mixing duration of about 60 min, a high efficiency for dye removal from textile wastewaters was registered (Figure 5).

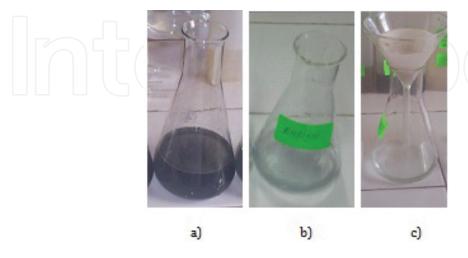


Figure 5. Variation of textile wastewater colour after treatment with (a) initial wastewater, (b) synthetic resin Purolite C100 and (c) chitosan.

#### 2.3. Chitosan as adsorbent of metal ions

Adsorption has been proven to be a reliable and economical alternative to remove the pollutants from wastewaters, and the use of chitosan as biosorbent for heavy metal ions is reported in a large quantity of literature studies.

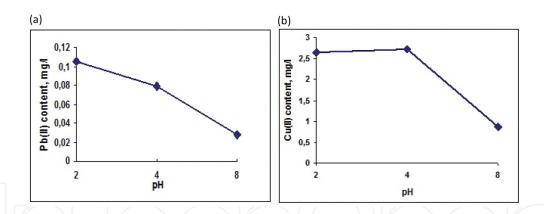
The bond between the metal ion and chitosan functional groups in the biosorption process involves different phenomena as complexation, electrostatic attraction, micro-precipitation and ion exchange. The mechanism of complex formation between chitosan and metal ions during adsorption process can be developed in two ways:

*Bridge model*: metal ions are bonded with various amino groups from the same chain or from different chains through complex inter- or intramolecular reactions.

Pendant model: metal ions are bonded with amino groups in a hanging manner.

In our experiments, we tested the adsorption ability of chitosan for heavy metal ions from textile wastewaters (Cu(II) and Pb(II)) and aqueous solutions (Zn(II) and Fe(III)).

The removal efficiency was 91.67 % for Pb ions and 54.15 % for Cu ions, being influenced by pH value which is a very useful parameter that affects the surface charge of wastewater solutions in terms of stability of suspensions. In our studies the maximum adsorption of Cu(II) and Pb(II) ions from textile wastewaters was obtained at pH value of 8 (**Figure 6 (a)** and **(b)**).



**Figure 6.** The influence of pH value on the adsorption of metal ions from wastewater: (a) Pb(II) content and (b) Cu(II) content.

The main functional groups of chitosan which are potential points for adsorption of metal ions are -OH and  $-NH_2$ . In pH acid conditions, these groups are protonated  $(-OH_2^+, -NH_3^+)$  and make the adsorption of metal ions to be reduced. As pH value increases, the degree of protonation of functional groups decreases. This influences the process forming of complex coordination bonds between the metal ions and functional groups.

In the experiments regarding the adsorption capacity of Zn<sup>2+</sup> ions in aqueous solution on the chitosan, we used three different samples of chitosan, a pure chitosan (having a 55.94 % acetylation degree) and two commercial products [36]. The influence of temperature (20, 40, 60 °C) on the dissociation process was verified by pH and conductivity measurements. The

effects of chitosan dosage (0.1 g, 0.2 g), heavy metal concentration (10–20 g L<sup>-1</sup> Zn<sup>2+</sup>), contact time (15–60 min) and mixing rate (450 rpm) on adsorption efficiency were studied. During the adsorption process, Zn<sup>2+</sup> ions were chelated by chitosan through the amine groups in the fibres. The duration of action of the metal ions on chitosan is the main factor affecting the final product. The complex formed between chitosan and Zn was analysed by spectrophotometric method at  $\lambda$  of 264 nm (**Figure 7(a)** and **(b)**).

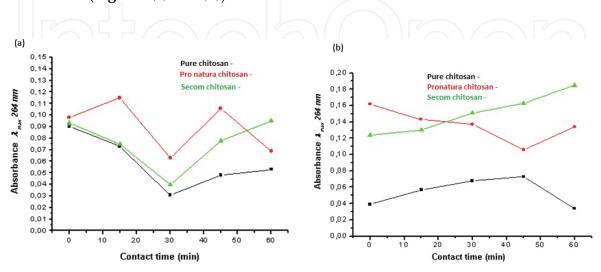


Figure 7. Chitosan-Zn<sup>2+</sup> ion interaction effects: (a) 0.1 g chitosan dosage and (b) 0.2 chitosan dosage.

