The Influence of Mixing Intensity on the Sorbent Particle's Distribution and the Efficiency of Adsorption of Cu^{2+} Ions from Aqueous Solutions

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Abstract

Industrial and human activity has a significant impact on the environment, contributing, among others, to the increase in the pollution of natural waters, including heavy metals. Their source may be sewage from the metallurgical, electroplating or mining industries. Particularly dangerous to the health and life of living organisms are, among others: Cr(VI), Zn(II), Cu(II), Cd(II), Fe(II) and Ni(II), because they have a significant ability to accumulate in soft tissues. Physicochemical methods, electrochemical, membrane and sorption processes or ion exchange are used to remove such pollutants. Applying the principles of waste-free economy in a closed circuit, selected biomass is increasingly used as a sorbent. The paper presents a theoretical analysis of the effect of mixing intensity on the efficiency of the sorption process under established process conditions in connection with the assessment of the degree of dispersion of solid phase particles in the reactor.

Keywords: *biosorbents, heavy metals, copper ions removal, spent coffee ground (SGC)*

INTRODUCTION

Adsorption of heavy metal ions from aqueous solutions by various sorbents is a critical area of research, especially in the field of environmental pollutant removal. Spent coffee grounds (SCG) have recently gained popularity as a readily available, cheap and effective adsorbent for remediation of contaminated water sources. SCG, as a by-product of the coffee brewing process, is rich in organic compounds such as cellulose, lignin and polyphenols, which contribute to its adsorption capacity [1-3] Frezzini et al. presented the methodology and effectiveness of using SCG for the removal of pharmaceutical products and volatile organic compounds (VOCs) through the adsorption process [4,5]. An unconventional application of SCG was presented by Shi et al., who developed superhydrophobic SiO2 nanoparticles produced from coffee grounds (SSD-SCG). This material adsorbed various oils in water, including viscous crude oil, both in seawater and under harsh chemical conditions, with a removal efficiency of 98.5–99.7%. After repeated use, SSD--SCG was used as a high-temperature fuel, thus realizing the goal of waste-to-energy conversion [6]. However, the classical application of SCG is their use for the removal of metal ions from water, including heavy metals under steady hydrodynamic conditions. Hence, the evaluation of the effect of mixing intensity as a parameter of adsorption efficiency is implied because it affects the geometrical distribution of particles as well as their surface interactions with metal ions. Effective mixing helps in achieving a more uniform distribution of active sites on the sorbent particles, which ultimately leads to improved sorption capacity. This is evident from studies showing that increased surface area is associated with increased sorption capacity for heavy metal ions such as Cu^{2+}, Zn^{2+}, and Cd^{2+} [7,8]. Furthermore, it helps in achieving a more uniform distribution of metal ions around active sites on the sorbent particles, which ultimately leads to improved sorption capacity. This is based on studies showing that increased surface area is associated with increased sorption capacities for heavy metal ions such as Cu^{2+}, Zn^{2+} and Cd^{2+} [7]. Similarly, Dávila-Guzmán et al. showed that SCGs can significantly reduce the heavy metal content in aqueous solutions, reaching maximum biosorption capacities under optimal conditions of 0.21 mmol/g for Cu^{2+} and 0.32 mmol/g for Pb^{2+}, respectively [9,10]. The effectiveness of SCGs as adsorbents can be influenced by various factors, such as pH, contact time, initial concentration of heavy metals, and the particulate size of the SCGs. Hunter reported that pH 5-6 is optimal for adsorption of Cu^{2+} onto spent coffee grounds [11]. Furthermore, Chwastowski et al. indicate, that a longer contact time enhances adsorption efficiency with equilibrium in adsorption established within 30 to 120 minutes [12]. The mechanism of the sorption process is identified by determining the adsorption isotherms. These are most often the Langmuir and Freundlich models. The first indicates the adsorption of a monolayer and the second indicates an inhomogeneous adsorption surface, which implies multilayer adsorption. The key role in this process is played by electrostatic interactions between active centres and metal ions. [10, 13, 14].

