

THE USE OF CHITOSAN FOR REMOVING SELECTED POLLUTANTS FROM WATER AND WASTEWATER – SHORT REVIEW

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Abstract

Chitosan is a natural product derived from chitin, which is mostly found in exo-skeletons of shrimp, crab and lobster shells. This paper presents a short review of the literature regarding the use of chitosan and its modifications for removing selected pollutants from water and wastewater. In particular, the examples of removal of metal ions, dyes, anions and phenols were described. Furthermore, the possibility of the use of chitosan as a coagulant and flocculant in water and wastewater technologies are also shown. Based on the literature review described in this article it can be concluded that chitosan and especially its modifications is a very promising sorbent for removing a broad spectrum of pollutants from aqueous solutions. It also presents directions for further research in order to obtain a better knowledge of the practical applications of chitosan.

Streszczenie

Chitozan jest naturalnym produktem pochodzącym z chityny, która najczęściej występuje w egzo-szkieletach krewetek i krabów oraz w muszlach homarów. W publikacji dokonano krótkiego przeglądu literatury odnośnie zastosowań chitozanu i jego modyfikacji do usuwania wybranych zanieczyszczeń z wody i ścieków. W szczególności, opisano przykłady usuwania jonów metali, barwników, anionów i fenoli. Przedstawiono również możliwości zastosowania chitozanu jako koagulantu i flokulantu w technologii wody i ścieków. Na podstawie przeglądu literatury opisanego w tym artykule, można stwierdzić, że chitozan a zwłaszcza jego modyfikacje, jest bardzo obiecującym sorbentem do usuwania szerokiego spektrum zanieczyszczeń z roztworów wodnych. Przedstawiono również kierunki dalszych badań w celu uzyskania lepszej wiedzy dotyczącej praktycznych zastosowań chitozanu.

Keywords: Chitosan; Chitosan modification; Adsorption; Metal ions; Dyes; Anions; Phenols.

1. INTRODUCTION

Chitosan is a natural product derived from chitin, which is mostly found in exo-skeletons of shrimp and crab and lobster shells. It is one of the most accessible renewable product in the natural environment, received in biosynthesis process [1]. In fact, chitosan mainly derives from the process of chemical or enzy-

matic deacetylation of chitin. This process results in partial or complete removal of acetyl groups from acetyl amino group of chitosan. The name of chitosan is applied to the modified chitin containing less than 25% of the acetyl groups [2]. The chemical structures of chitin and chitosan was shown on the Figure 1.

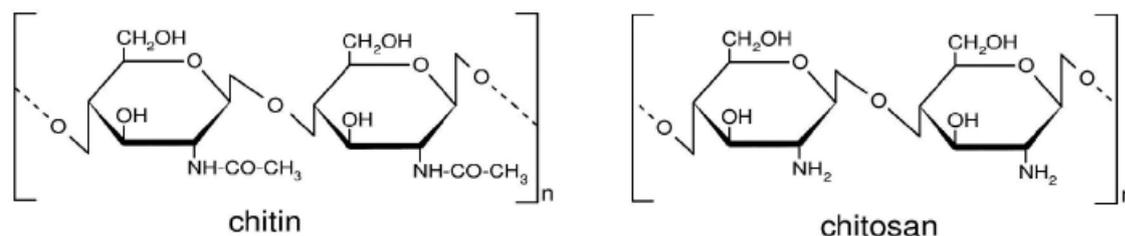


Figure 1.
Chemical structure of chitin and chitosan

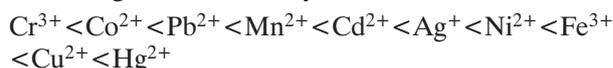
Several chitosan modification methods have been applied to improve its sorption capacity, mechanical strength and resistance to low pH values. We can distinguish physical and chemical modifications of chitosan. The physical modifications include the preparation of chitosan in various forms such as powder, nanoparticles, gel beads, membranes, sponges, “honeycomb” type structure and various types of fiber for all applications [3]. Chemical modifications include cross-linking using glutaraldehyde, oxidized β -cyclodextrin, ethylene glycol diglycidyl ether or epichlorohydrin [4]. Chitosan has found many applications in various industries, e.g. textile, paper, cosmetic, pharmacy, in agriculture, medicine and environmental engineering [5, 6].

