

STUDY OF THE KINETICS OF COPPER ION SORPTION BY CHITOSAN SPHERES

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Abstract

Chitosan, a polysaccharide derived from chitin, has adsorption capacity, particularly towards heavy metal ions. The aim of this study was to produce chitosan spheres with and without CCP 90 activated carbon and then to evaluate their adsorption ability and kinetics using an aqueous copper(II) solution. The research was conducted using ultraviolet–visible spectrophotometry, examining the surface morphology of the obtained spheres after copper ion (Cu^{2+}) adsorption, along with elemental analysis with an energy dispersive spectrometric probe. The results confirmed an increase in the adsorption of Cu^{2+} on chitosan spheres with CCP 90 activated carbon.

Keywords: chitosan, sorption, hydrogel spheres, UV–Vis

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1. Introduction

Industrial waste and sewage pose a threat to the natural environment and living organisms, which necessitates the need to limit their negative impact through effective utilisation or complete neutralisation. Industrial sewage may contain environmentally harmful compounds such as metal ions, including nickel(II), copper(II), lead(II), chromium(III), cadmium(II) and organic substances such as pesticides or dyes. These compounds can be removed using chitosan or modified forms of chitosan [1–10]. Chitosan is a copolymer produced by the deacetylation of chitin, consisting of randomly distributed β -(1 \rightarrow 4)-D-glucosamine and N-acetyl-D-glucosamine. It can be used as an adsorbent in engineering and environmental protection. The currently used wastewater treatment methods include mineralisation [11], flotation [12], ion exchange [13], catalysis and photocatalysis [14–17] and adsorption [18, 19]. Adsorption is considered one of the most effective and economical methods of removing metal ion contaminants from watercourse systems. When chitosan is used, its adsorption efficiency is increased by mixing it with various materials – perlite [20], zeolites [21], cellulose [22], diatomaceous earth [23], titanium dioxide [24] and montmorillonite [25], among others. The production of fertilisers, paints and pigments as well as galvanisation processes produce waste containing copper ions (Cu^{2+}), which are harmful to the natural environment. This study aimed to modify chitosan with CCP 90 activated carbon, to produce chitosan hydrogel spheres and evaluate the ability of these spheres to adsorb copper(II) sulfate (CuSO_4).

2. Materials and methods

2.1. Materials

The following reagents were used to produce hydrogel spheres: commercial chitosan ($\text{C}_6\text{H}_{11}\text{NO}_4$)_n (CAS number 9012-76-4) with a deacetylation degree of 90% procured from POL-AURA (Poland); acetic acid (CH_3COOH) and sodium hydroxide (NaOH) obtained from Chempur (Poland); and activated carbon, namely Carbopal CCP 90 from Donauchem (Poland) obtained from carbonisation of coconut shells. The ion adsorption tests used $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ from Avantor Performance Materials Poland S.A. (Poland), from which a 1% solution was prepared. All other materials used were of analytical grade.

2.2. Methods

2.2.1. Preparation of Chitosan Hydrogel Spheres

Chitosan hydrogel spheres without and with the addition of 5% and 10% CCP 90 activated carbon were obtained from a 3% chitosan solution prepared in 2% acetic acid. The percentage of activated carbon added was based on the weight of the applied chitosan.

The prepared solutions were placed in a syringe and added to a 10% NaOH solution, which constituted a coagulation bath, using an infusion pump. A mechanical stirrer was used to enhance gelation of the obtained chitosan spheres and to prevent the spheres from sticking to each other. The resulting spheres were rinsed several times with distilled water until a neutral pH was obtained. Figure 1 presents photographs of the obtained chitosan hydrogel spheres. Figure 2 presents photographs of the obtained chitosan spheres after drying at room temperature.

