

Optimizing modified rice bran for treating aqueous solutions polluted by Cr (VI) ions: isotherm and kinetics analyses

Zahra Ameri¹, Mehran Hoodaji^{1*}, Majid Rajaie², Mitra Ataabadi¹

¹Department of Soil science (soil chemistry and fertility), Isfahan (Khorasgan) Branch, Islamic Azad University, Isfahan, Iran; ²Department Soil and Water Research, Fars Agricultural and Natural Resources Research and Education Center, AREEO, Shiraz, Iran

*Corresponding author: Mehran Hoodaji, Department of Soil Science (Soil Chemistry and Fertility), Isfahan (Khorasgan) Branch, Islamic Azad University, Isfahan, Iran. Email: mehran.hoodaji1@gmail.com

Received: 20 July 2021; Accepted: 7 August 2021; Published: 26 August 2021

© 2021 Codon Publications

OPEN ACCESS 

ORIGINAL ARTICLE

Abstract

This study investigated the possibility and efficiency of absorbing chromium (VI) (Cr [VI]) ions from the polluted solutions by employing the chemically modified adsorbents (alkali, biochar, and acid rice bran), focusing on the possible impacts of the solution's pH values, adsorbent's dosages, concentrations, and contact times. The colorimetric method was used for Cr determination by employing an ultraviolet/visible spectrophotometer. The scanning electron microscope and Fourier transform infrared spectroscopy were used to analyze the characteristics of the modified adsorbents. The findings indicated that the optimized acid, biochar, alkali, and unmodified rice bran removal efficiency for Cr (VI) were 94.50%, 94.27%, 88.60%, and 90.18%, respectively. The increase of adsorbent dosage up to 2 g/L led to a rise in removal effectiveness (82.06%). Furthermore, the highest removal efficiency was obtained (94%) at the pH of 2.0, the contact duration of 100 min, Cr (VI) concentration of 50 mg/L, and dosage of 2 g/L, which was statistically the optimal condition for the modified rice bran. The adsorption kinetics was agreeably suited to pseudo-second-order, whereas the Freundlich isotherm equation was also suitably expounded the study's findings. The findings implied that the acid and biochar rice bran performed remarkably in the remediation of the wastewater compared with alkali rice bran for reuse for industrial, agricultural, and environmental purposes.

Keywords: absorbing Cr (VI) ions; isotherm and kinetics studies; modified rice bran; organic adsorbents; water treatment

Introduction

Improper wastewater discharge and waste management causing water pollution dangerously affect human health (Montanher *et al.*, 2005). Heavy metals are one of the most significant contaminations in the Earth's resources. The entry of heavy metals into the ecosystem with anthropogenic origins has significantly increased (Almasi *et al.*, 2016). Heavy metals will be transferred to living organisms and eventually to humans because of their accumulation properties (Alavi *et al.*, 2016). Amongst heavy metals, chromium (VI) (Cr [VI]) is usually known

to be outstandingly hazardous to humans (Esfahani *et al.*, 2020).

Cr is present in contaminated water and soil mostly in the form of 3 and 6 valence electrons. They threaten human health because of their nondegradability, carcinogenic, and mutagenic properties. Cr (VI) is reported to be 500–1000 times more poisonous than Cr (III) (He *et al.*, 2020). Hence, considering its harmful effects, several methods are used to absorb it from industrial effluents including biological methods, adsorption, reverse osmosis, and solvent extraction (Almasi *et al.*, 2016). Conventional

processes to remove Cr from industrial effluents are very costly (Dargahi *et al.*, 2015). Because of its efficiency and ease of use, “adsorption” has been introduced as a prevalent refining method (Wang and He, 2020). Here, the toxic materials stick to the surface of the water-insoluble adsorbent pores. Inexpensive and natural adsorbents use instead of the expensive commercial activated carbon is necessary (Munyengabe *et al.*, 2020).