Chitosan is mainly used as an effective bio-sorbent in environmental engineering. The main advantage of chitosan over the common activated carbon and other bio-sorbents is its low price, high affinity for a number of contaminants (due to the presence of amino and hydroxyl groups), chemical stability, high reactivity and selectivity in relation to pollutions [3]. Chitosan and its modifications have been successfully used for the removal of metal ions, dyes, phenols, various anions, pesticides, fungicides and humic substances by adsorption [7]. This paper presents a brief overview of applications of chitosan in the field of water and wastewater treatment.

2. REMOVAL OF METAL IONS

Heavy metals are one of the most dangerous and toxic water pollutants. They are not only dangerous by the direct consumption of water but also because of their accumulation in food, creating a secondary risk during the consumption of meat, vegetables or fish. The high adsorption potential of chitosan in relation to the heavy metals can be attributed to the significant hydrophilicity due to the large number of highly reactive hydroxyl and functional groups and the flexibility of the polymer chain [8]. Koshijima et

al. [9] provide the following number of the efficiency of binding of metal ions by chitosan:



The following is a brief summary of the use of chitosan for the sorption of selected heavy metals.

2.1. Cadmium

Cadmium and cadmium compounds are very toxic even in small concentrations. They have the ability to bioaccumulate in organisms and ecosystems. Benguela et al. [10] applied chitin to removal of cadmium ions from water solutions. Obtained sorption capacity was equal to 14 mg Cd (II)/g of chitin. On the basis of scanning electron microscope (SEM) analysis combined with X-ray radiation the presence of cadmium on the surface of chitin after the sorption process was revealed.

Jha et al. [11] removed of cadmium in the sorption process using chitosan. The pH in the range of 4.0-8.3 resulted in sorption capacity equal to 5.93 mg of Cd (II)/g chitosan. The presence of EDTA increases the efficiency of the removal of cadmium, as EDTA, and other aminopolycarboxylic acids form stable complexes with heavy metals. Rorrer et al. [12] reported an increase in the sorption capacity of chitosan with respect to cadmium by the use of chitosan beads. The beads were precipitated in sodium hydroxide solution, and then cross-linked with glutaraldehyde and freeze dried. Obtained chitosan beads had a diameter of 1 and 3 mm. For the 1 and 3 mm diameter chitosan beads maximum sorption capacity was 518 and 188 mg Cd(II)/g, respectively. Smaller beads had the surface area of 150 m²/g and an average pore size of 560 Å, which is equivalent to 56 nm. The modified chitosan (beads) have a larger surface area and mechanical strength in comparison with unmodified chitosan.

2.2. Arsenic

Arsenic occurring in natural water is a global problem. Its toxicity, adverse effects on human health and the methods of removing arsenic (V) from the water have been the subject of many studies. Dambies et al. [13] removed arsenic (V) using chitosan beads impregnated with molybdates. The optimal pH of the sorption process was pH = 3, and the sorption capacity of the beads 160 mg AsO₄³⁻/g. The sorbent was subjected to the process of successful regeneration with phosphoric acid. Three cycles of adsorption/desorption resulted in a reduction of sorption capacity of chitosan beads.

Kwok et al. [14] investigated the use of chitosan flakes to remove arsenic (V). They applied the 96 hours contact time of chitosan with the solution containing arsenic. The increase of the initial pH resulted in decrease of the amount of absorbed arsenic. This was explained by the decrease in the number of the positive amine groups with increasing pH, which combined with the arsenates ions. Achieved sorption capacity was 1.331 µg AsO₄³⁻/g of chitosan with initial pH = 5.5 and 14160 µg AsO₄³⁻/g of chitosan with initial pH = 3.5.

To remove arsenic (III) and arsenic (V), the chitosan powder received from the chitin shells of shrimps was applied [15]. Most favorable pH of the sorption process was pH = 5 for both forms of arsenic ion. Under these operating conditions, the sorption capacity of the chitosan amounted to 1.83 mg As(III)/g of chitosan and 1.94 mg As(V)/g chitosan.

2.3. Chromium

Aydin and Aksoy [16] investigated the removal of chromium (IV) on chitosan flakes. The process was conducted in following conditions: pH 1.5-9.5, dose of sorbent 1.8-24.2 g/dm³. For initial concentration 30 mg Cr/dm³, the highest removal degree was achieved under conditions: pH equal to 3 and dose of sorbent equal to 13 mg/dm³. Under these conditions sorption capacity was 22.09 mg Cr(VI)/g of chitosan flakes. Schmuhl et al. [17] used cross-linked and unmodified chitosan for the removal of chromium from the water solution. For the optimal pH = 5, sorption capacity of cross-linked and unmodified chitosan were 78 and 50 mg Cr (VI)/g of chitosan.

