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THE APPLICATION OF WHEAT BRAN FOR THE REMOVAL OF COPPER IONS FROM POLLUTED WATER

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Abstract. The purpose of the study underlying the present paper was to determine the adsorption of copper ions which happens to be one of the most important toxic heavy metals in the environment; for that purpose a test was carried out under laboratory conditions using wheat bran as adsorbent. The object of the test was to examine the effect of solution pH, contact time, adsorbent dose and initial copper ions concentration (2 mg/L to 20 mg/L) on adsorption yield and uptake. Three masses of wheat bran (0.5 g, 1.0 g and 2.0 g) were used for this experiment. 1.0 g of wheat bran gave a maximum adsorption efficiency at pH 5.0. At this pH, the adsorption efficiency for initial copper ions concentration of 5 mg/L was found to be 65.8% at room temperature for a contact time of 60 min. The adsorption of copper ions slowly reached equilibrium at 30 mins. With an adsorbent dose of 0.5 g of wheat bran, a maximum uptake of 0.277 mg/g of copper ions was recorded. With increasing mass of adsorbent dose from 0.5 g to 2.0 g. the adsorption uptake of copper ions decreased from 0.273 mg/g to 0.087 mg/g The highest removal efficiency of copper ions was found to be at a metal concentration of 5 mg/L. With the metal concentration increasing the adsorption of copper ions by 0.5 g of wheat bran decreased from 52.0% to 39.9%.

Keywords: adsorption, adsorbent, wheat bran, copper ions.

Introduction

Water plays an important role in our lives and the global economy as a whole. Water covers 71% of the surface of the Earth, and 3% of which is fresh water. Fresh water is most fit for human consumption and can be derived from lakes, rivers, groundwater etc. Approximately, 70% of the fresh water is used in agriculture sector (Kanamarlapudi et al., 2018).

This natural resource is becoming scarce in many parts of the world, which is becoming a problem, causing severe social and economic concerns. As pointed out by Vardhan et al. (2019), the World Water Council has assessed that by 2030, the number of people living in water scarce areas will increase to around 3.9 billion. Though over the last few years access to safe drinking water has improved, it is estimated that about five million people per year die due to the consumption of polluted drinking water. In many developing countries, 90% of all wastewater are discharged in freshwater bodies without having undergone any treatment, to the detriment of the natural resources and human population. The concern to protect freshwater bodies for a healthy population is becoming a challenge in recent times (Kanamarlapudi et al., 2018).

The wastewater discharged from industries contains several organic and inorganic pollutants, including heavy metals which can be toxic or carcinogenic, and whose even very low concentrations can cause harm to people and other living beings (Renu et al., 2017). For instance, studies conducted by Mustapha and Agunloye (2016) showed that copper concentration between 0.01–0.02 mg/L is toxic to fish. The most concerning heavy metals discharged by a range of industries include copper (Cu), lead (Pb), cadmium (Cd), chromium (Cr), zinc (Zn), arsenic (As), nickel (Ni) and mercury (Hg) (Renu et al., 2017). Mining, mineral processing and metallurgical activities generate wastewater containing heavy metals, and they end up finding their way into the aquatic environment which can easily be absorbed by living cells (Pawar & Bhosale, 2018). Also electroplating, textile, battery manufacturing, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries are considered as main sources of heavy metal ion pollution (Ahmaruzzaman, 2011).

Scientists and environmental engineers are facing a tough challenge of cost-effective treatment methods of wastewater from industries containing suchheavy metals (Pawar & Bhosale, 2018). For example, copper found in large quantities in nature as an element, or in other forms a have metal regulated by the Environmental Protection Agency andnormally used for anti-corrosion as well as a decorative coating on metal alloys (Basci et al., 2004). The conventional treatment methods which have been employed for removing heavy metals such as copper from polluted water include chemical precipitation, ion exchange, coagulation, reverse osmosis, membrane filtration and electrochemical methods (Bashir et al., 2018). However, such conventional methods have low removal efficiencies, contribute to the generation of toxic sludge, high energy consumption and are generally expensive (Kumar et al., 2019).

Adsorption, however, has been found to be one of the most effective methods for the removal of heavy metal ions from wastewater. Activated carbon is the most widely used adsorbent in industries; but the high cost of the activation process limits the use of activated carbon in treating wastewater (Ahmaruzzaman, 2011). Using low-cost adsorbents for the removal of heavy metals have been reported in recent times and they have been found to be very effective, efficient, abundant and cost effective (Kumar et al., 2019).