High quantity of chitosan in complex formed between chitosan and Zn involves longer contact time to reach the adsorption equilibrium. The obtained results showed that chitosan can be used to retain Zn<sup>2+</sup> ions in certain systems (e.g. farmlands and industrial wastewater). Chitosan as adsorbent could be regenerated and reused, being an effective adsorbent for zinc ions and other metal ions from wastewater [36].

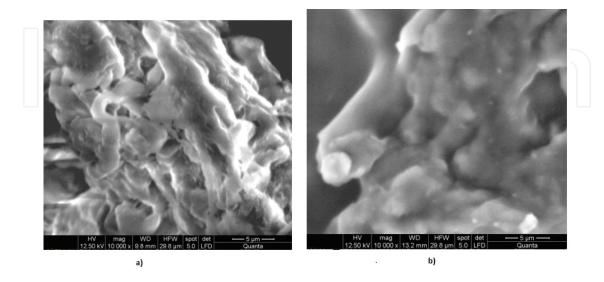


Figure 8. SEM structural analysis of chitosan (a) and chitosan-Fe(III) chelated complex (b).

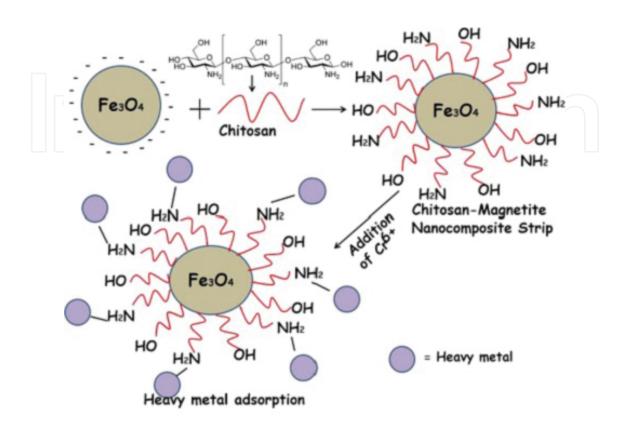
In other research studies, the removal of Fe(III) ions from aqueous solution using chitosan was studied [37]. Retention of Fe(III) ions on chitosan is influenced by factors as contact time, the concentration ratio of the phases, pH and mixing rate. Retention of Fe(III) ions on chitosan is strongly dependent on the pH changes. For pH lower than 3, chitosan is dissolved, and for pH higher than 4.5, a colloid solution is obtained. The equilibrium of the chitosan adsorption is established relatively quickly, after 60 min, and the adsorption capacity for retaining the Fe(III) ions is more than 80 % (mg/g). Scanning electron microscope (SEM) images showed the formed complexes and the chemical modification of chitosan depends on the ion concentration. Structural analysis by SEM provides an indication that the mechanism of adsorption of Fe(III) ions on chitosan is a complex phenomenon involving the formation of nodosities on the chitosan structure. The mechanism of retention of Fe(III) ions on chitosan is a complex phenomenon and involves the formation of lumps on the structure of chitosan through the surface adsorption of metal ions and strong coordination with functional groups (Figure 8).

### 3. Chitosan composites in wastewater treatment

Chitosan is a very promising adsorbent, which can be modified in many ways (grafting, cross linking, functionalisation for forming composites, etc.). Because chitosan is very sensitive to pH, forming either gel or dissolve depending on pH values, some cross linking reagents such as glyoxal, formaldehyde, glutaraldehyde, epichlorohydrin, ethylene glycon diglycidyl ether and isocyanates have been used to improve its performance as adsorbent [38]. This process of cross linking stabilises chitosan in acid solutions becoming insoluble and enhances its mechanical properties [39]. A large volume of works has been published during the last three years, presenting results of chitosan-modified adsorbents for the removal of various pollutants (dyes, metals/ions, others).

Recently, chitosan-based metal particle composites have been studied increasingly as an alternative adsorbent in water treatment, such as using metals [40], metal oxides [41], magnetite [42] and bimetals [43], to adsorb heavy metals and dyes from wastewater. For example, chitosan-coated magnetite nanoparticles (CMNP) were prepared and used as bactericidal agent to remove organic contaminants and bacteria from water [14].

Moradi Dehaghi et al. [44] in their research have developed the chitosan-ZnO nanoparticle composites by sonication process. The dissolution and swelling studies were performed on these composites, and crystallinity and surface morphology characterisation using X-ray diffraction, Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscope of nanocomposite samples were studied. The testing of sorbent performance of these materials was carried out on pesticide adsorption from aqueous solution of permethrin 25 % using a column of chitosan-ZnO nanocomposite beads. It was demonstrated that the CS/ZnONP beads had an excellent adsorption performance. In comparison with chitosan beads, the removal efficiency of CS/ZnONP beads was increased from 49 % to 99 %. The adsorption and regeneration studies of permethrin demonstrated that the CS/ZnONP beads could be reused effectively with 56 % regeneration after three cycles in on-line column. Based on the high sorbent capacity, CS-ZnONP beads could explore a new biocompatible and eco-friendly strategy for pesticide removal and could be used in water treatment process.