Studies conducted by Rojas et al. [18] focused on Cr(VI) and Cr(III) removal by cross-linked chitosan. Test results revealed that for Cr(III) sorption capacity was only 6 mg/g of chitosan and for Cr(VI) as much

as 215 mg/g in optimal pH conditions (pH = 4). Such high removal efficiency of Cr(VI) has been explained by the presence of a large number of protonated amino groups of chitosan at low pH values of the reaction.

2.4. Lead

Barbusiński et al. [19] investigated the use of chitosan and its modifications for lead adsorption from aqueous solutions. Chitosan has been used in form of powder and beads (unmodified, cross-linked with glutaraldehyde or epichlorohydrin optionally conditioned with NaHSO₄). The most effective sorbent proved to be unmodified chitosan. The highest Pb adsorption capacity (39.24 mg/g) was achieved for pH = 6 and reaction time between 360 and 720 min of process. The adsorption of Pb was described by the Langmuir isotherm equation.

Based on those results, they presented chain of efficiency of chitosan sorbents in relation to lead:

(chitosan) > (beads+NaHSO₄) > (beads+ECH) > (beads+GLU) > (beads+ECH+NaHSO₄) > (beads unmodified)

3. REMOVAL OF DYES

Wastewater containing dyes is very difficult to purify. Dyes are usually resistant to biological oxidation and, in some cases, to the chemical oxidants. Adsorption at a low cost and by the means of widely available natural adsorbents is an alternative to conventional processes, but also for advanced oxidation methods which are very effective and efficient in the degradation of dyes in wastewater, but relatively expensive. Chitosan is one of the promising bio-sorbents used to remove dyes from aqueous solutions.

3.1. Acid dyes

The ability of chitosan, derived from deacetylated crab shell chitin, to remove five acid dyes (Acid Green 25, Acid Orange 10, Acid Orange 12, Acid Red 18, Acid Red 73) from aqueous solution by adsorption has been studied by Wong et. al. [20]. The deacetylation degree (DD) of the chitosan was 53% and the size fraction used in the experiments was 355-500 µm. The initial pH of the sorption was pH = 4.0. Based on the Langmuir isotherm analysis, the extremely high monolayer adsorption capacities were determined to be 645.1, 922.9, 973.3, 693.2 and 728.2 mg/g chitosan for Acid Green 25, Acid Orange 10,

Acid Orange 12, Acid Red 18 and Acid Red 73, respectively.

The performance of nanochitosan (with particle size range from 0.0663 to 1.763 μm) as an adsorbent to remove four acid dyes from aqueous solution has been investigated by Cheung et al. [21]. Nanochitosan emulsion has been produced in a suspension form by adding tripolyphosphate solution into the chitosan solution drop-wise. Studies have shown that the nanochitosan suspension has a concentration of 0.3% by volume, which is equivalent to 3 mg/cm^3 . The emulsion is adjusted to pH 3.5 by the addition of dilute acetic acid. Based on the Langmuir isotherm analysis, the monolayer adsorption capacities were determined to be 1.77, 4.33, 1.37 and 2.13 mmol/g of nanochitosan for Acid Orange 10, Acid Orange 12, Acid Red 18 and Acid Red 73, respectively.

In both studies [20, 21] the differences in adsorption capacities were explained as the differences in the particle size of dye molecules and the number of sulfonate groups on each dye molecule. The authors concluded that these differences have been associated with the different size; monovalent and smaller dye particle having superior capacities due to the increase in dye/chitosan ratio in the system, enabling a deeper penetration of dye molecules to the internal pore structure of nanochitosan or chitosan. The results have demonstrated that efficiency of adsorption may be attributed mainly to the chemical structure of each dye.

Likewise Salwiczek et al. [22] conducted research on the usage of chitosan and its modifications to remove acid dyes (Acid Red 18 and Acid Green 16) from aqueous solution. Most effectively absorbing modification in the case of both dyes, which achieved the highest sorption capacity turned out to be cross-linked chitosan beads ECH and conditioned NaHSO_4 . It was found that each of the applied modifications increases the sorption capacity of the modified sorbents compared to the unmodified chitosan. The best results of sorption process were achieved for pH = 3. Equilibrium adsorption for each modification of chitosan was reached after 360 minutes of contact time with the wastewater.

