

Sulfonated *Lagenaria vulgaris* shell as a potent biosorbent for copper at low pHs

Maja N. Stanković^{1*}, Vladimir D. Dimitrijević¹, Dragan M. Djordjević¹, Aleksandar Lj. Bojić¹

*1- University of Niš, Faculty of Sciences and Mathematics, Department of Chemistry,
Višegradaska 33, 18000 Niš, Serbia*

ABSTRACT

Lagenaria vulgaris shell is composed of lignocellulosic material with the ability to bind metal cations due to hydroxyl, carboxylic, lactonic, and phenolic groups present in its structure. To introduce a greater amount of sulphonic groups characterized by significant ion-exchanging capacity, oxidation, and successive sulfonation were performed. The efficiency of biosorbent based on chemically modified *Lagenaria vulgaris* shell for Cu(II) ion removal from aqueous solution was studied in batch conditions on various initial pHs. Results showed that removal efficiency (95%) did not change in the pH range from 2.0 to 5.0.

Keywords: sulfonation, Lagenaria vulgaris shell, biosorption, Cu(II) ions

* Corresponding author: maja.stankovic@pmf.edu.rs

Introduction

Among the chemical industries, those that hold heavy metals are the most dangerous in terms of discharging large amounts of wastewater containing toxic metals that living organisms can adsorb. As members of the food chain, these contaminated organisms can increase the concentration of toxic metals in humans (Barakat, 2011). While some heavy metals (iron, manganese, copper, zinc, etc.) are essential for the proper functioning of the human body, ingesting amounts greater than recommended can lead to significant health problems, even death. Mining, refining ores, electroplating, electrolysis deposition, and anodizing cleaning produce significant amounts of wastewater containing copper. Exposure to increased doses of copper causes weakness, lethargy, anorexia, and damage to the gastrointestinal tract (Theophanides & Anastassopoulou, 2002).

Adsorption is a well-known purification technique used in industrial wastewater treatment. Mineral materials (zeolites, activated alumina, *etc.*), activated carbon, industrial by-products, agro-food industry wastes (biosorbents), polymeric materials, *etc.*, can be used as the adsorbents (Akpomie & Conradie, 2020; Kurniawan et al., 2005). The adsorption process is influenced by pH, temperature, adsorbent dose, and contact time (Das et al., 2008). The main advantages of this technique are simple equipment, a wide variety of target contaminants, and effectiveness with fast kinetics. But disadvantages such as the high cost of materials (activated carbon is the most used), usual requirements for several types of adsorbents, and rapid saturation that requires expensive regeneration followed by a loss of materials make adsorption economically non-feasible for some chemical industries (Crini & Lichtfouse, 2019).

Natural substances that occur as agricultural, r food-industry waste have been widely studied in the past two decades for wastewater treatment. This process, called biosorption, became popular due to its efficiency and environment-friendly characteristics. The biosorption has found an application in removing heavy metals, phenols, dyes, and other organic pollutants from wastewater. It is a proven alternative to current technologies for the efficient removal of low concentrations of metal ions from aqueous solutions due to cost-effectiveness, simplicity, and high capacity for removing inorganics such as organic pollutants (Karaouzas et al., 2021).

Cellulose is the most abundant polysaccharide on the earth. It is the main structural component of plants and seaweed cell walls and is mainly obtained from the forest, agricultural, industrial, and animal waste. The biomass obtained from all these sources has three main components: cellulose, hemicellulose, and lignin, which content highly depend on the obtained source (Bezerra et al., 2015). Despite the fact that cellulose has many hydroxyl groups which can be complex with metal ions, it has no good adsorption properties. But chemical modifications on cellulosic material surface introducing reactive agents improve its ability to adsorb contaminants from an aqueous medium. The oxidation of cellulose by sodium periodate followed by the sulfonation reaction is a well-known procedure for improving the dry and wet tensile strength and water absorbency and solubility properties of cellulose (Rajalaxmi et al., 2010; Shet & Wallajapet, 1997; Zhang et al., 2008). Nowadays, this procedure was also used for improving the adsorption of heavy metals from water solutions (Suopajarvi et al., 2015). Our attempts with paper pulp showed that this material is not practical because it is challenging to remove swelled cellulose from water. On the other hand, oxidized and successive sulfonated cotton fibers could not reach significant adsorption capacity for copper ions. Therefore, we used the shell of *Lagenaria vulgaris* as starting lignocellulosic material.