**Figure 9.** Schematic representation of removal mechanism of chromium ions by chitosan-magnetite nanocomposite strip [42].

In their studies, Sureshkumar et al. [42] have synthesised magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub>) using co-precipitation method. After UV-VIS, X-ray diffraction and atomic force microscopy characterisation, these nanoparticles were mixed with chitosan solution to form hybrid nanocomposites. The affinity of hybrid nanocomposite for chromium was studied using  $K_2Cr_2O_7$  (potassium dichromate) solution as the heavy metal solution containing Cr(VI) ions. Adsorption tests were carried out using hybrid nanocomposite strips at different time intervals compared with chitosan-only strip (**Figure 9**).

The chromium removal efficiency of chitosan strip is 29.39 % and that of the chitosan-magnetite nanocomposite strip is 92.33 %. Based on these results, the chitosan-magnetite nanocomposite strips are highly efficient for chromium removal from tannery wastewaters.

Abd-Elhakeem et al. [14] have prepared chitosan-coated magnetite nanoparticles and used it as adsorbent, chelating agent or bactericidal agent to remove organic contaminants, heavy metals and bacteria from water. In their research they find that the adsorption capacities of the different contaminants considerably increased with chitosan-magnetite nanoparticle concentration. The highest affinity was found for petroleum impurities, where 1 g of CMNP removed about 98 % from it, while the lowest capacity was recorded by heavy metals (**Figure 10**).

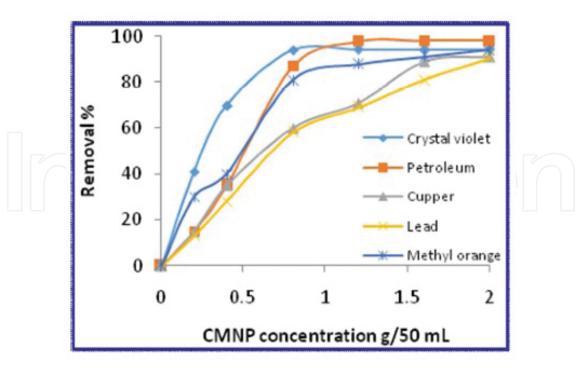


Figure 10. The influence of CMNP concentration on the removal % of different contaminants [14].

In the same studies, the influence on the bacterial growth was partially inhibited at concentration 0.1 g/ml of CMNP. The complete growth inhibition has occurred at concentration of 0.5 g/10 ml.

Hritcu et al. [45] in their research have evaluated the performances of composite chitosan-magnetite microparticles (Fe-Cc) as a new adsorbent for cobalt and nickel ion separation from aqueous solutions. Their sorption batch experiments were conducted for optimising the pH, initial target ion concentration and adsorbent amount. The experimental data have emphasised that Langmuir isotherm model is the best fit; the material has a maximum adsorption capacity of 588.24 mg/g for cobalt ions and, respectively, 833.34 mg/g for nickel ions. Regeneration study demonstrated that Fe-Cc particles might be reused up to three times without significant loss in adsorption capacity.

Saifuddin and Dimara [46] have investigated the potential and effectiveness of applying chitosan-magnetite nanocomposite particles as a primary coagulant and flocculants compared with chitosan for pretreatment of palm oil mill effluent (POME). The experiments were carried out under different conditions of dosage and pH, and the performance was assessed in terms of turbidity, total suspended solids (TSS) and chemical oxygen demand (COD) reductions. At the optimum conditions of pH and chitosan-magnetite, dosage was obtained about 98.8% reduction of turbidity, 97.6% of TSS and 62.5% for COD level. The synergistic effect of cationic character of both the chitosan amino group and the magnetite ion in the pretreatment process for POME brings about enhanced performance for effective agglomeration, adsorption and coagulation. It is important to mention that the chitosan-magnetite nanocomposite has a high efficiency (about 99%) to remove the oil residue from POME, better than chitosan only. The results showed that coagulation with chitosan-magnetite or chitosan was an effective and

environmentally friendly pretreatment technique for palm oil mill effluent wastewater compared to alum and alum polychloride-PAC which creates hazardous residual waste.