3.2. Direct (anionic) dyes

Chiou et. al. [23] investigated the use of cross-linked chitosan beads to remove direct dye (Direct Red 81) from aqueous solution. The beads were prepared by precipitation of a 1% solution of chitosan in a 1%

solution of sodium tripolyphosphate (TTP). The solution of TPP was used in the beads formation stage to produce more rigid beads via its ionic cross-linking effect. After that, the beads were cross-linked by epichlorohydrin (ECH). The maximum monolayer adsorption capacity was 2383 g/kg at 30°C and pH = 4. The result was of 9.9 and 16.7 times higher than the results obtained using the activated carbon and chitin respectively. The adsorption capacity increases along with the decreasing pH of the reaction. For Direct Red 81 dye, the maximum value of adsorption capacity obtained at pH 4 was 4.6 times higher than the capacity obtained at pH 8.

The studies revealed that the major adsorption site of chitosan is an amine group, $-\text{NH}_2$, which is easily protonated to form $-\text{NH}_3^+$ in acidic solutions. The strong electrostatic interaction between the $-\text{NH}_3^+$ group of chitosan and dye anions can be used to explain the high adsorption capacity of dye onto chemically cross-linked chitosan beads. The Langmuir model agreed very well with experimental data.

3.3. Reactive dyes

Wu et al. [24, 25] conducted research on the removal of three reactive dye: Reactive Red 222, Reactive Blue 222 and Reactive Yellow 145. In all cases, the adsorption capacities of dye using chitosan flakes, chitosan beads and swollen chitosan beads have been examined. The adsorption capacity of Reactive Red 222 obtained 239 mg/g of flakes and 1103 mg/g of chitosan beads. Higher efficiency of chitosan beads in comparison to chitosan flakes can be explained by higher specific surface area (measured by BET, *Brunauer-Emmett-Teller*, isotherm) which has more loose pore structure. However, the efficacy of dye adsorption using swollen chitosan beads was five times greater than using chitosan flakes (up to 1653 g/kg).

The efficacy of the adsorption of the Reactive Red 189 dye by using the cross-linked chitosan beads has also been studied [26]. The tripolyphosphate was used in cross-lined process to receive appropriate stiffness of beads. In order to improve the stability of the beads in the acidic environment, epichlorohydrin, glutaraldehyde and ethylene glycol diglycidyl ether were applied cross-linkers. Chitosan beads which were cross-linked with epichlorohydrin has demonstrated the greatest affinity to the dye Reactive Red 189, the maximum sorption capacity was in the range 1802–1840 $\text{g dye}/\text{kg}$ of sorbent at pH = 3 and a tem-

perature of 30°C. Moreover it was observed that the beads undergoing the desorption process had the ability of the re-sorption of the dye with the efficiency equal to the efficiency from before the desorption process.

4. OTHER APPLICATIONS OF CHITOSAN

4.1. Anions removal

In recent years, chitin and chitosan has been successfully used to remove anions from water. Chatterjee et al. [27] have used chitosan beads to remove nitrates (V) from aqueous solutions. The best results were obtained for pH = 3, the initial nitrate concentration of 1 g/dm³ and temperature 30°C. Under these operating conditions, the sorption capacity of 92.1 mg NO³-/g sorbent was achieved. Also carried out experiments on the desorption of nitrates absorbed earlier on chitosan beads. The greatest results has been obtained for pH in range 11-12. The efficacy of desorption was 86% and 87%, respectively.

Usage of protonated cross-linked chitosan gel beads by glutaraldehyde was studied in relation to removal of nitrate (V) from treated solution, resembling water present in an environment [28]. The greatest result of the sorption process was obtained in the range of pH from 3 to 5. However, it has been shown that without modifying the pH, sufficiently good results of nitrate removal from water were reached. The impact of ions naturally found in groundwater and surface water (Cl⁻, SO₄²⁻, F⁻) on the degree of sorption of nitrate, was also tested. The greatest influence on the sorption process has been demonstrated by F⁻ ions, which most significantly decreased the degree of the sorption of nitrate in relation to the other used anions.

The usage of protonated chitosan beads (PCB) as a defluorinating medium has been studied by Viswanathan et al. [29]. They proved that the sorption process was not dependent on pH and varied in the presence of other co-existing anions. The maximum value of sorption process was in the range from 4.72 mg/g to 7.32 mg/g. The hydrogen bonds between positively charged amino groups of chitosan and fluoride ions were indicated as a sorption mechanism. Different research were conducted by Jagtap et al. [30]. They used the metal-binding properties of chitosan, the metal used was titanium (Ti) in order to remove the fluoride ions. Titanium loading varied from 5 to 50 wt%. It was observed that an increase in

titanium loading from 5 to 15% has improved fluoride removal from 61 to 89%. The highest value of sorption capacity 7.2 mg/g has been achieved at neutral pH = 7. The presence of other anions have a negative affect on sorption of fluorides. The sharp drop in the concentration of fluoride was observed within the first 20 minutes of conducting the process, but after that time the dynamics of sorption rapidly decreased.