Experimental

Materials

The *Lagenaria vulgaris* fruit used in this study was harvested in the vicinity of Leskovac, Serbia, where it grows in controlled conditions without using fertilizers. The fruit sample was washed with deionized water, air-dried in sunlight, cut into 5 cm pieces, and ground using a crusher mill (Waring 8010 ES, Germany). Then it was dried at 55 °C for 24 h and sieved to fractionize particle sizes ranging from 0.8-1.25 mm using successive sieving.

Sodium periodate was purchased from Merck (Germany) and sodium bisulfite was purchased from Sigma–Aldrich (Germany). Copper(II) sulfate was obtained from Zorka (Serbia). All chemicals were of p.a. purity grade, and all solutions were prepared using deionized water.

Preparation of biosorbent

The native biomass (lignocellulosic substrate) was oxidized by soaking 3.00 g biomass in 200 mL of NaIO₄ (16.4 mmol) in the absence of light. Periodate ions react with the cellulose without destroying its fibrous nature and result primarily in the conversion of cellulose C2 and C3 secondary hydroxyl groups to dialdehyde groups (Kim et al., 2000; Kim et al., 2004). The suspension was heated at 55 °C because, at temperatures below 20 °C, the reaction proceeds too slowly, and at temperatures greater than 55 °C, periodate decomposes and the reaction is too fast, causing non-uniformity of the product (Shet, 1996). Different reaction time (3h, 5h, and 24h) was used to enhance dialdehyde content. Sulfonation was carried out by adding the dialdehyde intermediate to 0.1M sodium bisulfite solution and stirred for 72h at room temperature. After filtration, this material was washed with deionized water until the pH reached a constant value close to neutrality and dried at 30 °C.

Characterization of modified material

The biosorbent surface functional groups were characterized using FTIR BOMEM MB-100 (Hartmann & Braun) spectrometer in the range of 4000-400 cm⁻¹. Samples of 100 mg KBr disks containing 1% of finely ground powder (<20 μm) of sulfonated *Lagenaria vulgaris* shell were stored in a vacuum dryer before recording. The point zero charges (pHpzc) and native pH of suspension (pH_{sus}) of the biosorbent were determined using methods described earlier in Stanković et al. (2016).

The batch adsorption studies

Copper removal from model wastewater was investigated using a batch adsorption process. The adsorption experiments were conducted in 250 mL Erlenmeyer flasks containing 125 mL of 50.0 mg/L Cu(II) model solution for 120 min. To maintain consistent experimental conditions, all experiments were carried out using a thermostatic orbital shaker at a shaking speed of 220 rpm. Aliquots of solutions (4.0 mL) were withdrawn at preset time intervals, filtrated, and the filtrates were analyzed for Cu(II) using a flame atomic adsorption spectrometer AAnalyst 300 (Perkin Elmer, USA).

The effect of initial copper concentration on the sorption performance of sulfonated *Lagenaria vulgaris* shell was investigated by immersing 0.5 g of biosorbent in 125 mL solution with initial Cu(II) ions concentrations of 20.0, 50.0, 100.0, 200.0, and 400.0 mg/L at 293 K and at initial solution pH value of 5.0 ± 0.2 during 120 min. The influence of pH on copper removal was

studied by adding 4 g/L of the biosorbent at 293 K at varying pH values (1, 1.5, 2, 3, 4, and 5). The initial pH of the solutions was adjusted using 0.1 M HNO₃ and 0.1 M NaOH solutions. The effect of temperature on copper removal was studied using a solution with initial Cu(II) concentration of 50 mg/L at 10, 20, 35, and 50 °C at fixed initial pH value of 5.0 ± 0.2, biosorbent dose of 4 g/L, and contact time of 120 min.