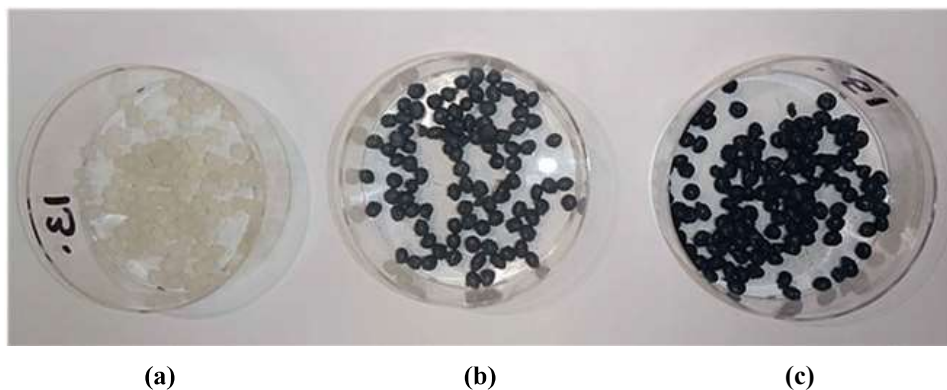


Figure 1. The photographs of chitosan spheres prepared from (a) 3% chitosan solution, (b) 3% chitosan solution with the addition of 5% activated carbon CCP 90, and (c) 3% chitosan solution with the addition of 10% activated carbon CCP 90.

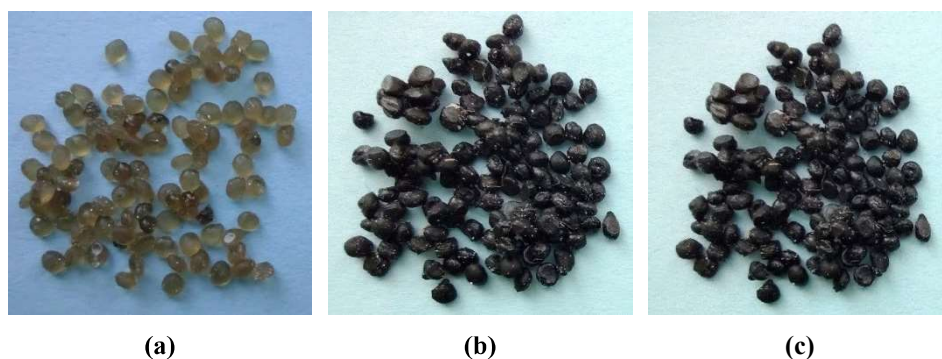


Figure 2. The photographs of chitosan spheres after drying at room temperature. They were prepared from (a) 3% chitosan solution, (b) 3% chitosan solution with the addition of 5% activated carbon CCP 90, and (c) 3% chitosan solution with the addition of 10% activated carbon CCP 90.

2.2.2. Investigation of the Adsorption Properties of the Obtained Chitosan Hydrogel Spheres

The adsorption properties of chitosan hydrogel spheres were tested using a CuSO_4 solution (prepared from 1 g of CuSO_4 in a volume of 100 cm^3). Approximately 2 g of wet chitosan spheres were placed in the beaker and 5 cm^3 of the CuSO_4 solution was added. The tests were carried out at neutral pH. Samples for testing were taken at 1, 2, 5, 10, 30, 60, and 120 min.

2.2.3. Analytical Methods

2.2.3.1. Ultraviolet–Visible Spectrometry

An Evolution™ 300 ultraviolet–visible (UV–Vis) spectrophotometer (Thermo Scientific, USA) was used to measure chitin suspensions in aqueous solutions obtained after the sonication steps. The absorbance was measured in the range of 625–850 nm. The blank was distilled water. The VISION pro™ software (Thermo Scientific, USA) was used to process the spectra.

2.2.3.2. Analysis of Morphology and Elements

A Phenom ProX scanning electron microscope (AM Eindhoven, the Netherlands) with a fully integrated energy dispersive X-ray spectroscopy (EDS) detector and software were used to assess morphology. The distribution of the different elements in the chitosan spheres was evaluated with the element identification (EID) software package and a specially designed and fully integrated energy dispersive spectrometer.

2.2.3.3. Optical Microscopy

The dimensions of the chitosan hydrogel spheres after adsorption were analysed using an optical microscope (Reichert, Austria) equipped with an ARTCAM CCD camera (Olympus, Japan), controlled by the Images Plus 2.0 software (Motic, China).