4.2. Removal of phenols

The phenols are one of the most dangerous water pollutant. In addition to the risk of loss of taste and aroma they are highly toxic to organisms even at low concentrations. The new methods have been researched, to replace the classic, well-known methods of phenols removal. The classic biological way or adsorption on activated carbon does not show high efficiency. The advanced oxidation methods of removing phenols are extremely effective but expensive. Barbusiński et al. [31] demonstrated that Fenton's reagent effectively degrade phenols, cyanides and thiocyanate contained in coke wastewater.

Other research focused on removal phenol and *o*-chlorophenol by using chitosan beads modified by sodium alginate and calcium chloride [32]. This modification improve the stability as well as the sorption capacity of the beads. The maximum sorption capacity for phenol was 108.69 mg/g, while for *o*-chlorophenol 97.08 mg/g. The impact of desorption process with 0.1 M NaOH solution for sorption ability has also been studied. Decrease in sorption capacity of the sorbent was observed after the second and third cycle of sorption-desorption. Li et al. [33] investigated the use of chitosan, chemically modified onto salicylaldehyde (CS-SA), β -cyclodextrin (CS-CD) and a cross-linked β -cyclodextrin polymer (EPI-CD) in the removal of phenol, *p*-nitrophenol and *p*-chlorophenol from aqueous solution. It was observed that adsorption capacity of phenol onto unmodified chitosan was minor (1.98-2.58 mg/g) in relation to sorbed impurities. Applying modification of CS-SA increased sorption capacity to respectively 8.50; 20.49 and 44.92 mg/g in the sorption of phenol, *p*-chlorophenol and *p*-nitrophenol,. On the other hand, sorption capacity of chitosan chemically modified by CS-CD was 34.93 mg/g, 179.73 mg/g and 20.562 mg/g in the sorption of phenol, *p*-chlorophenol and *p*-nitrophenol. The last modification by EPI-CD has led to the following results: 131.50 mg/g, 74.25 mg/g and 41.11 mg/g at the sorption of phenol,

p-chlorophenol and *p*-nitrophenol, respectively. Adsorption experiments were performed at pH = 7 and temperature 30°C. However, it was noted that the increase of the pH and temperature of the process undermines the effectiveness of the sorption process. The desorption process was carried out with ethanol. The efficiency of the desorption process varies between 80-94.2%, while the regenerated sorbent is characterized by the sorption capacity in the range of 69.4-78.9% of the original sorption capacity. The number of effective sorption/desorption cycles was 6.

4.3. Chitosan as a coagulant and flocculant

Recently, there is growing interest in developing natural low-cost alternatives to synthetic polyelectrolytes. Numerous biological products have recently been proposed and studied as effective coagulants and flocculants for replacing conventional materials [34-36]. Some of the reported products named “bioflocculants” include biopolymers (starches, chitosan, alginates) and microbial materials produced by microorganism including bacteria, fungi and yeast [37]. Chitosan as a comprehensive polymer was used in environmental engineering as an effective coagulant and/or flocculant (bioflocculant) [38-44]. It is possible because chitosan has many characteristics of coagulants and flocculants, such as high density of positive charges, the long chains of the polymer and the ability to precipitate (in a neutral and alkaline environment). Chitosan is appreciated for two important advantages: first of all, for its non-toxic properties and biodegradability and secondly, the ability to chelate [17]. Moreover, its unique physico-chemical and biological properties make it very effective in the reaction of the solid particles and dissolved. Moreover, compared with conventional chemical flocculants, bioflocculants produce no secondary pollution. Chitosan as a coagulant has been applied for the treatment of wastewater from breweries, paper mills, fatty plants, for treatment of wastewater containing metals, dyes, humic substances and the treatment of drinking water. Chitosan is widely applied in water and wastewater treatment (Table 1) because it can be conditioned and used for pollutant complexation in different forms, from water soluble forms to solid forms (gels, beads membranes, fibers, etc.) [45].