All the experiments were carried out in duplicates, and the average values were used for further calculations.

The removal efficiency at time t , RE (%), was obtained as follows:

$$RE = (C_0 - C_t) / C_0 * 100\%$$

where C_0 and C_t (mg/L) are the liquid-phase concentrations of Cu(II) ions at initial and any time t , respectively.

Results and Discussion

To determine the optimal time of the oxidation reaction, three systems were performed under the same conditions but with varying reaction times (3h, 5h, and 24h). After filtration, the material was washed with deionized water to remove the used oxidant and freeze-dried providing a 96-98% yield. The dialdehyde content was determined using an alkaline dissolving technique which is consistent with the redox reaction named after Cannizzaro (Hofreiter et al., 1931, Wang et al., 2008). It was observed that oxidation during 5h yielded material with the highest dialdehyde content (80%, 36%, and 32% for treatment during 5h, 24h, and 3h, respectively), which means that the material was more active for further modification, in this case, sulfonation.

The FTIR analysis was used to identify the characteristic functional groups present on the biosorbent. The band of medium intensity at about 1735 cm⁻¹ observed on the FTIR spectrum (Fig. 1) may be attributed to C=O stretching vibrations, probably due to aldehyde formation. This peak is also noticeable on the FTIR spectrum of refined *Lagenaria vulgaris* biomass but of much lower intensity (Mitić-Stojanović et al., 2011). The peaks at about 1350 and 1159 cm⁻¹ might be assigned to the stretching vibrations of the S-O (SO₃-H) groups (Ahsan et al., 2018; Yuen et al., 2005), confirming the incorporation of sulphonic groups into the structure of *Lagenaria vulgaris* shell.

Symmetric stretching vibrations of the hydroxyl group of primary alcohols from lignin give a strong band at about 1040 cm^{-1} , such as the symmetric stretching vibration of the S-O ($\text{SO}_3\text{-H}$) group. The strong, broadband in the $3700\text{-}3000\text{ cm}^{-1}$ region corresponds to the stretching vibrations of -OH functional groups. This band originated from numerous alcoholic and phenolic -OH groups in the cellulose and lignin (Iqbal et al., 2009). The relatively weak band at $3000\text{-}2800\text{ cm}^{-1}$ indicates C-H stretching vibrations in -CH and -CH₂ groups in the lignin, while the band at 1250 cm^{-1} could be due to stretching C-O vibration.