This study presents the experimental analysis of the influence of hydrodynamic conditions (mixing methods) on the efficiency sorption process under established conditions using SCG.

MATERIALS AND METHODS

Sorbent preparation

The tests used a various of portion sorbent (0.5-10 g) in the form of dried and unmodified spent coffee ground (SCG). The

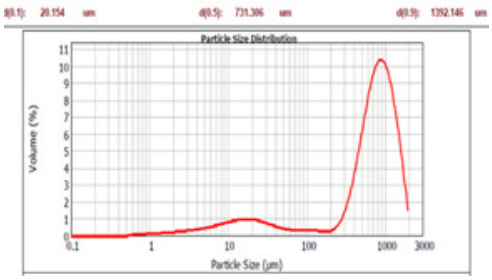

Fig. 1. Particle size distribution of SCG
Rys. 1. Rozkład wielkości cząstek SCG

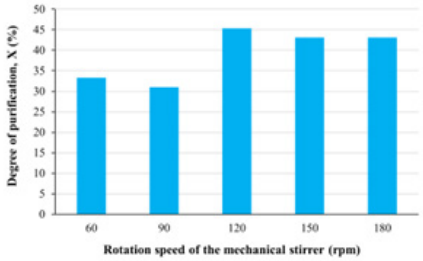

Fig. 2. Sorption removal of Cu^{2+} ions on 1 g SCG using a mechanical stirrer
Rys. 2. Sorpcyjne usuwanie jonów Cu^{2+} dla 1 g SCG za pomocą mieszadła mechanicznego

sorption material was waste from brewing roasted coffee in a pressure coffee machine with a grinding option. The particle class (0.8-1.0) mm was used for the tests, which was indicated based on the evaluation of the SCG particle size distribution. Granulometric analysis was performed using Mastersizer 2000 - Malvern Instruments. The obtained results are shown in Fig. 1. The physical properties of SCG were assumed as [15]: moisture 1.71%; organic compounds 97.13%; mineral compounds 1.16%; BET surface area 298.60 m^2/g; pHzc (pH of zero charge) 5.70.

Adsorption test

Model solutions of copper (II) ions were prepared based on copper (II) nitrate, $[Cu(NO_3)_2\ 3H_2O]$, from ACROS ORGANICS. The pH of the tested solutions was 4.0 (±0.1). A total of 0.02 mol/L HNO_3 was used to correct the pH. The tests were performed for the range of initial concentrations of 10–1000 mg/L. The sorption process was carried out in 150 mL beakers using 100 mL of copper (II) ion solution sample. Both phases were mixed using a mechanical laboratory mixer with the possibility of smooth correction of the rotor speed with mixing speed 120 rpm. The distance from the bottom of the vessel was 0.02 m and was equal to the length of the movable arm of the rotor. Sorption was carried out at room temperature (295 K). It was assumed that the time to achieve sorption equilibrium was 60 min. The suspension was separated by gravity filtration on a hard filter. The filtrate was analysed for the content of copper (II) ions. The initial and final concentrations of the tested solutions before and after sorption were determined by the cuprizone method using a Cadas 200 Dr. Lange UV-VIS spectrophotometer. The standard curve method was used. The measurements were carried out in ammonia- citrate medium at pH 8.0-9.5. The absorbance of the solutions was measured at a wavelength of 600 nm [16]. The obtained sorption results were compared with the values from mixing the system using a laboratory shaker [14]. The initial concentrations of copper solutions and the conditions of the sorption process (temperature, shaking time, volume of the tested solution, sorbent mass) were identical for both experiments.

The procedure for performing the sorption process included: placing a dose of SCG in a beaker, adding a measured portion of the tested model solution and starting the laboratory mixer. An agitator with one movable blade of 0.02 m length was used, which was positioned horizontally during movement. The height of the rotor position from the beaker bottom was 0.02 m.