The use of agricultural waste, especially those which contain cellulose, demonstrates potential adsorption capacity for various pollutants. The basic components of agricultural waste products are hemicellulose, lignin, lipids, starch, hydrocarbons, water, simple sugars, and proteins which contain a number of functional groups (Bhatnagar & Sillanpaa, 2010).

The production of wheat is increasing every year and the quantity of by-products from the wheat process is also increasing (Katileviciute et al., 2019). Wheat bran, a by-product of the wheat process is a great source for adsorption process because it possesses large amounts of dietary fibre which contains carbohydrates, proteins, starch, sugars, and celluloses and works as a good adsorbent material (Basci et al., 2004; Katileviciute et al., 2019).

The aim of the study covered by the present paper wasto assess the use of wheat bran to remove copper ions from aqueous solutions and its capability in terms of the most popular adsorption parameters.

Methodology

Preparation of wheat bran

For the purpose of an experiment a sample of wheat bran was collected from Malsena-Vievis, a wheat processing company in Lithuania. The sample was placed in the oven and heated at 105 °C for 24 h until it became dry for the purpose of the experiment, was allowed to cool to the room temperature and later sieved through a 1 mm sieve. The dried samples were weighed using the “Radwag” analytical balance in the laboratory and stored in clean and dry screw-cap containers according to the samples needed for the experiment. These samples were 0.5 g, 1.0 g and 2.0 g. The containers were labelled and tightly closed to prevent the adsorbent from absorbing moisture.

Preparation of the adsorbate solution

The standard solution of Cu (II) was prepared by dissolving copper standard solution (Cu $(NO_3)_2$ in HNO_3, 1000 mg/L Cu) in deionized water. Deionized water was manually contaminated with Cu (II) with initial concentrations of 20 mg/L, 10 mg/L, 5 mg/L and 2 mg/L of copper. These concentrations were chosen based on the maximum permitted concentrations (MPC) in the sewage collection system which is 2.0 mg/L. The reference value was chosen from the Lithuanian wastewater management regulation (Ministry of Environment…, 2006), as it was the nearest official standard that specifies the permissible concentrations of pollution that are appropriate for the experiment concerned. 0.1 M concentration of HNO_3 and 0.1 M concentration of NaOH was also prepared to control the pH of each adsorbate solution.

Experiment

The effect of the pH on the adsorption of Cu (II) ions on wheat bran was investigated using a constant mass of 1.0 g of adsorbent with 50 ml of 5 mg/L solution of individual Cu (II) ions adsorbate at different pH values (2.0, 3.0, 4.0, 5.0, 6.0 and 7.0) at room temperature, 21.3 °C. Copper ions solutions with concentration of 5 mg/L were prepared for six different pH solutions at room temperature, 21.3 °C. The variable pH was adjusted with 0.1 M NaOH and 0.1 M HNO_3 and measured with the Hanna pH meter. This was repeated three times and the average value was used for each solution.

1.0 g of wheat bran was placed in individual screw-cap containers and the various adsorbate solutions with different pHs of 50 ml was poured in the screw-cap containers containing the wheat bran, was tightly closed and put in the rotating drum shaker "Labos shake-Gerhardt" for 60 min. After 60 min., the solutions were filtered using an F1001 Grade filter and the filtrate was checked for the remaining metal ion concentration. The "Buck Scientific 210 VGP" Atomic Absorption Spectrometer (AAS) was used to measure the final concentration of Cu (II) ions. This process was employed for contact time, adsorbent dose and initial metal ion concentration experiments.

The effect of contact time on the adsorption of Cu (II) ions was investigated for three different masses of the adsorbent 0.5 g, 1.0 g and 2.0 g and 50 mL of each 5 mg/L individual adsorbate solution. Six different contact times (5, 10, 15, 30, 60 and 120 min) were studied at room temperature and optimal pH.

The effect of adsorbent dose on the adsorption of Cu (II) ions was studied using three different adsorbent masses, 0.5 g, 1.0 g and 2.0 g. The adsorbent dose was mixed with 50 mL of 5 mg/L Cu (II) concentration of each adsorbate solution at room temperature and with optimum pH of the copper ion solution.

The effect of initial Cu (II) ions concentration on adsorption was examined by mixing 0.5 g, 1.0 g and 2.0 g of adsorbent with 50 mL of individual adsorbate solution in varying concentrations (20 mg/L, 10 mg/L, 5 mg/L, 2 mg/L) of copper ions at room temperature and optimal pH. The individual ion mixtures were then placed in the rotating drum shaker "Labos shake-Gerhardt" for 60 min.