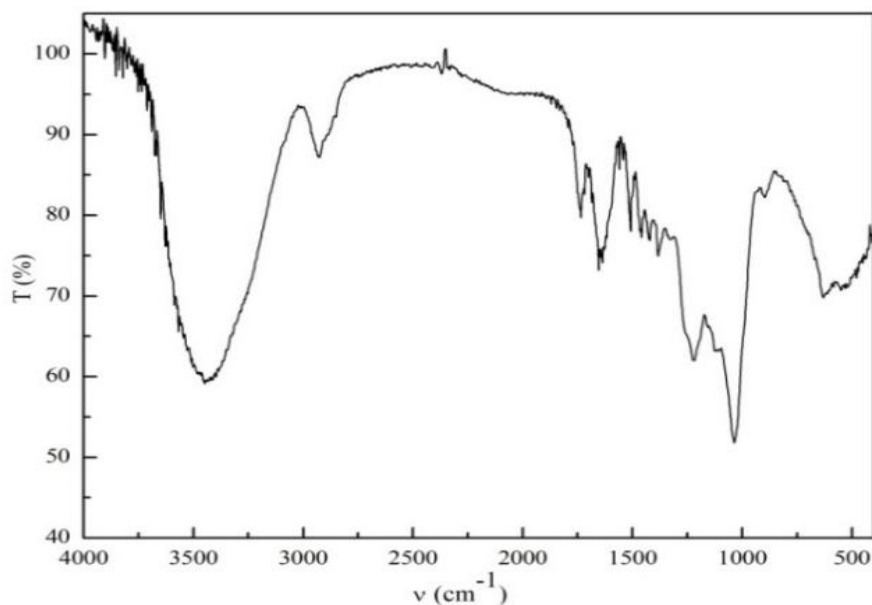


Figure 1. The FTIR spectrum of sulfonated *Lagenaria vulgaris* shell

Within the characterization of the material, the native pH of the suspension (2.78) was determined, as well as the point of zero charges, pH_{pzc} , of the material (3.76). The latter is widely used in characterizing the ionization behavior of a surface. Thus, based on pH_{pzc} , the surface of the biosorbent is expected to be positively charged at low pH values, which indicates that the removal of copper from the model solution is not only a consequence of electrostatic interactions and ion exchange. It can be assumed that complexation with incorporated sulphonic groups plays a significant role in removing Cu(II) ions. It is worth mentioning that the pH_{pzc} value of our material is lower compared to starting material (pH_{pzc} 6.10) or even *Lagenaria vulgaris* shell treated with sulfuric acid (pH_{pzc} 4.95, pH_{sus} 5.65) (Bojić et al., 2016; Ljupković et al., 2011).

Effect of pH

The adsorption experiments focused on studying the influence of solution pH on the removal of copper(II) ions from an aqueous medium. The solution pH is important in the biosorption process and affects not only surface charges and dissociation of functional groups but also solubility, chemical speciation, and diffusion rate of solute (Alothman et al., 2019). Therefore, we investigated the removal efficiency of sulfonated *Lagenaria vulgaris* shell in the pH range of 1.0-5.0 (Fig. 2). It could be assumed that at lower pH, sulphonic groups would be protonated, and competition of H⁺ ions is significant, which would result in poor Cu(II) ions adsorption. But, in this case, the removal efficiency was up to 95% at pH 5.0 and did not change even at pH 2.0. A considerable fall in removal efficiency was observed at pH 1.5 (75%), while at pH 1.0, it reached 23%. Even at very acid conditions (pH 1.5), when the competition of H⁺ ions is significantly strong, the removal efficiency of sulfonated *Lagenaria vulgaris* shell for Cu(II) ions is around 75%. This behavior significantly differs from the starting material, which shows a pronounced dependence of the removal efficiency on the pH values, as seen in Mitić-Stojanović et al. (2011). On the other hand, sulfuric acid-treated *Lagenaria vulgaris* biomass showed comparing results, *i.e.*, variation of pH (in the range from 3-6) caused a small effect on Cu(II) ions sorption onto biosorbent (Ljupković et al., 2011). Authors assumed that the acidic -SO₃ groups on the surface of the biosorbent could not be protonated on investigated pH values, so it does not lead to electrostatic repulsion of positively charged particles that would reduce the ability of copper removal. They also cited the Ozer et al. (2007) suggestion that sulfuric acid reacted with hydroxyl groups in the lignin, forming the sulfuric esters as a non-ionic functional group, which may complex copper(II) cations. Such behavior indicates that this material can be used, with unchanged productivity, to remove copper from wastewater of different sources, without previous pH preparation.