Table 1.
Principal properties of chitosan in relation to its use in water and waste treatment application [45]

Principal characteristics	Potential applications
• Non-toxic	• Flocculant to clarify water (drinking water, pools)
• Biodegradable	• Reduction of turbidity in food processing effluents
• Renewable resource	• Coagulation of suspended solids, mineral and organic suspensions
• Ecologically acceptable polymer (eliminating synthetic polymers, environmentally friendly)	• Flocculation of bacterial suspensions
• Efficient against bacteria, viruses, fungi	• Interactions with negatively charged molecules
• Formation of salts with organic and inorganic acids	• Recovery of valuable products (proteins...)
• Ability to form hydrogen bonds intermolecularly	• Chelation of metal ions
• Ability to encapsulate	• Removal of dye molecules by adsorption processes
• Removal of pollutants with outstanding pollutant-binding capacities	• Reduction of odours • Sludge treatment • Filtration and separation • Polymer assisted ultrafiltration

On the basis of [45] and references cited therein it can be concluded that the following are the main reasons of the success of chitosan used as coagulant and/or flocculant in field of water and wastewater treatment:

- chitosan has the advantage of being a non-toxic material,
- non corrosive,
- safe to handle (non hazardous product, not irritating for skin and eyes),
- safe for live organisms,
- does not pollute the natural environment,
- is efficient in cold water and at much lower concentrations than the metal salts,
- it does not leave residual metals in the water, which could be a secondary contamination problem,
- reduce the volume of sludge produced compared to the sludge obtained with alum,
- considerably increases the density of the sludge and facilitates its drying compared to the traditional coagulants,
- the sludge can be efficiently degraded by microorganisms,

- does not add much to the salinity of the treated water and is useable at alkaline pH.

The usage of chitosan as a flocculant cause the increment of the flocs size, which favours the floc settling speed and therefore reduces the settling time [17]. Nonetheless, there are also disadvantages of using chitosan as a coagulant and flocculant. Among all: chitosan is only efficient over a limited pH range, overdosing can restabilize a dispersion and affect other process aspects, chitosan differs by various parameters e.g. degree of deacetylation or molecular weight which may affect its capability of the pollutant coagulation. You should perform research and find the right process conditions, every time when introducing a new provider or chitosan with other parameters [3].

5. CONCLUSIONS

Based on the review of the literature quoted in this article it can be concluded that chitosan and especially its modifications is a very promising sorbent for removing a broad spectrum of pollutants from water and wastewater. Chitosan can effectively remove metal ions, dyes, anions and phenols. Moreover, chitosan can be used as a coagulant and/or flocculant in the field of water and wastewater technologies. Chitosan is not only an effective sorbent but also has additional advantages: it is inexpensive, non-toxic and biocompatible.

The economic aspect is very important because it can cause a significant reduction in the technical application. From this point of view, chitosan has many advantages [2, 46, 47]: chitin is a material obtained from natural raw resources; chitin and chitosan are now produced commercially at low cost; the production of the chitosan-based materials is economically feasible, as they are easy to prepare with relatively inexpensive chemical reagents; moreover, relatively harmless chemicals are used in the production processes.

Possible applications of chitosan in water and wastewater technologies require further intensive research. Directions for further research should cover, among others, the following aspects:

- studies on the removal of other impurities from aqueous solutions using chitosan and its modifications, including substances from the group of persistent organic pollutants;
- use of higher temperature of sorption to determine its influence on the sorption capacity of chitosan

and its modifications;

- studies on the effectiveness of contaminant removal by chitosan beads in a flow column reactor;
- studies of chitosan beads to determine the best modification, from the point of view of their mechanical strength;
- use of chitosan and its modifications for the sorption of pollutants from real wastewater and aqueous solutions containing different kinds of contaminants.

REFERENCES

- [1] *Patil R.S., Ghormade V., Deshpande M.V.*; Chitinolytic enzymes: an exploration. *Enzyme Microb. Tech.*, Vol.26, No.7, 2000; p.473-483
- [2] *Crini G., Badot P.M.*; Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. *Progress in Polymer Science*, Vol.33, 2008; p.399-447
- [3] *Guibal E.*; Interactions of metal ions with chitosan-based sorbents: a review. *Separation Purification Technology*, Vol.38, 2004; p.43-74
- [4] *Lee S.T., Mi F.L., Shen Y.J., Shyu S.S.*; Equilibrium and kinetic studies of copper (II) ion uptake by chitosan-tripolyphosphate chelating resin. *Polymer*, Vol.42, 2001; pp.1879-1892
- [5] *Struszczyk M.H.*; Chitin and chitosan. Part II. Applications of chitosan. *Polimery*, Vol.47, No.6, 2002; p.396-403
- [6] *Mucha M., Miśkiewicz D., Pawlak A.*; Chitozan i jego mieszaniny. Właściwości i zastosowanie (Chitosan and its mixtures. Properties and applications). *Przemysł Chemiczny*, Vol.82, No.8-9, 2003; p.1138-1142 (in Polish)
- [7] *Bhathangar A., Sillanpää M.*; Applications of chitin and chitosan-derivatives for the detoxification of water and wastewater – A short review. *Advances in Colloid and Interface Science*, Vol.152, 2009; p.26-38
- [8] *Crini G.*; Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in Polymer Science*, Vol.30, 2005; p.38-70
- [9] *Koshijima T., Tanaka R., Muraki E., Yamada A., Yaku F.*; Chelating polymers derived from cellulose and chitin. *Cellulose Chemistry and Technology*, Vol.7, 1973; p.197-208
- [10] *Benguella B., Benaïssa H.*; Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies. *Water Research*, Vol.36, No.10, 2002; p.2463-2474