Theoretical analyse for copper ions adsorption

The degree of purification of studied solutions from copper (II) ions, X, %, was determined using formula (1):

$$X = \frac{c_0 - c_e}{c_0} \cdot 100\% \quad (1)$$

where: c_o and c_e – initial and equilibrium concentration of $Cu2^+$ ions in solutions, mg/L

The sorption capacity was calculated using formula (2):

$$q_e = \frac{V(c_0 - c_e)}{m} \quad (2)$$

where: q_e is the amount of adsorbed ions per unit mass of the sorbent in the equilibrium state, (mg/g), V is the volume of the solution (L) and m is the amount of dry mass of the sorbent (g)

The removal of $Cu2^+$ ions on unmodified ground coffee was described by often used the Langmuir isotherm model. The equation of this isotherm and their linear form were described in detail in our previous study [14].

RESULTS AND DISCUSSION

The influence of the rotational speed of mechanical stirrer on efficiency of ions copper adsorption

Based on preliminary studies [14], two doses of SCG were selected for further testing at 0.5 and 1.0 (g). In the first step, a sorption

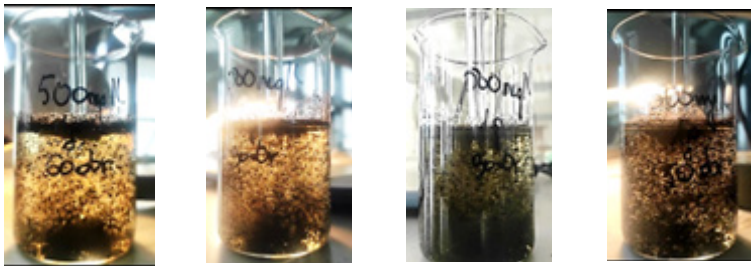

Fig. 3. Sample images of spent coffee grounds distribution. C_o = 500 mg/L; 1 g SGC; rotation speed of the mechanical stirrer: a) 60 rpm, b) 90 rpm, c) 120 rpm, d) 150 rpm

Rys. 3. Przykładowe obrazy dystrybucji ziaren zużytych fusów kawy. C_o = 500 mg/L; 1 g SGC, prędkość obrotowa mieszadła mechanicznego: a) 60 rpm, b) 90 rpm, c) 120 rpm, d) 150 rpm

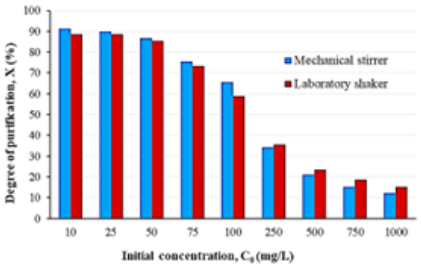

Fig. 4. Sorption removal of Cu^{2+} on 0.5 g SCG using a laboratory shaker and a mechanical stirrer

Rys. 4. Usuwanie sorpcyjne jonów Cu^{2+} dla 0,5 g SCG przy użyciu wstrząsarki laboratoryjnej i mieszadła mechanicznego

experiment was performed under the established process conditions (section 2.2: V=100 mL; pH = 4.0; T=295 K; contact time-1h) for a variable range of stirrer rotational speeds (60-180 rpm). The initial concentration of copper ions in the solution was 500 mg/L, and the SCG dose was 1 g. The obtained results are shown in Fig. 2.

Analysing the purification degree values of the water samples (Fig. 2), it can be indicated that the maximum efficiency of the sorption process close to 45% was obtained for a mixing speed of 120 rpm. Increasing the rotor speed to 150 rpm and 180 rpm caused a slight decrease in the purification degree of the water solution from copper (II) ions, simultaneously causing excessive turbulence on the suspension surface, which is not a favourable phenomenon due to the risk of pulp aeration. The obtained results indicate that the rotational speed of 120 rpm is optimal for carrying out the sorption process of Cu^{2+} ions on spent coffee grounds. For this reason, subsequent experiments were performed for this mixing speed.

Fig. 3 presents sample images showing suspension of spent coffee beans under low to high rotational speed conditions.

The images reveal a much denser distribution of SCG throughout the solution tank with increased mixing. The distribution of coffee beans throughout the solution volume occurs for rotor speeds above 120 rpm (Fig.2c). Uneven suspension of sorbent grains while retaining a significant number of SCG particles near the bottom of the tank was noted for speeds below 80 rpm. The fluid movement in these conditions is insufficient to keep the beans in suspension for a longer period of time. This causes the process of their settling to dominate.