Each experiment was repeated three times, deriving the average outcome. The adsorption capacity (mg/g) and percentage adsorption (%) were calculated.

Statistical analysis

The results obtained having conducted the experiments needed to be processed to derive the actual values employing for the purpose the relevant statistical parameters. All statistical data, namely arithmetic mean, variance, standard deviation etc. were calculated using Microsoft Excel program 2016.

Results and discussions

The adsorption of copper (II) ions on wheat bran was examined as a function of the initial pH, contact time, adsorbent dose, and initial metal ion concentration.

The effect of initial pH on copper ions adsorption

One of the most important environmental factors influencing not only binding site of the adsorbent but also the solution chemistry of heavy metals is pH. The pH strongly influences the speciation and the adsorption of heavy metals (Ozer et al., 2004). Table 1 presents the results of the experiment of the effect of solution pH on the adsorption of copper (II) ions on wheat bran at room temperature and 5 mg/L of initial metal ion concentration and 1.0 g of adsorbent dose with contact time of 60 min.

Table 1. Experimental results for copper ions removal using wheat bran

Experimental pH values	Cu (II) ion concentration (mg/L)	Adsorption efficiency (%)	Adsorbed amount (mg/g)
2.0	2.50	50.1	0.125
3.0	1.87	62.5	0.156
4.0	1.82	63.7	0.159
5.0	1.71	65.8	0.165
6.0	1.60	68.1	0.170
7.0	1.55	69.0	0.173

The effect of pH on copper ions adsorption is shown in Figure 1 below providing evidence that the adsorption of Cu (II) ions is very low at acidic pH values. Adsorption efficiency was 50.1% at pH 2.0 then sharply increased to 62.5% at pH 3.0. At lower pH, hydronium ions tend to surround the surface of the adsorbent thereby decreasing the interaction of copper ions with the binding sites of the wheat bran by greater repulsive forces (Ozer et al., 2004). This supports the findings in Table 1. Also, according to (Wang et al., 2009), the concentration of hydronium ions is higher in lower pH and this results in less ligands that is found in the wheat bran for copper ions removal. As the pH increases there are more ligands available for an efficient adsorption of copper ions from the solution and this explains the process developing under pH 5.0 to 7.0, as shown in Table 1.

As seen in Figure 1, the adsorption efficiency increases with increase in pH value till 5.0 with a following gradual increase at pH 6.0. With pH greater than 6.0 the amount of OH^- ions in the solution is increased and metal ions react with these OH^- ions and are precipitated as metal hydroxides. In general, metal ions are precipitated in alkaline pH range and do not contribute towards adsorption (Farooq et al., 2010). It can be said that both adsorption and precipitation played a role in the removal of copper ions at pH above 6.0.

According to Ozer et al. (2004) experimental studies have shown that copper cations at around pH 5.0 would be expected to interact more strongly with negatively charged binding sites of wheat bran. This result was consistent with the results in the report of Kumar et al. (2019) where the adsorption of copper ions was effective at a pH of 5.0 using a number of low-cost adsorbents as groundnut seed cake, sesame seed cake and coconut seed cakel. The adsorption efficiency at this pH value in this experiment was 65.8%.

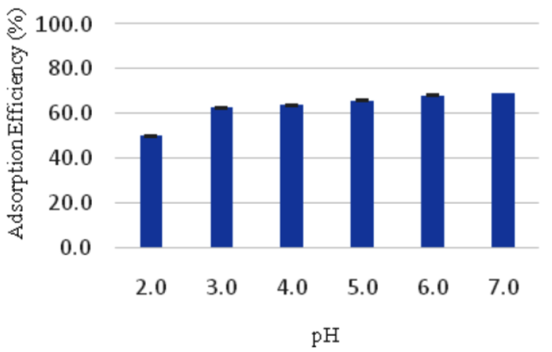

Figure 1. Relationship between copper ion adsorption efficiency and pH of solution, n = 3, ±SD

In this study, the optimum pH for copper (II) ions adsorption was found at pH 5.0 and the other adsorption experiments were performed at that pH value.

The effect of contact time on copper ions adsorption

The study of the effect of contact time is important because it gives information about the minimum time required to adsorb maximum amount of the metal ions from the solution on the adsorbent (Farooq et al., 2015). The results of contact time for adsorbed amount of copper ions on wheat bran are shown in Figure 2.