- [11] Jha I., Iyengar L., Rao A.; Removal of cadmium using chitosan. *Journal of Environmental Engineering-ASCE*, Vol.114, 1988; p.962-974
- [12] Rorrer G., Hsien T-Y., Way J.D.; Synthesis of porous-magnetic chitosan beads for removal of cadmium ions from wastewater. *Ind. Eng. Chem. Res.*, Vol.32, 1993; p.2170-2178
- [13] Dambies L., Roze A., Guibal E.; As(V) sorption on molybdate-impregnated chitosan gel beads (MICB). In: *Advances in Chitin Science*, Vol.4, 2000; p.302-309. Edited by: Peter M.G., Domard A. and Muzzarelli R.A.A. (University of Potsdam, 2000. ISBN 3-9806494-5-8)
- [14] Kwok K., Lee V., Gerente C., McKay G.; Novel model development for sorption of arsenate on chitosan. *Chemical Engineering Journal*, Vol.151, 2009; p.122-133
- [15] Chen C.C., Chung Y.C.; Arsenic removal using a biopolymer chitosan sorbent. *Journal of Environmental Science and Health. Part A, Toxic/Hazardous Substances & Environmental Engineering*, Vol.41, 2005; p.645-658
- [16] Aydin Y., Aksoy N.; Adsorption of chromium on chitosan: optimization, kinetics and thermodynamics. *Chemical Engineering Journal*, Vol.151, 2009; p.188-194
- [17] Schmuhl R., Krieg H. M., Keizer K.; Adsorption of Cu(II) and Cr(VI) ions by chitosan: kinetics and equilibrium studies. *Water SA*, Vol.27, 2001; p.1-8
- [18] Rojas G., Silva J., Flores J.A., Rodriguez A., Ly M., Maldonado H.; Adsorption of chromium onto cross-linked chitosan. *Separation and Purification Technology*, Vol.44, 2005; p.31-36
- [19] Barbusiński K., Salwiczek S., Kozik V.; Zastosowanie chitozanu i jego modyfikacji do usuwania ołowiu i kadmu z roztworów wodnych (Use of chitosan and its modifications for removal of lead and cadmium from aqueous solutions). *Przemysł Chemiczny*, Vol.94, No.12, 2015; p.2304-2307 (in Polish)
- [20] Wong Y.C., Szeto Y.S., Cheung W.H., McKay G.; Adsorption of acid dyes on chitosan – Equilibrium isotherm analyses. *Process Biochemistry*, Vol.39, 2004; p.695-704
- [21] Cheung W.H., Szeto Y.S., McKay G.; Enhancing the adsorption capacities of acid dyes by chitosan nano particles. *Bioresource Technology*, Vol.100, 2009; p.1143-1148
- [22] Salwiczek S., Szymura E., Barbusiński K.; Zastosowanie chitozanu i jego modyfikacji do usuwania barwników (Use of chitosan and its modifications for dyes removal). *Monografia: Inżynieria Środowiska Młodym Okiem: Wody Powierzchniowe i Podziemne*, red. Skoczko I. i in. Oficyna Wydawnicza Politechniki Białostockiej, Białystok, 2014 (in Polish)
- [23] Chiou M.S., Ho P.Y., Li H.Y.; Adsorption of anionic dyes in acid solutions using chemically. *Dyes and Pigments*, Vol.60, 2003; p.69-84
- [24] Wu F., Tseng R., Juang R.; Comparative adsorption of metal and dye on flake- and bead types of chitosan prepared from fishery wastes. *Journal of Hazardous Materials*, Vol.B73, 2000; p.63-75
- [25] Wu F., Tseng R., Juang R.; Enhanced abilities of highly swollen chitosan beads for color removal and tyrosinase immobilization. *Journal of Hazardous Materials*, Vol.B81, 2001; p.167-177
- [26] Chiou M., Li H.; Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads. *Chemosphere*, Vol.50, 2003; p.1095-1105
- [27] Chatterjee S., Woo S.H.; The removal of nitrate from aqueous solutions by chitosan hydrogel beads. *Journal of Hazardous Materials*, Vol.164, 2009; p.1012-1018
- [28] Jaafari K., Elmaleh S., Coma J., Benkhouja K.; Equilibrium and kinetics of nitrate removal by protonated cross-linked chitosan. *Water SA*, Vol.27, 2001; p.9-13
- [29] Viswanathan N., Sundaram C.S., Meenakshi S.; Removal of fluoride from aqueous solution using protonated chitosan beads. *Journal of Hazardous Materials*, Vol.161, 2009; p.423-430
- [30] Jagtap S., Thakre D., Wanjari S., Kamble S., Labhsetwar N., Rayalu S.; New modified chitosan-based adsorbent for defluoridation of water. *Journal of Colloid and Interface Science*, Vol.332, 2009; p.280-290
- [31] Barbusiński K., Główkowska, J., Tomys, K.; Coke plant wastewater treatment by Fenton reagent. *Archives of Environmental Protection*, Vol.32, No.3, 2006; p.21-28
- [32] Nadavala S., Swayampakula K., Boddu V., Abburi K.; Biosorption of phenol and o-chlorophenol from aqueous solutions on to chitosan-calcium alginate blended beads. *Journal of Hazardous Materials*, Vol.162, 2009; p.482-489
- [33] Li J-M., Meng X-G, Hu Ch-W, Du J.; Adsorption of phenol, p-chlorophenol and p-nitrophenol onto functional chitosan. *Bioresource Technology*, Vol.100, 2009; p.1168-1173
- [34] Chen Y., Lian B.; Progress of microbial flocculant study and its application. *Bull. Mineral Petrol Geochem.*, Vol.23, 2004; p.83-89
- [35] Jiang J.Q.; Development of coagulation theory and new coagulants for water treatment: its past, current and future trend. *Water Supply*, Vol.1, 2001; p.57-64
- [36] Salehizadeh H., Shojaosadati S.A.; Extracellular biopolymeric flocculants – recent trend and biotechnological importance. *Biotechnol. Adv.*, Vol.19, 2001; p.371-385