While increased agitator speeds generate vortices directly under the rotor at first and cause particles to be lifted from the bottom of the tank. Over time, the SCG grains are distributed throughout the solution volume, which means that the thermodynamic conditions are stabilized. This state should be understood as a balance between the suspension of beans caused by fluid movement and their settling due to hydrophilicity.

Additionally, the lack of turbulence above the impeller, limited the mechanical pulling process of SCG grains originally floating on the surface of the solution into the interior of the tank. For this reason, a significant number of grains did not participate in the sorption process. This is confirmed by the low result of the process efficiency index (Fig.2a).

Assessment of the effect of mixing method on the results of copper (II) ions sorption from aqueous solutions

A comparison of the degree of copper ion purification in model solutions depending on the type of mixing method used is shown in Fig. 4. The sorption experiment was performed under the established process conditions (V=100 mL; pH = 4.0; T=295 K; contact time-1h mixing speed 120 rpm; shaking speed 200 rpm)

It was observed that there is a small difference (on average about 2.5%) in the degree of purification of aqueous solutions from copper (II) ions, depending on the hydrodynamic conditions in the vessel. In the range of low concentrations of the tested solutions (10-100 mg/L), slightly more favourable sorption results were obtained using a mechanical stirrer, while in the concentration range of 250-1000 mg/L an opposite trend was noted. In both cases, the sorption efficiency decreases with the increase in the initial concentration of Cu^{2+} ions in the solution. The highest sorption efficiency (over 90%) was noted for the lowest concentration of the contaminant (Cu^{2+} ions), while the lowest value equal to 15% of the degree of ion removal was determined for the initial concentration of 1000 (mg/L)

The obtained test results interpreted in accordance with the Langmuir equation are presented in Figure 4. The values of the coefficients qmax and b of the equation are listed in Table 1.

To determine the capacity of the obtained monolayer, i.e. the amount of adsorbate covering the adsorbent surface with a layer of single molecules, the linear form of the Langmuir isotherm was used. The calculated value of the correlation co-

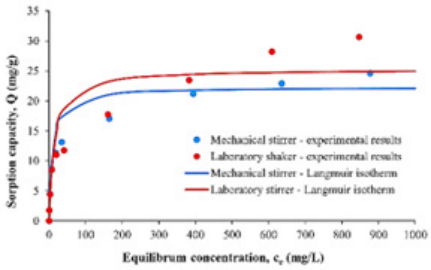

Fig. 5 Langmuir isotherms for Cu^{2+} ions sorption from aqueous solutions on 0.5 g SCG using a laboratory shaker and a mechanical stirrer
Rys. 5. Izotermy Langmuira dla sorpcji jonów Cu^{2+} dla 0,5 g SCG przy użyciu wstrząsarki laboratoryjnej i mieszadła mechanicznego

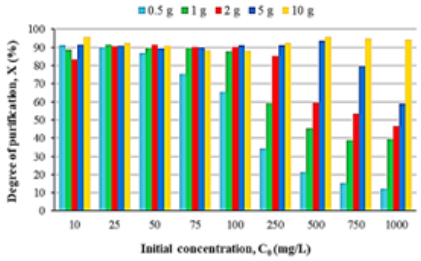

Fig. 6. Sorption removal of Cu^{2+} ions from aqueous solutions using various sorbent dose
Rys. 6. Usuwanie sorpcyjne jonów Cu^{2+} z roztworów wodnych przy użyciu różnych dawek sorbentu

Tab. 1. Langmuir adsorption isotherm coefficients for Cu^{2+} ions on the SCG with different mixing types
Tab. 1. Współczynniki izoterm adsorpcji Langmuira dla jonów Cu^{2+} na SCG przy różnych sposobach mieszania