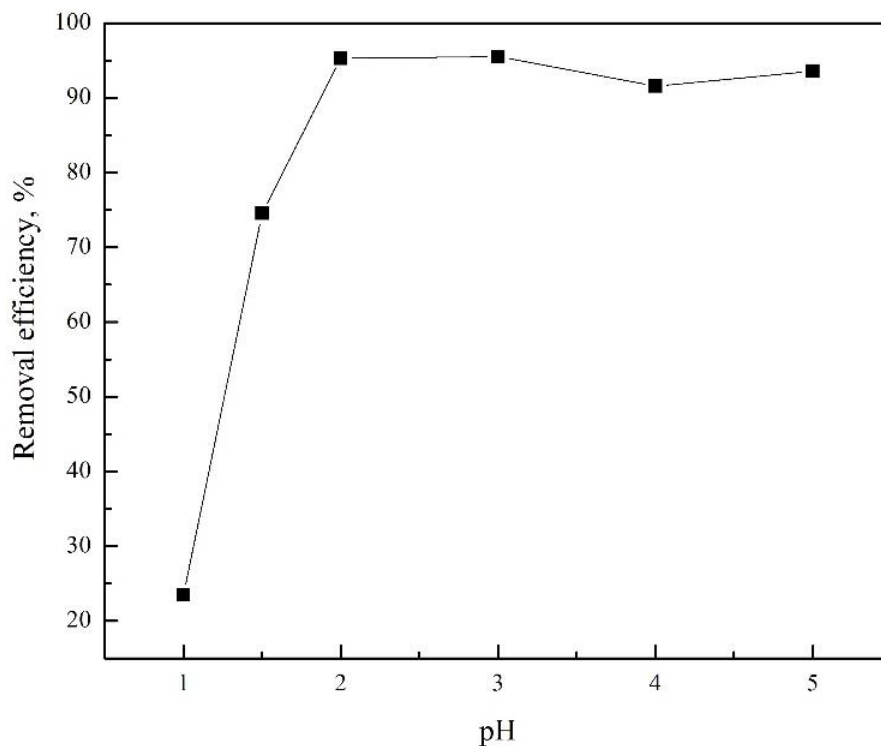


Figure 2. Effect of pH on removal efficiency of sulfonated *Lagenaria vulgaris* shell (Cu(II) conc. 50.0 mg/L, biosorbent dose 4.0 g/L, temp. $20\pm 0.5^{\circ}\text{C}$, 120 min)

Effect of initial Cu(II) concentration

Examination of the influence of the initial concentration of copper(II) ions on the removal efficiency of sulfonated *Lagenaria vulgaris* shell, was performed with initial concentrations of Cu(II) ions in the range from 20.0 to 400.0 mg/L in contact with 4.0 g/L of biosorbent granulation 0.8-1.25 mm at $20 \pm 0.5^{\circ}\text{C}$ and $\text{pH } 5.0 \pm 0.2$. As expected, results indicate a decrease in efficiency with increasing concentration of pollutants. At low initial metal ion concentrations, a large number of available, active sites on the adsorbent surface react rapidly and bind all Cu(II) ions present, allowing almost 100% adsorption (94% for initial concentrations of 20.00 and 50.00 mg/L, Fig. 3). On the other hand, at higher concentrations, a larger number of Cu(II) ions remain unabsorbed due to the saturation of a limited number of available, binding sites on the surface of the biosorbent. Contrariwise, the adsorption capacity increased from 4.7 mg/g at an initial Cu(II) concentration of 20.0 mg/L to 76.4 mg/g at an initial Cu(II) concentration of 400.0 mg/L.