Good water quality is essential to human health, social and economic development, and the ecosystem. However, as populations grow and natural environments become degraded, ensuring sufficient and safe water supplies for everyone is becoming increasingly challenging (Acharya *et al.*, 2018). The availability of safe and abundant water supplies is directly linked to wastewater management (Tahir *et al.*, 2017). Globally, 80% of wastewater flows back into the ecosystem without being treated or reused, contributing to a situation where around 1.8 billion people use a source of drinking water contaminated with feces, putting them at risk of contracting cholera, dysentery, typhoid, and polio (Wu and Yu, 2006).

The organic and natural adsorbents (including chitosan, oxyhumilite, volatile ash, charcoal, peach kernels, rice, barley, wheat straw, and sawdust to remove organic and inorganic contaminants) instead of commercial activated carbon have been employed prevalently by the researchers because of their abundance and low cost (Tahir *et al.*, 2017). Determining the type of adsorbent is critical in the adsorption process; many factors such as high adsorbent capacity, economic cost, environmental friendliness, high efficiency, and effectiveness should be taken into account (Butt *et al.*, 2003). Various agricultural by-products can be good options for removing Cr (VI) because these biological wastes are very abundant and available (Samadani Langeroodi *et al.*, 2015; Bhatti *et al.*, 2017).

Chemically modified agricultural adsorbents may have higher adsorption capacities than unmodified ones (Wannagah and Hanafiah, 2008). Pretreatments using different modifying chemicals like sodium hydroxide, sulfuric acid, hydrochloric acid, tartaric acid, and formaldehyde have been utilized to remove soluble organic compounds and increase the efficiency of metal adsorption (e.g., Bansal *et al.*, 2009; Acharya *et al.*, 2018). Biochar is another low-cost organic adsorbent, recently employed for removing heavy metals for its unique external surface specifications (Zhang *et al.*, 2018).

This article aims to study the Cr (VI) removal efficacy of the modified rice bran (acid, alkali, and biochar) from the polluted aqueous solutions under experiment. The possible effects of different pH values, the adsorbent’s dosages, initial concentrations, and contact times were analyzed

to achieve the optimal condition for the adsorbing process, and the isotherms and kinetics analyses of the modified adsorbents were also investigated accordingly.

This study attempted to answer the following questions:

- Does the chemically modified rice bran (acid, alkali, and biochar) function properly for removing Cr (VI) from polluted aqueous solutions?
- How do different pH values, the adsorbent’s dosages, initial concentrations, and contact times affect the removal efficiency of the modified adsorbents?
- Which one of the modified adsorbents and under which conditions can be used as the optimal adsorbent for removing Cr (VI) from polluted aqueous solutions?
- Which isotherm and kinetic models describe the removal efficiency of the adsorbents?

Materials and Methods

Potassium dichromate, sodium hydroxide, nitric acid, and 1,5-diphenylcarbazide ($C_{13}H_{14}N_4O$; CAS Number 140-22-7; molecular weight, 242.28 g/mol) were the chemicals and reagents utilized for the study prepared from valid, academic laboratories. Potassium dichromate was dissolved in 1000 mL of deionized water to make the Cr (VI) stock of 1000 mg/L. The desired concentration of Cr (VI) solution (50, 150, and 200 mg/L) was set by attenuating the solution immediately before utilization. The pH of the solution was adjusted using 0.1 N sodium hydroxide or nitric acid. A scanning electron microscope (model S-4160) was used to examine the surface morphology of the adsorbents’ samples. Fourier transform infrared (FT-IR) spectrometer (model TENSOR, Bruker, Billerica, MA) was employed to record the FT-IR spectra of the acid, alkali, and biochar modified rice bran. The pH regulation in Cr (VI) solutions was carried out by a pH meter (Eutech, pH 5500 model, Waltham, MA). The Cr (VI) concentration was measured after the adsorption process by an ultraviolet-visible spectrophotometer (DR 5000, HACH, Loveland, CO) at 540 nm.

