

Efficient Removal of Cr(VI) Ions from Aqueous Solutions using Arabinogalactan Coated Magnetic Nanoparticles

Katja Vasić^{a,b}, Mateja Primožič^a, Željko Knez^{a,c}, Maja Leitgeb^{a,c,*}

^aUniversity of Maribor, Faculty of Chemistry and Chemical Engineering, Laboratory of Separation Processes and Product Design, Smetanova ulica 17, 2000 Maribor, Slovenia

^bUniversity of Maribor, Faculty of Electrical Engineering and Computer Science, Institute of Electrical Power Engineering, Laboratory for applied electromagnetics, Koroška cesta 46, SI-2000 Maribor, Slovenia

^cUniversity of Maribor, Faculty of Medicine, Taborska ulica 8, 2000 Maribor, Slovenia
 maja.leitgeb@um.si

Heavy metals being the most common pollutants of water and soil pose a risk for the ecosystems due to their non-degradable nature. Especially, chromium (Cr) is widely used in metal plating, pigmentation, printing, textile dyeing, wood preservation and other industries, therefore being a very common pollutant in surface and underground waters. The elimination of such pollutants from wastewater is highly important because of their carcinogenic and toxic nature. Among many methods for the removal of Cr(VI) ions from wastewater, adsorption is the most common and effective physiochemical method, because of its high efficiency, recyclability, cost-effectiveness and simplicity. Polysaccharides have been extensively employed in synthesis of magnetic nanoparticles (MNPs) as coating materials for constructing an adsorptive material, mainly due to their high adsorptive ability and low-cost. They are also environmentally friendly, renewable, biodegradable, biocompatible and can easily be modified. Arabinogalactan (AG) is a polysaccharide, that has high adsorption capacity for Cr(VI) ions. AG modified magnetic nanoparticles (AG-MNPs) were prepared by co-precipitation method using ferric and ferrous ions and later used as the adsorptive material for efficient Cr(VI) removal. The optimum conditions for Cr(VI) ions adsorption were found to be at pH 4, with contact period of only 30 min at 200 rpm, resulting in 92.9% adsorption efficiency and 99.6% maximum adsorption efficiency after 120 min at 200 rpm, using Cr(VI) ions at concentration of 0.5, 1.0 and 5.0 mg/L.

1. Introduction

Rapid world industrialization is causing contamination of freshwater by different pollutants, such as heavy metals. Therefore, treating and recycling of wastewater is becoming a vital part of obtaining a precious commodity as is fresh water. Wastewater from industrial processes is often contaminated with dyes, antibiotics, heavy metals and others (van Loosdrecht and Brdjanovic, 2014; Almomani et al., 2020; Wu et al., 2022). Heavy metals are trace elements with relatively high density of more than 4000 g/L and are often poisonous. Many heavy metals easily accumulate in different tissues, which are toxic and carcinogenic and can cause disorders (Enfrin et al., 2020). Chromium (Cr) is widely used in industrial activities and one of the heavy metal pollutants. Hexavalent chromium Cr(VI) is the predominant species of dissolved Cr in water, as well as a suspected carcinogen, which is toxic to humans and animals, as it can freely move through the cell membranes and its high oxidation potential (Kumar and Dwivedi, 2021). Additionally Cr(III) is considered to be less toxic form of Cr due to its low mobility and relatively low solubility (Liu and Yu, 2021; Wu et al., 2022). Many reports were published investigating various treatments for water decontamination. Some of the treatments include membrane filtration, ion exchange and chemical precipitation, reverse osmosis, solvent extraction and adsorption (Barakat, 2011; Yao et al., 2022). The simple, feasible and less expensive method is adsorption. In adsorption method, the wastewater is in contact with an adsorbent material, which captures pollutants, because of its characteristic properties, such as surface area, porosity, magnetic properties, surface charge and others (Wu et al., 2022). Various nanoparticles were investigated for the removal of contaminants from wastewater, because of their specific surface area and porosity. Different polymer-modified magnetic nanoparticles of nano-

size, such as ferric, aluminium or magnesium oxide are considered to be the most effective adsorbent materials for the removal of heavy metals from aqueous systems (Singh et al., 2023). Arabinogalactan (AG) is a highly branched natural polysaccharide with 70% water solubility, which displays high added-value functionalities, especially their adsorptive ability. Surface properties of AG are unique, since it has the ability to decrease the interfacial tension between different interfaces and to stabilize these interfaces through steric and electrostatic interactions and hydration forces. Such properties can be used to stabilize nanoparticles, as well (Davantès et al., 2019). AG exhibits high water solubility, biocompatibility and biodegradability, which renders AG attractive as a potential multifunctional nano-vehicle. Such nanoparticles are highly effective adsorbents for the removal of heavy metals, since they have numerous advantages, such as high ability, rapid kinetics, unsaturated surfaces, acceptable sorption and ease of use (Kim et al., 2013; Bhatia and Singh, 2019). In our study, AG-MNPs were used as adsorptive nanomaterial for efficient removal of Cr(VI) from aqueous solution. Effect of pH, adsorbent concentration and Cr(VI) concentration were investigated and isotherm model was analyzed using Freundlich isotherm model.