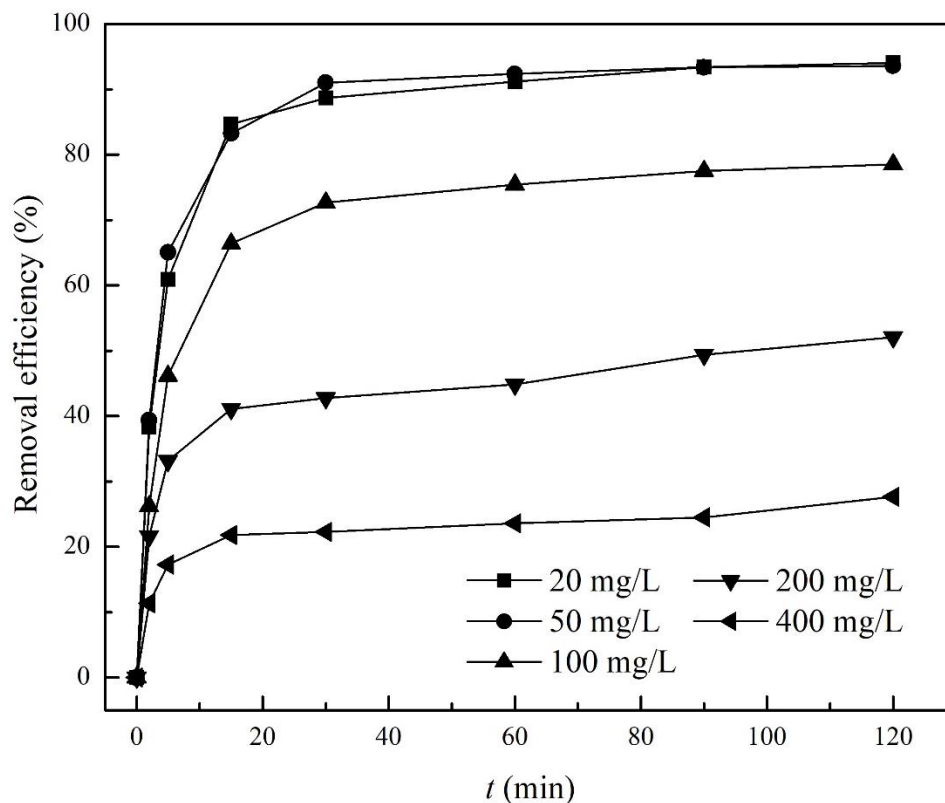


Figure 3. Effect of initial concentration of Cu(II) ions on removal efficiency of sulfonated *Lagenaria vulgaris* shell (biosorbent dose 4.0 g/L, 0.8-1.25 mm sized, pH 5.0±0.2, temp. 20±0.5 °C, 120 min).

Effect of initial temperature

The effect of temperature was examined with initial Cu(II) concentrations of 50.00 mg/L in contact with 4.0 g/L of biosorbent sized 0.8-1.25 mm during 120 minutes at 10, 20, 35, and 50 °C. The highest efficiency of copper removal (94%) from the model solution was at 20 °C, while at 10 °C it was 85%. The removal efficiency increases with increasing temperature from 10 °C to 20 °C and then decreases with increasing temperature up to 35 °C, while further heating to 50 °C does not change the removal efficiency. Such behavior suggests that a higher temperature does not favor the removal of copper from the model solution, which might be due to the desorption of copper from the biosorbent surface or adsorbent degradation at higher temperatures. Therefore, the optimal temperature range of copper removal from solution using sulfonated *Lagenaria vulgaris* shell vary between 10-20 °C.