3. Results and Discussion

Quantitative calculations of the Cu^{2+} adsorption process were conducted based on data extracted from UV–Vis absorption spectra at the characteristic points of the local absorption band maxima, considering background scattering (Figure 3). The absorption value A was determined for the CuSO_4 solution at 820 nm. According to the Beer–Lambert law, the absorption value is directly proportional to the concentration of the solution. For a solution prepared from 1 g of CuSO_4 in 100 cm^3 , the A value was 0.5397, which was the starting value to assess Cu^{2+} adsorption from the CuSO_4 standard solution and the solutions after adsorption on chitosan hydrogel spheres without the addition of carbon for 1, 2, 5, 10, 30, 60 and 120 min. The spectra appeared similar when using chitosan hydrogel spheres containing 5% or 10% CCP 90 activated carbon.

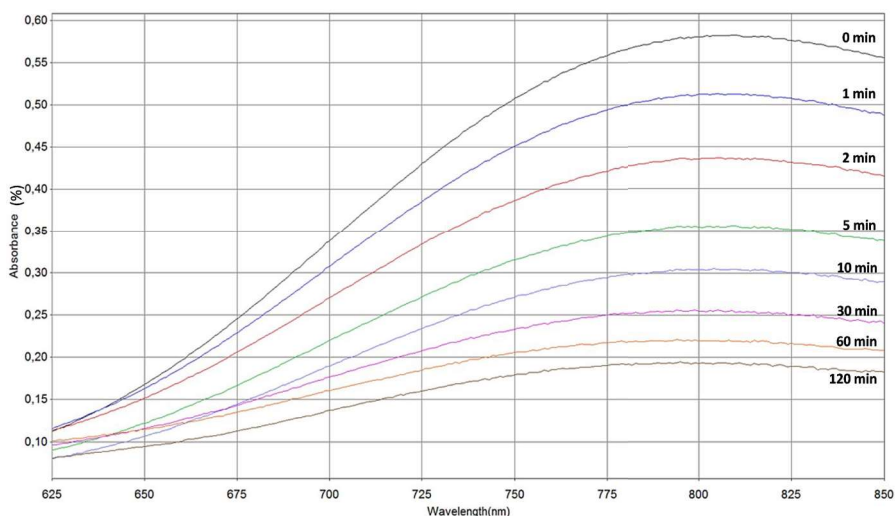


Figure 3. Ultraviolet–visible spectra (625–850 nm) for the standard copper sulfate solution and the solutions after adsorption on chitosan hydrogel spheres without CCP 90 activated carbon for 1, 2, 5, 10, 30, 60 and 120 min.

The adsorption isotherms of Cu^{2+} on chitosan spheres (Figure 4), precipitated in gel form with a significant water content, follow a course similar to the absorption patterns described in the literature [26–28].