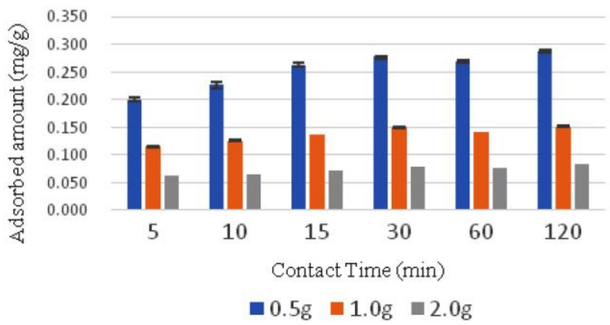

Figure 2. Influence of contact time on adsorption of wheat bran adsorbent, n = 3, ±SD

The adsorption process undergoes two stages, in Stage I there is a sharp increase in the adsorption capacity because at the beginning of the process there is a high availability of active binding sites in the adsorbent, whereas in Stage II the adsorption capacity changes at a slower rate when the time increases until due to the enrichment of the adsorbent there is no more significant change in adsorbed amount of metal ions (Farooq et al., 2015).

This same trend is observed in Figure 2 where there was a fast removal of copper ions in the solution at the earlier stages of the time before slower removal of copper ions in the solution to reach equilibrium. The adsorption of copper ions by wheat bran slowly reached equilibrium at 30 min. In view of this, a 120 min contact time was sufficient for the adsorption of copper ions on wheat bran. It is observed that with an adsorbent dose of 0.5 g, the adsorbed amount of copper ions was 0.277 mg/g at 30 min, then was fairly stable after 60 min and 120 min recording 0.269 mg/g and 0.288 mg/g respectively.

With an adsorbent dose of 1.0 g, the adsorbed amount of copper ions was 0.150 mg/g at 30 min then adsorption became fairly stable after 60 min and 120 min recording, respectively, 0.141 mg/g and 0.152 mg/g.

When the adsorbent dose was increased to 2.0 g, the adsorbed copper ions amount was 0.079 mg/g and adsorbed copper ions amount in the solution remained constant for 60 min and 120 min of contact time recording, respectively, 0.077 mg/g and 0.083 mg/g.

In conclusion, equilibrium of adsorption was reached at 30 min of contact time for all masses of adsorbent. Wang et al. (2009) also reported the adsorption of Cu (II) ions by wheat bran, rice bran and walnut hull slowly reaching equilibrium at 30 min.

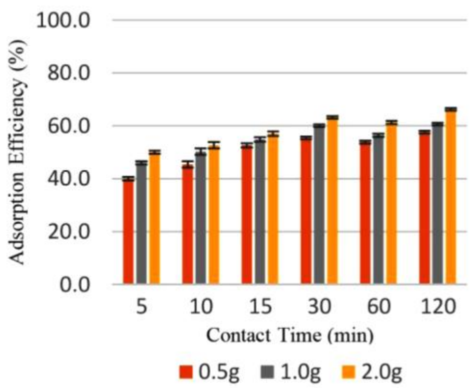

Figure 3. Influence of contact time on Cu (II) ions removal using wheat bran as adsorbent, n = 3, ±SD

In Figure 3, it can be observed that maximum adsorption efficiency occurred at 120 min with adsorbent doses 0.5, 1.0, and 2.0 g recording efficiencies of 57.6%, 60.6% and 66.2%. Equilibrium adsorption efficiency was reached at 30 min since this is when adsorption starts to settle down and remains fairly constant after 30 min.

The effect of adsorbent dose on copper ions adsorption

The adsorbent dose in the solution affects the specific uptake and efficiency, which needs to be taken into consideration when using any adsorbent (Wang et al., 2009). The influence of adsorbent dose in percentage adsorption and equilibrium uptake is indicated in, respectively, Figure 4 and Figure 5. As adsorbent dose is increased from 0.5 g to 1.0 g, there was an increase in the removal of copper ions from 54.6% to 57.2%. When the adsorbent dose was further increased to 2.0 g, the removal efficiency increased from 57.2% to 69.8%. This is as a result of the availability of more binding sites for the adsorption of copper ions (Ozer et al., 2004).