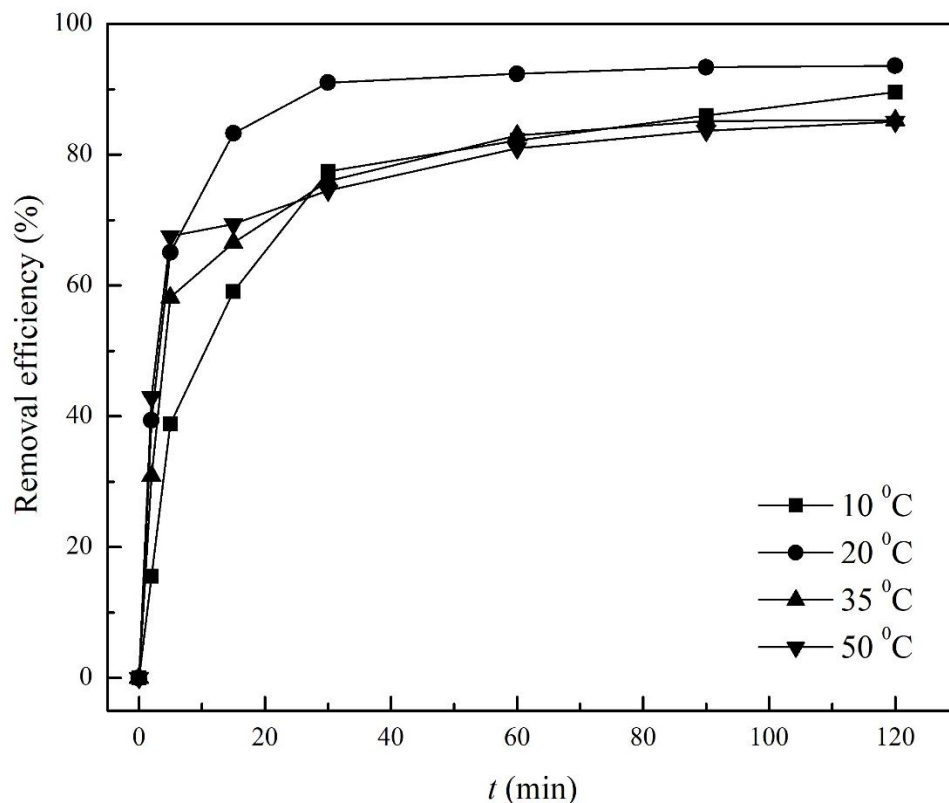


Figure 4. Effect of temperature on removal efficiency of sulfonated *Lagenaria vulgaris* shell (Cu(II) conc. 50.0 mg/L, biosorbent dose 4.0 g/L, pH 5.0, 120 min)

Conclusion

The chemical modification (oxidation and successive sulfonation) of the *Lagenaria vulgaris* shell is very important for the application in the removal of copper ions and other contaminants from aqueous solutions because materials prove new chemical properties that are more approving than the starting materials. These new properties improve the interactions between the modified material and copper ions during adsorption processes in aqueous solutions. Results showed that solution pH does not strongly influence these interactions. Therefore, the sulfonated *Lagenaria vulgaris* shell is promising for removing copper ions from natural and industrial wastewater.

Acknowledgment

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, Contract No. 451-03-68/2022-14/200124.

Conflict-of-Interest Statement

Declarations of interest: none.

References

- Ahsan, A., Islam, T., Imam, M. A., Hyder, A.H.M. G., Jabbari, V., Dominguez, N., & Noveron, J. C. (2018). Biosorption of bisphenol A and sulfamethoxazole from water using sulfonated coffee waste: Isotherm, kinetic and thermodynamic studies. *Journal of Environmental Chemical Engineering*, 6(5), 6602-6611.
- Akpomie, K. G., & Conradie, J. (2020). Banana peel as a biosorbent for the decontamination of water pollutants a review. *Environmental Chemistry Letters*, 18, 1085–1112.
- Allothman, Z. A, Bahkali, A. H., Khiyami, M. A., Alfadul, S. M., Wabaidur, S. M., Alam, M., & Alfarhan, B. Z. (2020). LoLow-costiosorbents from fungi for heavy metals removal from wastewater. *Separation Science and Technology*, 55(10), 1766-1775.
- Barakat, M. A. (2011). New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry*, 4(4), 361-377.
- Bezerra, R. D.S., Teixeira, P. R. S., Teixeira, A. S. N. M., Eiras, C., Osajima, J. A., & Silva Filho, E. C. (2015). Chemical functionalization of cellulosic materials – main reactions and applications in the contaminants removal of aqueous medium. In M. Poletto, H. L. Ornaghi Jr. (Eds.), *Cellulose - Fundamental Aspects and Current Trends*, Rijeka: InTech.
- Bojić, D., Nikolić, G, Mitrović, J., Radović, M., Petrović, M., Marković, D., & Bojić, A. (2016). Kinetic, equilibrium and thermodynamic studies of Ni(II) ions sorption on sulfuric acid treated *Lagenaria vulgaris* shell. *Chemical Industry & Chemical Engineering Quarterly*, 22(3), 235-247.

Crini, G., & Lichtfouse, E. (2019). Advantages and disadvantages of techniques used for wastewater treatment. *Environmental Chemistry Letters*, 17(1), 145-155.

Das, N., Vimala, R., & Karthika, P. (2008). Biosorption of heavy metals—an overview. *Indian Journal of Biotechnology*, 7, 159–169.

Hofreiter, B. T., Alexander, B. H., & Wolff, I. A. (1955). Rapid estimation of dialdehyde content of periodate oxystarch through quantitative alkali consumption. *Analytical Chemistry*, 27(12), 1930–1931.