#### 3.1. Chitosan-zeolite composites in wastewater treatment

Due to their thermal and chemical stability and great potential for the separation of ions by cation exchange, zeolites are especially appealing among all kinds of inorganic fillers. The cation exchange capacity of the zeolites therefore depends on the framework Si/Al ratio and decreases with an increase of the Si/Al ratio.

Chitosan-zeolite composites have shown good adsorption properties for different pollutants such as dyes, phosphates, nitrates, ammonium and humic acids [47–49] as well as for the removal of heavy metal cations [50, 51].

Nesic et al. [52] in their research presented data about synthesis of chitosan-zeolite composite films and its application on adsorption of anionic dye (Bezactive orange 16 (BO16)) from aqueous solutions. The equilibrium data were fitted to Langmuir and Freundlich models, presenting Qm = 305.8 mg/g. This value was taken at pH = 6, which based on preliminarily results was found to be optimum.

Wan Ngah et al. [53] in their studies have prepared chitosan-zeolite (CZ) composite adsorbent to remove Cu(II) ions from aqueous solutions. The kinetic, adsorption isotherm and desorption studies have been completed. The optimum pH value was 3 and the best isotherm was fitted by the Redlich-Peterson and Langmuir models. The percentage of Cu(II) desorption was only 47.97%, which indicated that the Cu(II) ions were strongly bonded to the CZ surface.

Our studies were focused on obtaining of chitosan-zeolite (CZ) composites using commercial chitosan and zeolites from local volcanic tuff deposits with 71–83.3% of clinoptilolite contents. These composites were applied on organic impurities adsorption from poultry farm wastewaters. Chitosan-zeolite composites have been prepared by the encapsulation method according to the procedure described by Wan Ngah et al. [53] as follows: chitosan and zeolite were mixed in acetic acid solution (5%) and stirred for 2 h. At this mixture acetic acid solution was added (5%) and stirring continued about 1 h. Aiming to form the composite beads, the obtained suspension was added dropwise into the precipitation bath containing NaOH, and the mixture was stirred for 3 h. The formed beads were filtered and washed with distilled water to remove excess of NaOH and finally air-dried. After drying the beads were grinded to obtain the desired size ( $<200 \,\mu m$ ). After this, the beads of chitosan-zeolite composite were structurally characterised by SEM image analyses and EDX spectral analyses and used as adsorbent for the organic impurities from wastewater (COD and greases and oil impurities).

From the SEM micrograph presented in **Figure 11**, chitosan-zeolite composite has rough and flaky surface. Zeolite is present as loose aggregates of micrometric octahedral crystals included in cavities of a continuous polysaccharide matrix, in the case of evaporative drying; the shrinkage of the polysaccharide gel has led to a physical separation between polymer and embedded zeolites.

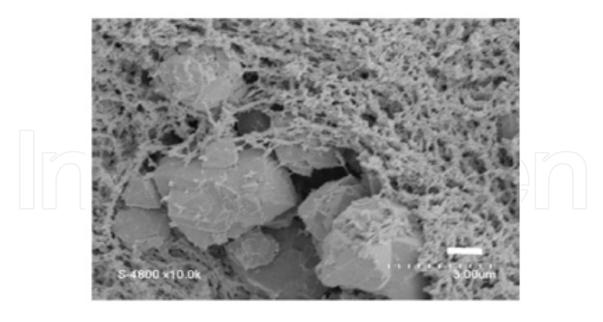


Figure 11. Chitosan-zeolite composite SEM images.

The EDX spectra (Figure 12) show the presence of sodium, which is originated from zeolite where the sodium ions counterbalance the negative charge of zeolite. Carbon, nitrogen, oxygen, aluminium and silicon were found in chitosan-zeolite composites since they are the major components of chitosan and zeolite.

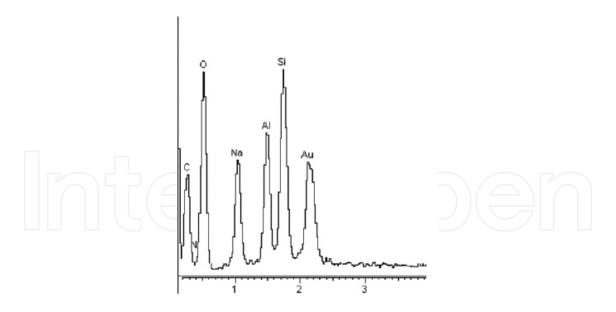


Figure 12. EDX spectra of chitosan-zeolite composites.