Preparation of the modified adsorbents

Rice bran samples were thoroughly washed and dried at 70°C for 24 hours and were placed in a desiccator for complete moisture removal with a relative humidity of about 20% and stabilized weight. Later, the adsorbents were powdered using an electric mill (devoid of chromium alloy) and passed through 50 and 100-micron meshes sieves.

Preparation of the acid-modified rice bran

Prepared rice bran was placed in a container saturated with 5 cm of 1 M hydrochloric acid on the adsorbent surface for 24 hours. The suspension was placed on a shaker for 1 hour at 150 rpm. The resultant was filtered by a filter paper and thoroughly rinsed with distilled water to equalize the electrical conductivity and the pH of the inlet and outlet water of the filter paper (Elhami and Bahadori, 2015). The final products were air-dried.

Preparation of the alkali-modified rice bran

The ingredients were exposed to saturated sodium hydroxide solutions (0.4 mol/L) in a container for 24 hours, rinsed twice, and dried at 70 for a whole day (Soltani *et al.*, 2012).

Preparation of the biochar rice bran

The samples and the carefully weighed rice bran were poured into containers with lids and placed in an electric furnace without oxygen. Candles were lit to create low or no oxygen furnace conditions for the remaining oxygen in the environment inside the furnace containing raw materials to be exhausted or minimized for providing conditions for the pyrolysis process. The oven door was also sealed with refractory grease, and the adsorbent samples were heated at 700°C for 3 hours (Kim *et al.*, 2012).

For scrutinizing the impact of Cr (VI) concentration: different concentrations of 50, 150, and 200 mg/L were chosen; contact duration influence was evaluated at 20, 40, 80, and 100 minutes; the effect of the adsorbent's dosage was checked at 0.5, 1, and 2 g/L, and for determining the effect of pH, the pH of 2, 4, and 6 were selected. The experiments were carried out in a batch reactor (with a volume of 100 mL). For the adsorption process, the samples with a specific Cr (VI) solution volume and the desired amount of adsorbent were placed in the reactor and then subjected to the adsorption process. All experiments were repeated in triplicates and performed at laboratory temperature. For proper mixing and appropriate contact between the adsorbent and hexavalent Cr, a shaker with a speed of 100 rpm was used.

Analytical procedure

The modified samples were filtered through a 0.45 µm membrane filter, and the residual concentration of Cr (VI) in the solution was measured at 540 nm in an ultraviolet-visible spectrophotometer. The concentration was detected by oxidizing the 1 and 5 diphenylcarbazide to 1:5-diphenylcarbazone that produces a purple color. About 250 mg of diphenylcarbazide was dissolved in 50 mL of acetone to prepare the 1:5 diphenylcarbazide solution. To a 10 mL flask, 200 µL of the prepared

solution and 1 mL of the equilibrium solution were added along with five droplets of 1N nitric acid solution to keep the pH constant at about 2. The resultant was made up to 10 mL and was incubated 5 to 10 minutes for the purple color development. A suitable amount of the purple-colored solution was transferred to the quartz cell for verifying the Cr (VI) concentration at 540 nm (Singh *et al.*, 2011). Finally, R and q_e , representing removal and adsorption efficacies, respectively, were estimated using Equations (1) and (2):

$$R(\%) = \frac{c_0 - c_t}{c_0} \times 100 \quad (1)$$

$$q_e = \frac{(c_0 - c_t)M}{V} \quad (2)$$

SAS software was employed for the statistical significance evaluation of the variable's impacts on the Cr (VI) removal and removal efficiencies of different experimental conditions. Linear regression was used to evaluate the isotherm and kinetic adsorption models.