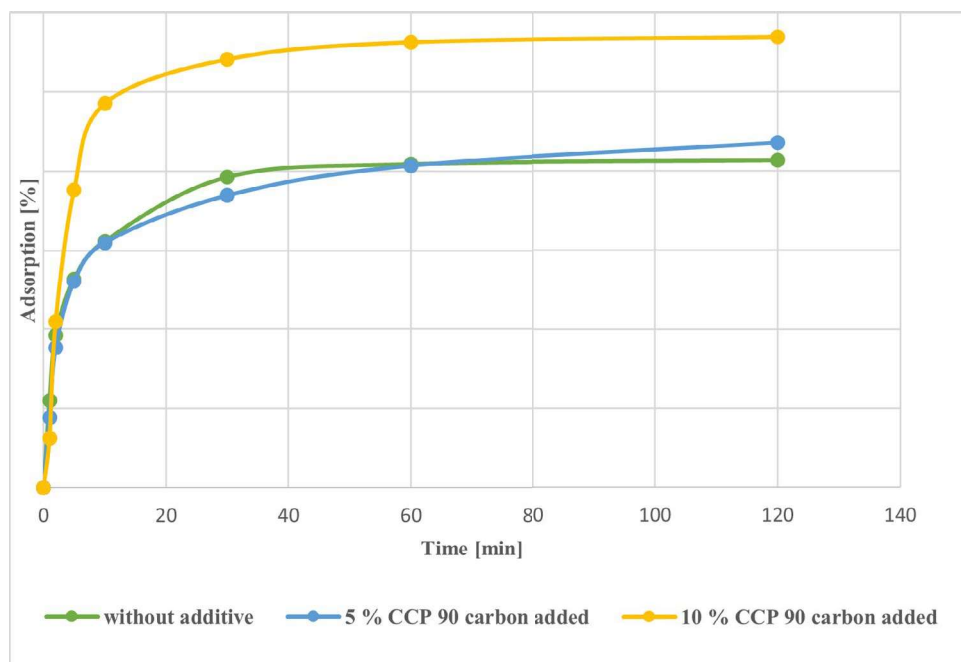


Figure 4. The course of the adsorption process of copper(II) ions for the obtained chitosan hydrogel spheres.

The adsorption value increases proportionally during the adsorption process. As time progresses, its value stabilises, indicating an equilibrium between adsorption and desorption. The adsorbent surface is saturated with the adsorbate layer and the adsorption curve is parallel to the time axis.

The fast speed of the process at the beginning of the process may be the result of strong swelling of chitosan. Interestingly, the addition of 5% activated carbon CCP 90 in the form of micropowder (60–70 μm) did not impact the process. This is probably due to the strong interaction between the ingredients and partial mutual absorption. However, the addition of 10% CCP 90 activated carbon significantly altered the course of absorption, leading to intensification. With the higher amount of activated carbon, there are additional active centres for the adsorption of Cu^{2+} . The tested chitosan hydrogel spheres presented type I isotherms, also known as the Langmuir isotherm, which is characteristic of microporous adsorbents.

Figure 5 shows scanning electron micrographs at different magnifications of the surface of the spheres obtained from a 3% chitosan solution after adsorption of Cu^{2+} , taken at different magnifications. Figure 6 shows the results of EDS analysis of chitosan hydrogel spheres without CCP 90 activated carbon after adsorption of Cu^{2+} . The main identified elements in the tested sample of chitosan sphere after adsorption of copper Cu^{2+} are oxygen (O), carbon (C), nitrogen (N), Cu and sulfur (S) (Table 1).

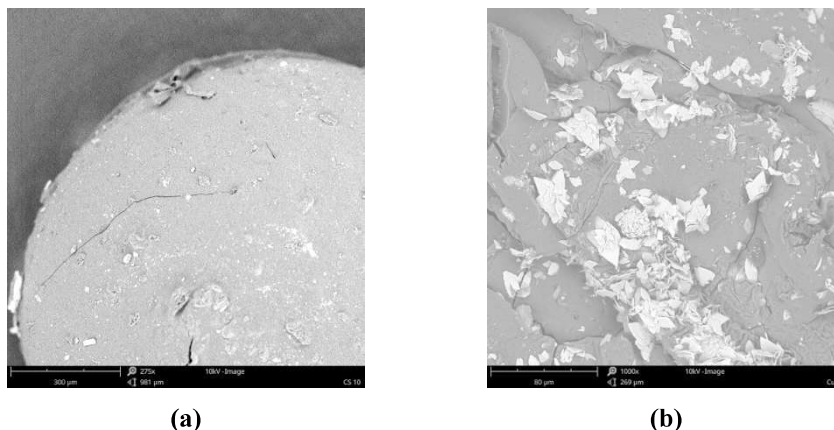


Figure 5. Scanning electron micrographs of the surface of spheres obtained from a 3% chitosan solution after adsorption of copper(II) ions without CCP 90 activated carbon at (a) 275× and (b) 1000× magnification.