2. Materials and methods

2.1 Materials

Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), orthophosphoric acid (85%), potassium dichromate, acetic acid, hydrochloric acid (37%), sodium hydroxide and ethanol were obtained from Merck, Germany. Arabinogalactan, 1,5-diphenylcarbazide and glutaraldehyde (25%) were obtained from Sigma Aldrich, Germany. Ammonium hydroxide was purchased from Chem-Lab, Belgium. All reagents were of analytical grade and used without further purification. In all experiments, deionized water was used.

2.2 Preparation of AG-MNPs

Ferric (III) ions ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and ferrous (II) ions ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) were combined in a 2:1 M ratio and dissolved completely in 40 mL of deionized water. 1 mg of arabinogalactan (AG) was dissolved in 30 mL of water and stirred. Both solutions were added into a three-neck flask equipped with a mechanical stirrer. Later on, 5 mL of ammonium solution (25%) was added dropwise to the mixture and vigorously stirred at 500 rpm under a nitrogen atmosphere and heated to 85 °C for 1 hour. After synthesis, AG-MNPs were obtained, washed two times with distilled water and two times with ethanol, using a magnet to remove any excess of ammonia and AG from the solution. Obtained AG-MNPs were dried overnight at 50 °C.

2.3 Preparation of analysis solutions

2.3.1 Preparation of Cr(VI) solution

The stock solution of Cr(VI) was prepared using 500 mg of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in 500 mL distilled water. The calibration curve for adsorption determination was performed using Cr(VI) ions solutions with concentrations of 1 mg/mL, 0.2 mg/mL, 0.1 mg/mL and 0.05 mg/mL.

2.3.2 Preparation of orthophosphoric acid solution

70 mL of orthophosphoric acid was diluted with 30 mL distilled water to prepare a 70% orthophosphoric acid solution.

2.3.3 Preparation of 1,5-diphenylcarbazide solution

0.5 g of 1,5-diphenylcarbazide was diluted in 50 mL of acetone.

2.4 Adsorption studies

2.4.1 Batch adsorption experiments

To investigate the adsorption capacity of AG-MNPs for Cr(VI) ions, a certain amount of the adsorbent AG-MNPs was used. Adsorption studies were performed in erlenmeyer flasks using AG-MNPs with 30 mL of Cr(VI) ions solution with concentration of 1mg/L. Continual agitation was applied using orbital shaker at 200 rpm and 22 °C. 2.5 mL of Cr(VI) solution was collected after 10, 20, 30, 60, 90, 120 min and analyzed.

2.4.2 Effect of pH on adsorption

To determine the optimal pH for adsorption of Cr(VI) ions, 30 mg of adsorbent AG-MNPs was placed into an erlenmeyer flask. 30 mL of Cr(VI) ions solution with concentration of 1mg/L was added into each flask with corresponding pH (3, 4, and 5). The solution was continually agitated at 200 rpm and 22 °C. 2.5 mL of Cr(VI) solution was collected after 10, 20, 30, 60, 90, 120 min and analyzed.

2.4.3 Effect of adsorbent AG-MNPs concentration on adsorption

To determine the optimal amount of adsorbent AG-MNPs, different amounts of AG-MNPs (using concentration of 0.5 mg/mL, 1 mg/mL, 1.67 mg/mL and 2.33 mg/mL) were placed into each erlenmeyer flask. 30 mL of Cr(VI)

ions solution with concentration of 1mg/L and pH 4 was added into each flask. The solution was continually agitated at 200 rpm and 22 °C. 2.5 mL of Cr(VI) solution was collected after 10, 20, 30, 60, 90, 120 min and analyzed.