After optimizing the test conditions for different parameters, isotherm analysis was performed for different initial Cr (VI) concentrations (two concentrations below (10 and 30) and two concentrations above (70 and 100) the optimal concentration of 50 mg/L). Kinetics experiments were also done at optimum test conditions at three intervals below (40, 60, and 80 minutes) and four intervals above (120, 240, 360, and 480 minutes) the optimum interval of 100 minutes. All these experiments were repeated in triplicates at laboratory temperature.

Results and Discussion

The modified rice bran adsorbent's characteristics

Figure 1 shows the FT-IR spectra of the acid, alkali, and biochar modified rice bran. A strong peak observed at 1031 cm⁻¹ for acidic rice bran, which is related to the extending oscillation of C-O in the structure of C-O-C. A moderate intensity peak at 13,300 cm⁻¹ is because of the stretching vibration of intermolecular O-H. The three-pronged peaks at 2921 cm⁻¹ can be related to the extending oscillation of C-H. The peak observed at 1740 cm⁻¹ is because of the extending oscillation of C=O that belongs to the carbonyl groups of acetyl and uronic esters present in the structure of hemicellulose. Binding between carboxyl structures of lignin structure is also possible.

The peaks observed from 1500 to 1600 cm⁻¹, and that observed at 1239 cm⁻¹ were because of the coupled stretching vibration C = O and the vibration in the O-H planes related to acidic structures. The peak at 1158 cm⁻¹