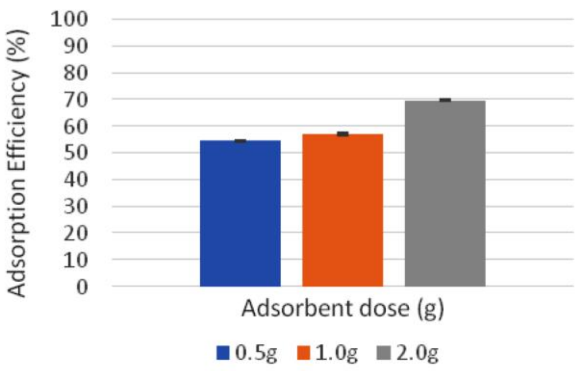

Figure 4. Influence of adsorbent dose on copper ions adsorption efficiency, n = 3, ±SD

The uptake of copper ions showed a reverse trend to the percentage adsorption as indicated in Figure 5. As the adsorbent dose was increased from 0.5 g to 1.0 g, the adsorption of copper ions per unit weight of adsorbent decreased from 0.273 mg/g to 0.143 mg/g. When further increased to 2.0 g, the adsorption of copper ions per unit weight of the adsorbent decreased from 0.143 mg/g to 0.087 mg/g. This is because of several factors which contribute to the effect of dosage of adsorbent. One of the crucial factors is that the adsorption sites remain less saturated during the adsorption reaction, as with the adsorbent dose increasing the because of the lower adsorptive capacity of the adsorbent adsorption capacity increases to a lesser (Ozer et al., 2004).

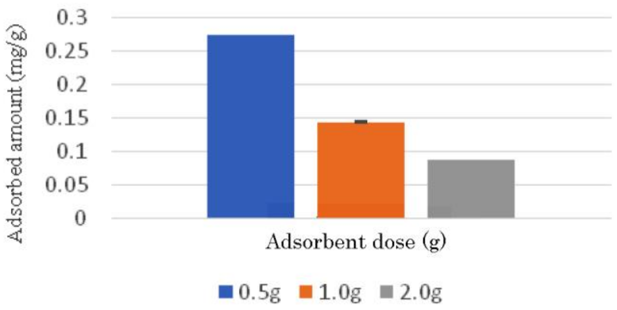

Figure 5. Influence of adsorbent dose on copper ions adsorption capacity, n = 3, ±SD

The effect of copper concentration on absorption

The results in Figure 6 show that the removal of copper ions from the solution decreases as the metal ion concentration increases from 5 mg/L to 10 mg/L and 20 mg/L. The maximum removal of copper ions was found to be at metal concentration of 5 mg/L when wheat bran is used as adsorbent. With the concentration increasing (5 mg/L to 20 mg/L) the percentage adsorption of copper ions by wheat bran decreased from 52.8% to 39.9% with the adsorbent dose standing at 0.5 g. When adsorbent dose was increased to 1.0 g, the adsorption decreased from 58% to 44% with increasing concentration from (5 mg/L to 20 mg/L) and when increased to 2.0 g, the adsorption percent rate decreased from 63% to 45.1%.

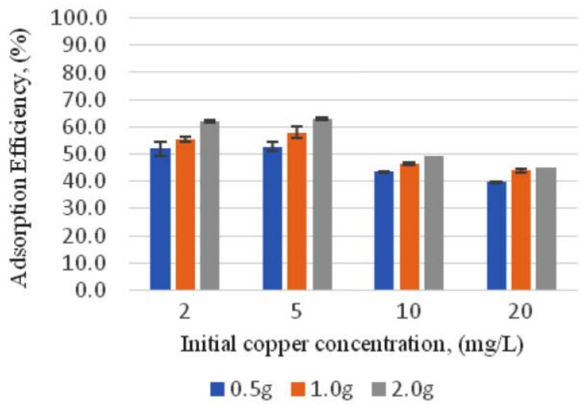

Figure 6. Influence of copper concentration on adsorption efficiency, n = 3, ±SD

At lower metal ion concentrations, all copper ions contained in the solution interact with the binding sites on the adsorbent, and as a result the percentage adsorption were higher than when the concentration of initial metal ions were high. Lower adsorption capacity is recorded at higher concentrations because of the saturation of adsorption sites (Ozer et al., 2004). This can be improved by diluting solutions or wastewater of high metal ion concentrations.

The adsorption efficiency of copper ions at higher concentrations shows a decreasing trend while the uptake of copper ions changes in the opposite direction. The uptake of copper ions in the solution increased in parallel to the increasing metal ion concentration.