2.4.4 Effect of Cr(VI) ions solution concentration on adsorption

To determine the optimal concentration of Cr(VI) ions solution, different concentrations of the solution were prepared (1, 5, 7 and 10 mg/mL). 1.67 mg/mL of adsorbent AG-MNPs was placed into each erlenmayer flask with 30 mL of Cr(VI) ions solution with corresponding concentration adjusted to pH 4. The solution was continually agitated at 200 rpm and 22 °C. 2.5 mL of Cr(VI) solution was collected after 10, 20, 30, 60, 90, 120 min and analyzed.

2.5 Adsorption analysis

To 2.5 mL of each adsorption sample, 23.5 mL of distilled water, 1 mL of orthophosphoric acid and 1 mL of 1,5-diphenylcarbazine solution was added. The solution was vigorously mixed in an erlenmayer flask and absorbance at 550 nm was determined using Varian UV-VIS spectrophotometer. The concentration was calculated according to the calibration curve for Cr(VI) determination. All the experimental data presented are averages of three replicates.

2.6 Non-linear isotherm model

In heavy metals removal investigations, the isotherm model is commonly used to explore adsorption mechanisms, as well as adsorption capacity and adsorbent properties. However, because of model limitations, not all isotherms can fit the experimental data and therefore cannot accurately present the heavy metals adsorption process. For the description of adsorption mechanism, the two-parameter adsorption isotherm is used. There are many non-linear adsorption isotherm models, that can be used for adsorption investigation. However, in our work, Freundlich isotherm was used.

2.6.1 Freundlich isotherm model

The Freundlich isotherm is applied to multilayer adsorption, which can explain the relationship between non-ideal and reversible sorption and is performed on a heterogenous surface. Eq(1) is expressed as follows:

$$q^e = K_F C_e^{1/n_F} \quad (1)$$

where

- q^e - removal capacity at equilibrium (mmol/g)
- K_F - Freundlich affinity coefficient (mmol/g / mmol/L)
- C_e - equilibrium concentration of Cr(VI) solution (mmol/L)
- n_F - Freundlich constant

3. Results and Discussion

3.1 Effect of pH on adsorption capacity

The initial pH of the solution affects the removal and adsorption efficiency of the adsorbent. Controlling the pH of the adsorption process is crucial among parameters, as the pH of the solution affects the oxidation state of Cr(VI), as well as the surface charge of materials selected for adsorption. Depending on the concentration and pH of the solution, Cr(VI) ions exist in different anionic forms, such as $Cr_2O_7^{2-}$, $HCr_2O_7^-$, CrO_4^{2-} and $HCrO_4^-$. Figure 1 shows adsorption capacity and removal efficacy for Cr(VI) at different pH. At strong pH, such as pH 3, it exists in H_2CrO_4 form, while at pH 4 and 5, it is usually in the form of $Cr_2O_7^{2-}$ and $HCrO_4^-$. As seen from Figure 1, adsorption capacity was determined at pH 3, 4, 5 with adsorbent concentration of 1mg/mL with initial Cr(VI) concentration of 1 mg/L. The adsorption was observed and determined throughout 120 min. The optimum pH is 4, where 45% of adsorption capacity was achieved after only 10 min. After 20 min the adsorption capacity increased to 67% and was above 90% just after 30 min. After 120 min, the adsorption capacity of AG-MNPs at pH 4 was 99%. While adsorption capacity of AG-MNPs at pH 3 was high as well, it reached 44% after 10 min, but resulted only in 92% after 120 min. The lowest adsorption capacity was observed at pH 5, where it reached only 33% after 10 min and resulted in 80% after 120 min. When the solution is acidic, the functional groups are protonated, which results in stronger electrostatic interactions between the adsorbent AG-MNPs and $Cr_2O_7^{2-}$ ions. However, at higher pH, which is between 5 and 7, the predominant species of Cr is CrO_4^{2-} , which means that the excessive OH^- ions in Cr(VI) solution compete with chromate (CrO_4^{2-}) ions for adsorption on the adsorbent AG-MNPs surface. Therefore, the adsorption capacity of adsorbent AG-MNPs decreases with increase in pH, which was also reported in previous studies (Singh et al., 2022).