Experiments were carried out at 25 °C where different amounts of chitosan-zeolite composite ranging from 30 to 150 mg were mixed with 50 ml wastewater and stirred at 250 rpm for 60 min. After adsorption, the mixture was filtered, and the removal percentage of chemical oxygen demand (COD) and fatty impurities was calculated using Eq. (1) formula.

$$\varepsilon = \frac{Ci - Cf}{Ci} \times 100\% \tag{1}$$

where Ci is the pollutant content before treatment [mg/l] and Cf is the pollutant content after treatment [mg/l].

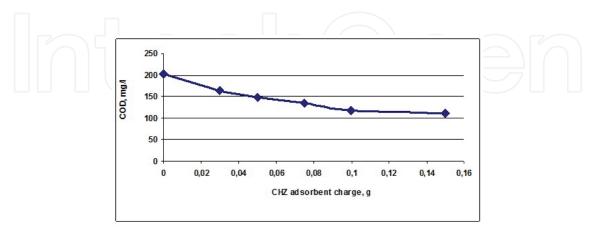


Figure 13. The effect of chitosan-zeolite composite dosage on the COD reduction.

The effect of adsorbent dosage on the removal of COD is shown in **Figure 13**. The quantity of COD removed increases as the chitosan-zeolite dosage increased. This was due to the increase in the number of active sites on chitosan-zeolite composites. The dosage of 0.10 g can be selected as the optimum dosage for further experiments. It can be observed that over this dosage, no further increase exists in the percentage removal of COD.

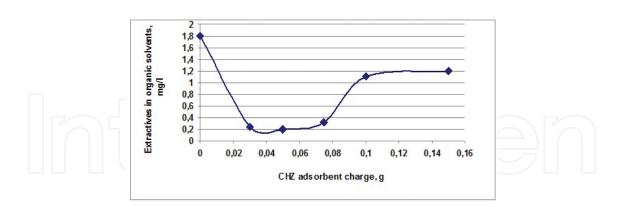
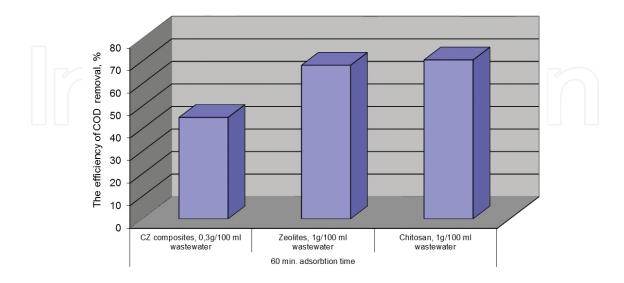


Figure 14. The effect of chitosan-zeolite composite dosage on the fatty and oil reduction.

The reduction of fatty and oil impurities increases with the chitosan-zeolite composite dosage, as it can be observed in **Figure 14**. It considers that the optimum dosage is at 0.05 g when the highest quantity of fatty impurities from wastewaters is eliminated.

Compared with the use of chitosan and zeolites only as adsorbents, it can be observed from **Figure 15** that the chitosan-zeolite composite performance is better. At the 60 min of adsorption

time and the 0.3 g adsorbent dosage, the COD reduction is 45% for chitosan-zeolite composites than 20–21% for chitosan and zeolites only [54].



**Figure 15.** The pollutant reduction performances for different natural adsorbents.

#### 4. Conclusions

Based on their proved properties, chitosan can be a very promising adsorption additive for wastewater pollutants. Aiming to improve their adsorption performances, chitosan can be modified by grafting, cross linking, functionalisation for forming composites, etc. Based on its origin product (chitin which can be found abundant in marine media, i.e. in the exoskeleton of crustaceans or cartilages of mollusks), the potential of chitosan to be used as (bio) adsorbent for wastewater pollutants is strong. However, the main drawback that limits the use of chitosan at industrial level is their low solubility in aqueous media. In this respect, the performances of chitosan can be improved by cross linking with different reagents, allowing chitosan composites to be used in acidic condition. To form composites with chitosan, different kinds of substances have been used.

The cationic nature of chitosan influences the adsorption mechanism of chitosan composites. In acid pH conditions, the amino groups of chitosan form protonated amines able to retain the metal ions or dye molecules from solutions or wastewaters. The interaction mechanisms can be through electrostatic attractions or/and complexation.

Although there is a wide range of chitosan derivatives with adsorption properties (raw chitosan, chitosan derivatives, chitosan composites, etc.), choosing the most suitable type of adsorbent in pollutant adsorption processes is still developed.

This field of research has a great area for improvement, and based on a large quantity of promising results, it is the hope that chitosan and their composites can be applied commercially instead of only at laboratory scale.

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