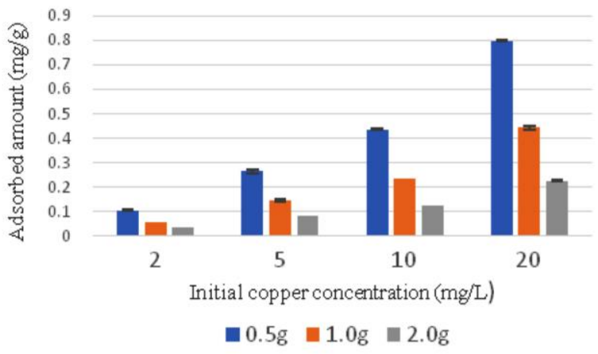

Figure 7. Influence of copper ions concentration on adsorption capacity, n = 3, ±SD

In Figure 7, the uptake of copper ions from solution increased from 0.104 mg/g to 0.797 mg/g when the adsorbent dose was 0.5 g, and the metal ion concentration increased. With adsorbent dose of 1.0 g, the uptake of copper ions increased from 0.055 mg/g to 0.442 mg/g and 0.031 mg/g to 0.225 mg/g with the adsorbent dose staying at 2.0 g.

Conclusions

1. The adsorption of copper ions using wheat bran was determined at a pH of 5.0 at room temperature with initial metal concentration of 5 mg/L and adsorbent dose of 1.0 g, and at this pH the maximum removal of Cu(II) ions was found to be 65.8%.

2. The adsorption of copper ions on wheat bran slowly reached equilibrium at 30 min and the uptake of Cu(II) ions was found to be 0.277 mg/g for adsorbent dose of 0.5 g, and, respectively, 0.150 mg/g at 1.0 g and 0.079 mg/g at of 2.0 g.

3. The adsorption of copper ions increased with increasing adsorbent dose but the adsorption of copper ions per unit weight of adsorbent decreased as adsorbent dose was increased. The removal yield of copper ions increased from 54.6% to 69.8% when adsorbent dose was increased from 0.5 g to 2.0 g. The uptake capacity of Cu(II) ions decreased from 0.273 mg/g to 0.087 mg/g with the increased of adsorbent dose from 0.5 g to 2.0 g.

4. The maximum removal of copper ions was found at metal concentration of 5 mg/L using wheat bran. Once the metal ion concentration increases the adsorption of copper ions decreased.. As concentration increased from 2 mg/L to 20 mg/L with adsorbent dose of 0.5 g, the adsorption decreased from 52% to 39.9%

5. The results showed that wheat bran can successfully be used to remove copper ions in polluted water and due to its abundant availability and low-cost wheat bran has significant advantages in respect of other natural materials.

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KVIEČIŲ KEVALŲ NAUDOJIMAS VARIO JONAMS IŠ UŽTERŠTO VANDENS ŠALINTI

G. M. N. A. Lomoko, D. Paliulis

Santrauka

Vario jonų, kurie yra vieni iš svarbiausių toksiškų sunkiųjų metalų aplinkoje, adsorbcija buvo ištirta laboratorijoje naudojant nemodifikuotas kviečių sėlenas kaip adsorbentą. Ištirtas tirpalo pH, kontakto trukmės, adsorbento dozės ir pradinės vario jonų koncentracijos poveikis adsorbcijos gebai ir absorbcijos efektyvumui. Šiame eksperimente buvo naudojamos trys nemodifikuotų kviečių sėlenų masės (0,5 g, 1,0 g ir 2,0 g). 1,0 g nemodifikuotų kviečių sėlenų įgavo didžiausią adsorbcijos gebą esant pH 5,0. Esant šiam pH ir pradinei vario jonų koncentracijai 5 mg/l, adsorbcijos geba kambario temperatūroje 60 minučių sąlyčio metu buvo 65,8 %, naudojant 1,0 g nemodifikuotų kviečių sėlenų. Vario jonų adsorbcija pasiekė pusiausvyrą maždaug per 30 minučių. Su adsorbuojančia 0,5 g nemodifikuotų kviečių sėlenų doze buvo užfiksuota maksimali 0,277 mg/g vario jonų geba. Vario jonų absorbcija sumažėjo nuo 0,273 mg/g iki 0,087 mg/g, didėjant adsorbento dozei nuo 0,5 g iki 2,0 g. Nustatyta, kad didžiausias vario jonų šalinimo efektyvumas pasiektas esant 5 mg/l metalo koncentracijai. Vario jonų adsorbcija, naudojant 0,5 g nemodifikuotų kviečių sėlenų, sumažėjo nuo 52,0 % iki 39,9 %, didėjant metalo koncentracijai (nuo 2 mg/l iki 20 mg/l).

Reikšminiai žodžiai: adsorbcija, adsorbentas, kviečių sėlenos, vario jonai.