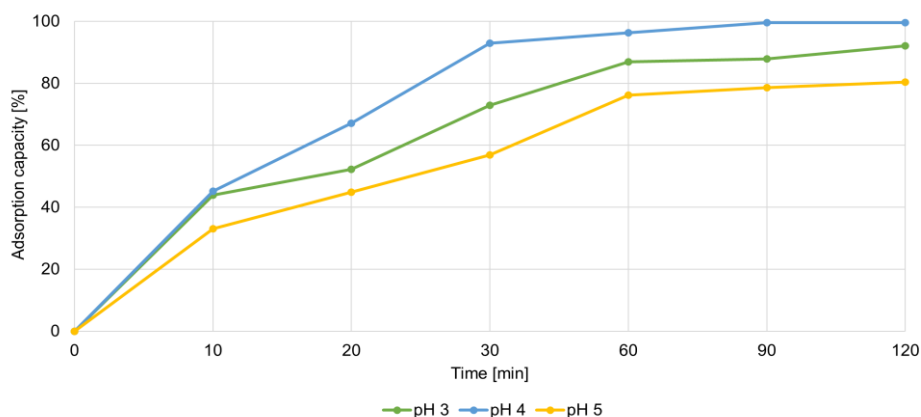


Figure 1: Effect of pH on adsorption capacity of adsorbent AG-MNPs.

3.2 Effect of adsorbent AG-MNPs dosage on adsorption capacity

The adsorption process can also be influenced by the adsorbent amount used in wastewater. The dose of adsorbent for our study was used in concentrations of 0.5 mg/mL, 1 mg/mL, 1.67 mg/mL and 2.33 mg/mL with optimum pH 4 and initial Cr(VI) concentration of 1 mg/L. The adsorption capacity of Cr(VI) increased with increased amount of adsorbent AG-MNPs, as can be seen in Figure 2.

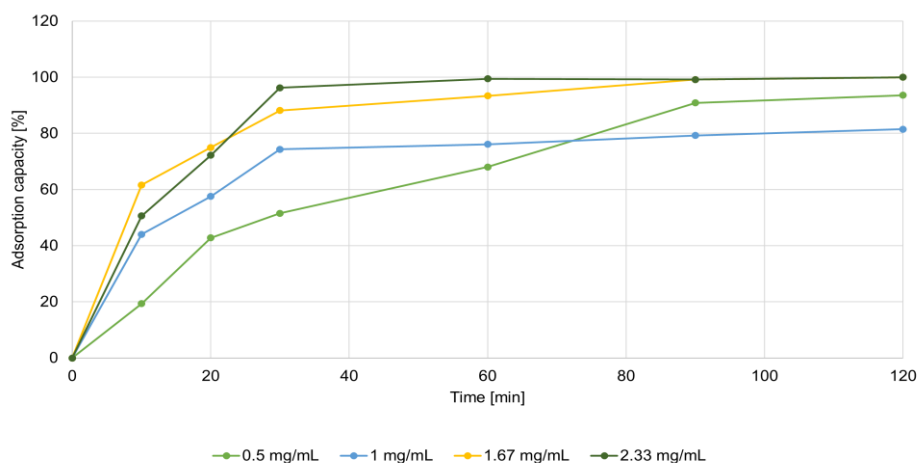


Figure 2: Effect of adsorbent AG-MNPs concentration on adsorption capacity.

Initially, AG-MNPs adsorbent concentration of 1 mg/mL was investigated, which resulted in 44% adsorption capacity after 10 min and increased to 76% after 60 min. After 120 min, the adsorption capacity of AG-MNPs reached 81%. The studies were continued with 0.5 mg/mL concentration of adsorbent and 1.67 mg/mL concentration of adsorbent AG-MNPs. While at concentration 0.5 mg/mL of adsorbent AG-MNPs, the adsorption capacity after 10 min was only 19% it reached 68% after 60 min and 78% after 120 min. However, when increasing the dosage of adsorbent AG-MNPs to 1.67 mg/mL, adsorption capacity increased as well. After 10 min it reached 61% and 93% after 60 min. After 120 min, the adsorption capacity was 100%. Additionally, the dosage of adsorbent AG-MNPs was further increased to concentration of 2.33 mg/mL, but retained similar results, when using concentration of 1.67 mg/mL of adsorbent. The adsorption capacity was 72% after 20 min and reached 96% after 30 min, while reaching 100% as well, after 120 min. In accordance with this, Figure 2 shows that the adsorption capacity of AG-MNPs increased with increased dosage of the adsorbent, as it provides additional active sites on the surface of the adsorbent, where it makes contact between each other to a considerably higher extent. The effective contact area between the adsorbent and Cr(VI) ions is increased, leading to an increase in adsorption capacity, consequently (Foroutan et al., 2021, 2022).

3.3 Effect of initial Cr(VI) ion concentration on adsorption capacity

The effect of Cr(VI) ions concentration on adsorption capacity of AG-MNPs from aqueous solution was studied under following conditions; pH 4, 1.67 mg/mL concentration of adsorbent AG-MNPs and contact time 120 min.