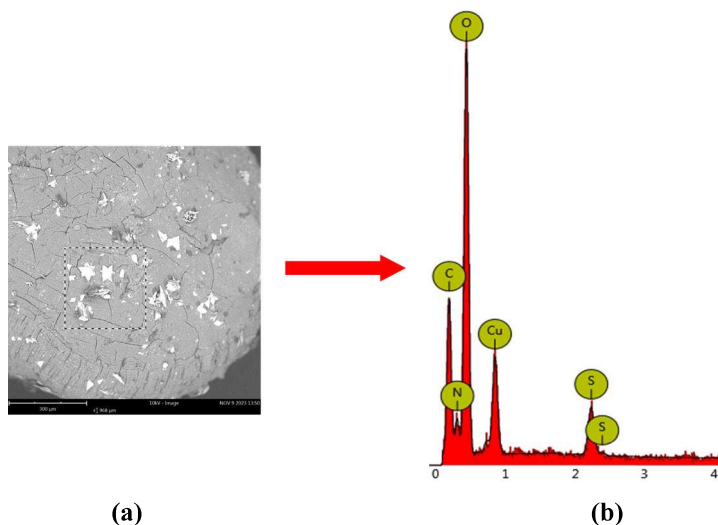


Figure 6. (a) Scanning electron micrograph of the surface of the chitosan spheres without CCP 90 activated carbon; the dashed line shows the scanning path of the energy dispersive X-ray spectroscopy (EDS) probe. (b) EDS analysis of the particles.

Table 1. Energy dispersive X-ray spectroscopy analysis of the chitosan spheres without CCP 90 activated carbon.

Element	Atomic percent [%] in the sample
Oxygen (O)	45.87
Carbon (C)	35.21
Nitrogen (N)	12.60
Copper (Cu)	4.38
Sulfur (S)	1.94

Figure 7 presents scanning electron micrographs of the surface of spheres obtained from a 3% chitosan solution with the addition of 5% CCP 90 activated carbon after adsorption of Cu^{2+} . The results of the EDS analysis are presented in Figure 8 and Table 2. The main identified elements in the tested sample are C, O, N, Cu and S.

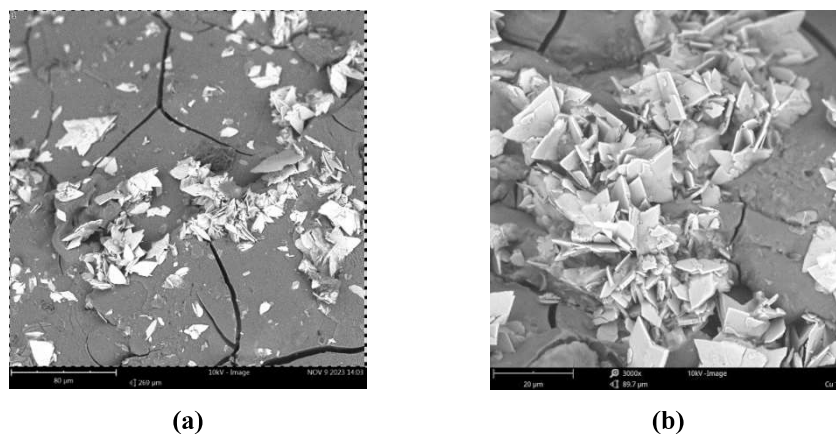


Figure 7. Scanning electron micrographs of the surface of spheres obtained from a 3% chitosan solution with the addition of 5% CCP 90 activated carbon after adsorption of copper(II) ions at (a) 269× and (b) 3000× magnification.

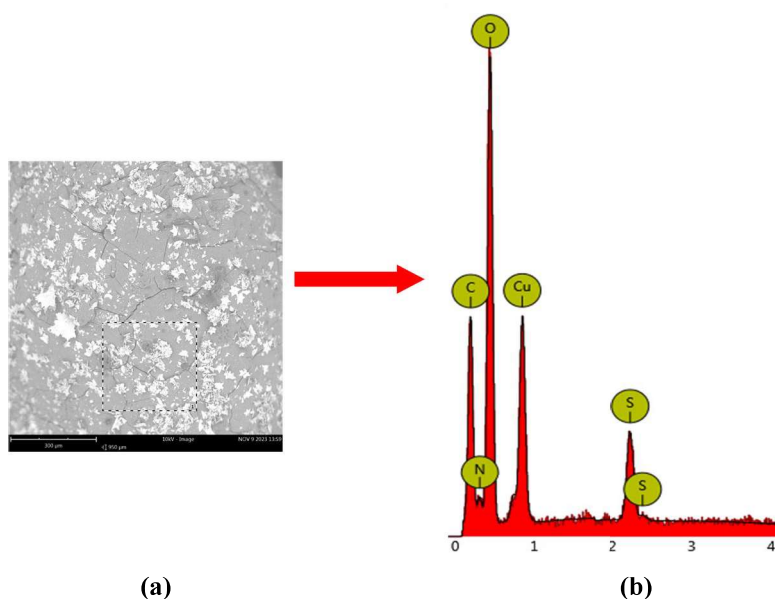


Figure 8. (a) Scanning electron micrograph of the surface of a chitosan hydrogel sphere containing 5% activated carbon; the dashed lines show the scanning area with the energy dispersive X-ray spectroscopy (EDS) probe. (b) EDS analysis of the particles.