Mechanical stirrer			Laboratory shaker		
q_{max} (mg/g)	b (L/mg)	R	q_{max} (mg/g)	b (L/mg)	R
22,3360	0,1004	0,9938	25.3165	0.0678	0,9924

efficient R is greater than 0.99 in both cases. This indicates a good fit to the experimental results. The maximum value of the sorption capacity (qmax) is high and amounts to 22.336 (mg/g), respectively, when using a mechanical impeller and 25.316 (mg/g), when using a laboratory shaker. This parameter provides information on the degree of occupation of all active sorbent centres (SCG). The parameter b was also determined, defining the affinity of the tested sorbent to Cu^{2+} ions. The higher its value, the greater the affinity of Cu^{2+} ions to the coffee grounds. A slightly higher value for b was obtained in the case of using a mechanical stirrer. This does not indicate a qualitative change in the sorbent used, but only a greater accessibility of its surface for the removed Cu^{2+} ions.

Comparison of the purification degree of aqueous solutions from copper (II) ions depending on the sorbent dose

To compare the efficiency of Cu^{2+} ion sorption from aqueous solutions depending on the sorbent mass, 0.5, 1, 2, 5 and 10 g of unprocessed coffee grounds were used, respectively. Each experiment was carried out using a mechanical stirrer for the following process conditions: solution volume 100 mL, pH = 4.0, room temperature, time of adsorption 1 h and mixing speed 120 rpm. The obtained results are presented in Fig. 6.

The obtained results indicate that the highest sorption efficiency (above 80%) was noted for initial concentrations of copper ions in the range of 10-50 mg/L, regardless of the sorbent dose (SCG). It should be noted that with the increase of the initial concentration of Cu^{2+} in the tested sample, the degree of ion removal decreases. This tendency is particularly visible in the case of using a dose of SCG in the amount of 0.5 g and 1 g. The efficiency of the sorption process for the highest concentration of 1000 mg/L reaches a value of about 12% for 0.5 g and 40% for 1 g, respectively. Only in the case of using 10 g of sorbent, the purification degree of solutions from copper ions remains at a high level (about 90%) in the entire tested concentration range.

CONCLUSION

Based on the conducted experiments, the following conclusions can be drawn:

- used coffee grounds after brewing in a coffee machine effectively removed copper (II) ions from model aqueous solutions.
- with the increase in the sorbent mass, the degree of purification of aqueous solutions from copper (II) ions increased, especially in the range of higher concentrations
- there is a slight difference (on average by approx. 2.5%) in the degree of purification of aqueous solutions from copper (II) ions depending on the type of mixing used (laboratory shaker and mechanical stirrer) and the speed of rotation of the stirrer.
- SCG can be an alternative and cheap sorbent for removing heavy metal ions.

ACKNOWLEDGEMENTS

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Wpływ intensywności mieszania na rozkład cząstek sorbentu i efektywność adsorpcji jonów Cu^{2+} z roztworów wodnych

Działalność przemysłowa i człowieka wywiera istotny wpływ na środowisko, przyczyniając się między innymi do wzrostu zanieczyszczenia wód naturalnych, w tym metalami ciężkimi. Ich źródłem mogą być ścieki z przemysłu hutniczego, galwanicznego czy górniczego. Szczególnie niebezpieczne dla zdrowia i życia organizmów żywych są m.in.: Cr(VI), Zn(II), Cu(II), Cd(II), Fe(II) i Ni(II), ponieważ wykazują znaczną zdolność do akumulacji w tkankach miękkich. Do usuwania tych zanieczyszczeń stosuje się metody fizykochemiczne, procesy elektrochemiczne, membranowe, sorpcyjne czy wymianę jonową. Stosując zasady gospodarki bezodpadowej w obiegu zamkniętym, coraz częściej jako sorbent wykorzystuje się wyselekcjonowaną biomasę. W artykule przedstawiono teoretyczną analizę wpływu intensywności mieszania na efektywność procesu sorpcji w ustalonych warunkach procesowych w powiązaniu z oceną stopnia dyspersji cząstek fazy stałej w reaktorze.

Słowa kluczowe: *biosorbenty, metale ciężkie, usuwanie jonów miedzi, mielone fusy z kawy*