Iqbal, M., Saeed, A., & Zafar, S. I. (2009). FTIR spectrophotometry, kinetics, and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd²⁺ and Pb²⁺ by mango peel waste. *Journal of Hazardous Materials*, 164, 161-171.

Karaouzas, I., Kapetanaki, N., Mentzafou, A. Kanellopoulos T. D., & Skoulikidis, N. (2021). Heavy metal contamination status in Greek surface waters: a review with application and evaluation of pollution indices. *Chemosphere*, 263, 128192.

Kim, U. J., Kuga, S., Wada, M., Okano, T., & Kondo, T. (2000). Periodate oxidation of crystalline cellulose. *Biomacromolecules*, 1(3), 488-492.

Kim, U. J., Kuga, S., & Wada, M., (2003). Solubilization of dialdehyde cellulose by hot water. *Carbohydrate Polymers*, 56(1), 7-10.

Kurniawan, T. A., Chan, G. Y. S., Lo, W. H., & Babel S. (2005). Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Science of the Total Environment*, 366(2–3), 409-426.

Ljupković, R. B., Mitrović, J., Radović, M., Kostić, M., Bojić, D., Mitić-Stojanović, D. L., & Bojić, A. Lj. (2011). Removal of Cu(II) ions from water using sulphuric acid-treated *Lagenaria vulgaris* shell (Cucurbitaceae). *Biologica Nyssana*, 2(2), 85-89.

Mitić-Stojanović D. L., Zarubica, A., Purenović, M., Bojić, D., Anđelković, T., & Bojić, A. (2011). Biosorptive removal of Pb²⁺, Cd²⁺, and Zn²⁺ ions from water by *Lagenaria vulgaris* shell. *Water SA*, 37(3), 303-312.

Ozer, D., Dursun, G., & Ozer, A. (2007). Methylene blue adsorption from aqueous solution by dehydrated peanut hull. *Journal of Hazardous Materials*, 144, 171-179.

Rajalaxmi, D., Jiang, N., Leslie, G., & Ragauskas, A. J. (2010). Synthesis of novel water-soluble sulfonated cellulose. *Carbohydrate Research*, 345(2), 284-290.

Shet, R. T. (1996). Sulfonated cellulose and method of preparation. US5522967 A.

Shet, R. T., & Wallajapet, P. R. R. (1997). Manufacture of sulfonated cellulose with improved absorbent properties. US 5703225.

Stanković, M. N., Krstić, N. S., Mitrović, J. Z., Najdanović, S. M., Petrović, M. M., Bojić, D. V., Dimitrijević, V. D., & Bojić A. Lj. (2016). Biosorption of copper(II) ions by methyl-sulfonated *Lagenaria vulgaris* shell: kinetic, thermodynamic and desorption studies. *New Journal of Chemistry*, 40(3), 2126-2134.

Suopajarvi, T., Liimatainen, H., Karjalainen, M., Upola, H., & Niinimaki, J. (2015). Lead adsorption with sulfonated wheat pulp nanocelluloses. *Journal of Water Process and Engineering*, 5, 136-142.

Theophanides, T., & Anastassopoulou, J. (2002). Copper and carcinogenesis. *Critical Reviews in Oncology/Haematology*, 42, 57-64.

Yuen, C.W.M., Ku, S.K.A., Choi, P.S.R., Kan, C.W. & Tsang, S.Y. (2005). Determining Functional Groups of Commercially Available Ink-Jet Printing Reactive Dyes Using Infrared Spectroscopy. *Research Journal of Textile and Apparel*, 9(2), 26-38.

Wang, X., Fang, G., Hu, C., & Du, T. (2008). Application of ultrasonic waves in activation of microcrystalline cellulose. *Journal of Applied Polymer Science*, 109(5), 2762-2767.

Zhang, J., Jiang, N., Dang, Z., Elder, T. J., & Ragauskas, A. J. (2008). Oxidation and sulfonation of cellulosic. *Cellulose*, 15, 489-496.