Table 2. Energy dispersive X-ray spectroscopy analysis for the chitosan spheres containing 5% CCP 90 activated carbon.

Symbol	Atomic percent [%] in the sample
Carbon (C)	42.01
Oxygen (O)	40.56
Nitrogen (N)	7.89
Copper (Cu)	6.70
Sulfur (S)	2.83

Figure 9 presents scanning electron micrographs of the surface of chitosan spheres containing 10% CCP 90 activated carbon after adsorption of Cu^{2+} .

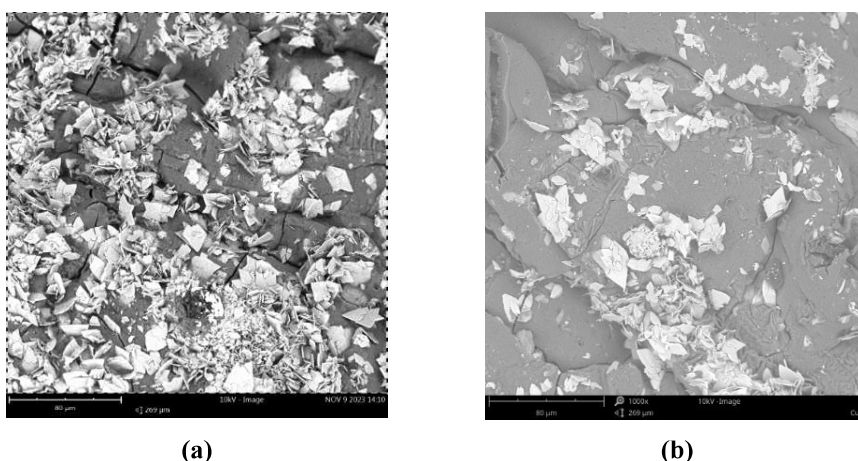


Figure 9. Scanning electron micrograph of the surface of spheres obtained from a 3% chitosan solution and 10% activated carbon after adsorption of copper(II) ions at (a) 269 \times and (b) 1000 \times magnification.

After Cu^{2+} adsorption, there were crystals of hydrated CuSO_4 visible on unmodified dried chitosan spheres. EDS analysis confirmed these observations. The adsorbed ions in the central ion system with chitosan amine ligands constitute a layer with that attracts sulfate anions. The resulting system constitutes the active centres of crystallisation nuclei. Salt probably diffuses from the inside of the hydrated gel spheres to the outside during drying. Stronger and increased diffusion and deposition of crystals outside the spheres may result from modification of the internal structure of the spheres with activated carbon. The number of hydrated CuSO_4 crystals increases with the addition of activated carbon.

EDS analysis was performed for chitosan hydrogel sphere after the addition of 10% CCP 90 activated carbon after adsorption of Cu^{2+} (Figure 10). The main identified elements are O, C, Cu, N and S (Table 3).