Figure 3 shows the results obtained, when investigating the adsorption capacity of adsorbent AG-MNPs and Cr(VI) ions solution with concentration of 1 mg/L, 5 mg/L, 7 mg/L and 10 mg/L. When the concentration of Cr(VI) was increased to 5 mg/L, the adsorption capacity increased as well. Because adsorption at lower concentrations ensures the availability of adsorption sites, fast adsorption is possible. As seen from Figure 3, when 5 mg/L concentration of Cr(VI) was used, the adsorption capacity of adsorbent AG-MNPs reached 88% after just 10 min. When concentration of Cr(VI) ions increased, the adsorption capacity reached its maximum. Since the adsorption capacity increased with increased concentrations, it is evident that a higher concentration of Cr(VI) has a bigger chance of accessing the interior active sites areas, when the starter concentration is higher. Because of Cr(VI) concentration increase, all of the adsorbent AG-MNPs active sites would be fully exposed and can become occupied by the Cr(VI) ions that are in excess of saturating. Therefore, the adsorption capacity is increasing with increasing the initial concentration of Cr(VI). There is a solvent potential difference, called a driving force, created between the pollutant solution and adsorbent. With increasing the concentration of Cr(VI) the abovementioned driving force is higher, which increases the adsorption capacity. Furthermore, an increase in concentration causes a larger potential energy difference, which generates a higher driving force and a higher adsorption capacity. The results are in agreement with previously reported works (Ahsan et al., 2018; Zhao et al., 2023).

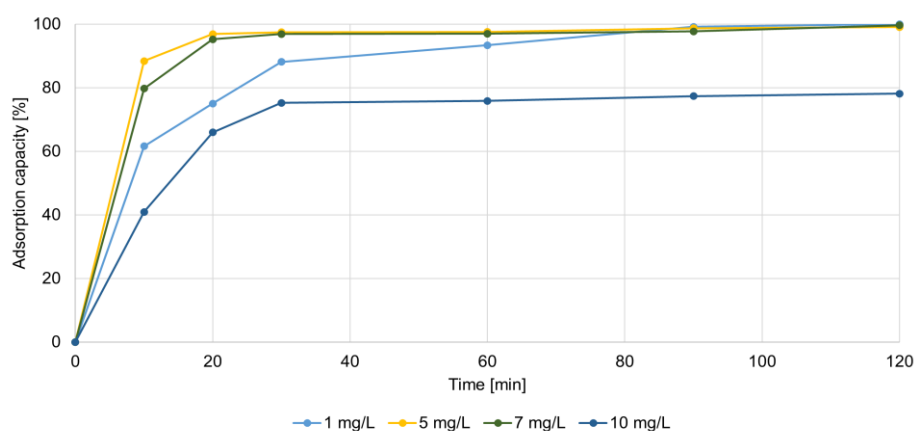


Figure 3: Effect of initial Cr(VI) concentration on adsorption capacity of AG-MNPs.

3.4 Adsorption isotherms

In our study, the isotherm results were examined using Freundlich isotherm model followed by Eq(1), where q_e is the removal capacity at equilibrium and the K_F is the Freundlich affinity coefficient. Non-linear regression of sorption data was performed using Eq(1). The model parameters from non-linear regression are reported in Table 1, where it is shown that the Freundlich isotherm is adequate to adsorption process. Freundlich kinetic model was used to determine the adsorption kinetic parameters, as presented in Table 1. AG-MNPs show $1/n$ coefficient value of 0.3916, while the Freundlich affinity coefficient was calculated to be 0.7621 and Freundlich constant was 2.5536. Linearity coefficient R^2 was 0.982, which indicates higher adsorption intensity.

Table 1: Summary of the isotherm parameters obtained from Freundlich model.

Isotherm	Parameters	Values
Freundlich	n	0.3916
	K_F	0.7621
	n	2.5536
	R^2	0.982

4. Conclusions

In this study, AG-MNPs were prepared by coprecipitation method, followed by functionalization with AG. The adsorption capacity of prepared adsorbent AG-MNPs was investigated, and adsorption studies were performed. Effect of pH of Cr(VI) solution, effect of adsorbent dosage and effect of initial concentration of Cr(VI) solution on adsorption capacity was determined. Additionally, by using Freundlich adsorption isotherm model it was concluded that adsorbent AG-MNPs exhibits excellent adsorption performance and high affinity for Cr(VI) ions. AG-MNPs were found to be highly adsorptive nanomaterial for efficient removal of Cr(VI) ions from aqueous solutions and show excellent potential for use in wastewater treatments.

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