- [37] Wang H.C., Li M.H., Tsang H.W., Wu M.M., Lin H.P.P.; Novel biological flocculants and production methods. United States Patent US20070062865 (2007)
- [38] No H.K., Meyers S.P.; Application of chitosan for treatment of wastewaters. Rev. Environ. Contam. Toxicol., Vol.163, 2000; p.1-28
- [39] No H.K., Meyers S.P.; Crawfish chitosan as a coagulant in recovery of organic compounds from processing streams. J. Agric. Food Chem., Vol.37, 1989; p.580-583
- [40] Johnson R.A., Gallanger S.M.; Use of coagulants to treat seafood processing wastewaters. J. Water Pollut. Control Fed., Vol.56, 1984; p.970-976
- [41] Senstad C., Almas K.A.; Use of chitosan in the recovery of protein from shrimp processing wastewater. In: Muzzarelli R.A.A., Jeuniaux C., Gooday G.W.; editors. Proceedings of the third international conference on chitin and chitosan. Senigallia, Italy; 1986; p.568-570
- [42] Moore K.J., Johnson M.G., Sistrunk W.A.; Effect of polyelectrolyte treatments on waste strength of snap and dry bean wastewater. J. Food Sci., Vol.52, 1987; p.491-492
- [43] Jun H.K., Kim J.S., No H.K., Meyers S.P.; Chitosan as a coagulant for recovery of proteinaceous solids from tofu wastewater. J. Agric. Food Chem., Vol.42, 1994; p.1834-1838
- [44] Sievers D.M., Jenner M.W., Hanna M.; Treatment of dilute manure wastewaters by chemical coagulation. Trans. ASAE, Vol.37, 1994; p.597-601
- [45] Renault R., Sancey B., Badot P.M., Crini G.; Chitosan for coagulation/flocculation processes – An eco-friendly approach. European Polymer Journal, Vol.45, 2009; p.1337-1348
- [46] Agullo E., Rodriguez M.S., Ramos V, Albertengo L.; Present and future role of chitin and chitosan in food. Macromolecular Bioscience, Vol.3, 2003; p.521-530
- [47] Ravi Kumar MNV.; A review of chitin and chitosan applications. Reactive and Functional Polymers, Vol.46, 2000; p.1-27