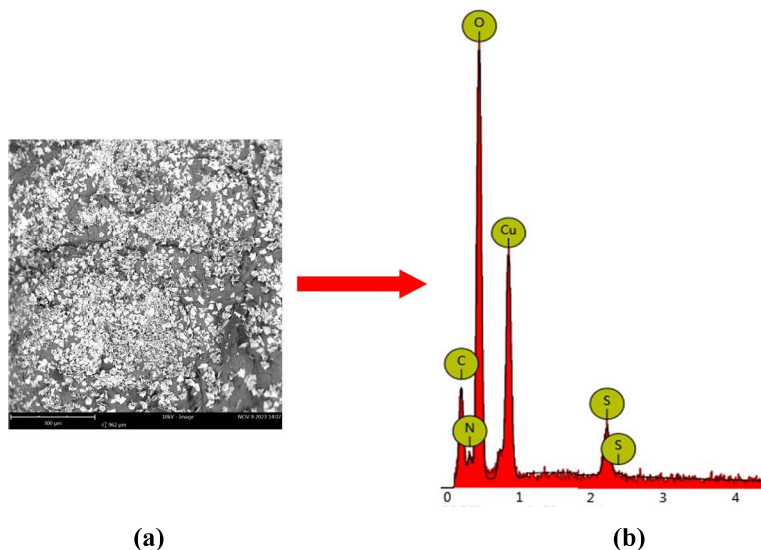


Figure 10. (a) Scanning electron micrograph of the surface of a chitosan sphere containing 10% activated carbon; the dotted lines show the scanning area with the energy dispersive X-ray spectroscopy (EDS) probe. (b) EDS analysis of particles.

Table 3. Energy dispersive X-ray spectroscopy analysis for the chitosan spheres containing 10% CCP 90 activated carbon.

Symbol	Atomic percent [%] in the sample
Oxygen (O)	49.37
Carbon (C)	29.18
Copper (Cu)	11.51
Nitrogen (N)	7.24
Sulfur (S)	2.70

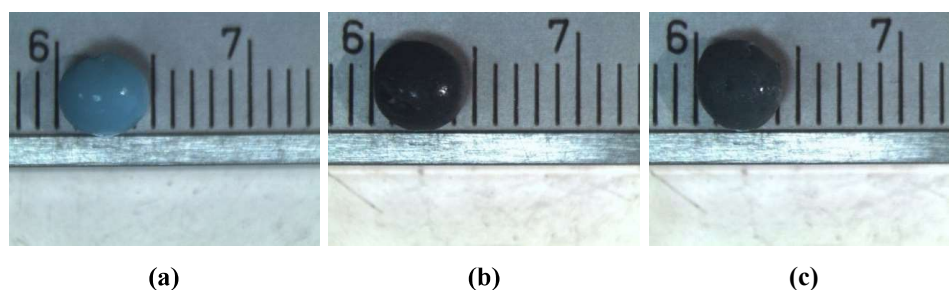


Figure 11. The photographs show chitosan spheres (a) without the addition of CCP 90 activated carbon after adsorption of copper(II) ions, (b) with the addition of 5% CCP 90 after adsorption of copper(II) ions and (c) with the addition of 10% CCP 90 after adsorption of copper(II) ions.

Figure 11 shows the sizes of the chitosan spheres after adsorption of Cu^{2+} . The addition of activated carbon affected the size of the formed chitosan spheres. Chitosan hydrogel spheres without activated carbon were 5 mm (Figure 11a). However, chitosan hydrogel spheres with 5% and 10% activated carbon (Figure 11b, c) were approximately 4.5 mm. There was also a noticeable change in the colour of the chitosan hydrogel sphere after adsorption of Cu^{2+} , from white to blue.

The addition of activated carbon in the form of a colloidal suspension of microparticles was intended to modify the spatial arrangement of chitosan chains through their initial adsorption and the largest possible surface area of chitosan and carbon available for ion migration. The addition of 5% activated carbon did not affect the adsorption of Cu^{2+} by chitosan. It is likely that the entire capacity of activated carbon was blocked by chitosan without blocking the active sites on the amine groups. The addition of 10% CCP 90 activated carbon improved the adsorption of Cu^{2+} due to the additional development of the chitosan adsorption surface or additional active centres on porous particles.

4. Conclusions

Chitosan hydrogel spheres without CCP 90 activated carbon were larger than those containing CCP 90 activated carbon after adsorption of Cu^{2+} . All chitosan hydrogel spheres effectively adsorbed Cu^{2+} . The adsorption of Cu^{2+} was similar for chitosan hydrogel spheres without CCP 90 activated carbon and chitosan hydrogel spheres with 5% CCP 90 activated carbon. However, chitosan hydrogel spheres with 10% CCP 90 activated carbon showed enhanced Cu^{2+} adsorption due to an increase in active centres.

5. References

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