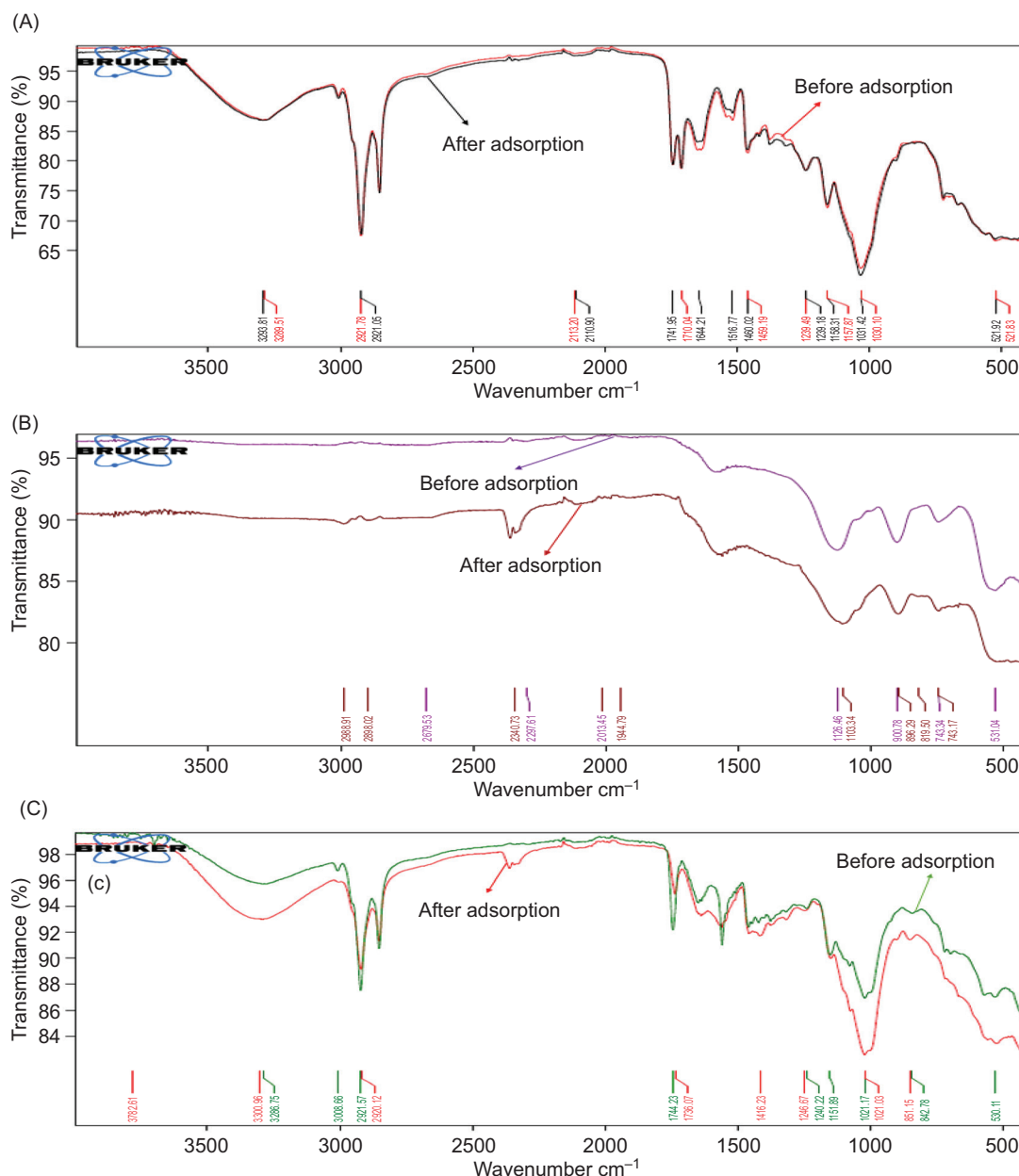


Figure 1. FT-IR spectra of the modified (A) acidic, (B) biochar, and (C) alkaline rice brans.

is the neutral vibration of C-OH. The pivotal substance in the rice bran structure is lignin and hemicellulose, which contain carboxyl and ester groups; by strengthening these groups, the interaction between the C=O functional groups and metals is increased, and the elimination of metals is possible only with this modified compound (Claoston *et al.*, 2014).

As discernible in the desired spectra for biochar, a weak peak seen at 3000 cm⁻¹ is associated with the extending oscillation of C-H. A wavelength of 2898 cm⁻¹ in this spectrum represents the asymmetric stretching of CH because the peak position at frequencies of 2700

to 3000 cm⁻¹ belongs to the CH group. Another peak detectable at 1696 cm⁻¹ was because of the asymmetric extending of C=O. The average peak observed in the range of 1600 cm⁻¹ is related to the N-H bending vibration. The peaks seen at 1103 and 1126 cm⁻¹ can be caused by the unfolding oscillation of the C-N bond of amine II and those at 700 to 1000 cm⁻¹ can be associated with the replacement of aromatic rings.

On the desired spectra for alkaline rice bran, a strong peak is detected at 1021 cm⁻¹, which relates to the asymmetric gravity of C-O in the structure of C-O-C. A moderate intensity peak also found at 13,300 cm⁻¹ could be

because of the extending vibration of intermolecular O-H. The strong three-pronged peaks at a frequency of 2921 cm^{-1} are related to the extending oscillation of C-H. The peak at 1744 cm^{-1} is because of the tensile vibration of C=O belonging to the carbonyl groups of acetyl and uronic esters present in the structure of hemicellulose. Binding between carboxyl structures of lignin structure is also possible. The peaks observed from 1500 to 1600 cm^{-1} are related to the coupled stretching vibration between C=O. The peak at 1240 cm^{-1} is because of the vibration in the O-H plane related to acidic structures, and that seen at 1151 cm^{-1} is the neutral vibration of C-OH. Now, since the pivotal substance in the barn structure is lignin and hemicellulose containing lignin, strengthening the carboxyl and ester groups present in the lignin structure enhances the interaction between the C=O functional groups and metals, and the elimination of metals is possible. Major changes in different areas of the graph before and after the adsorption process, especially at 1700 cm^{-1} indicate that the C=O bond activity of carbonyl groups is

higher than other functional groups in the rice bran surface during the adsorption process.

The results of the modification of adsorbents before and after adsorption of hexavalent Cr are represented in the form of scanning electron microscope (SEM) images in Figure 2. SEM images show changes in all adsorbents after adsorption of hexavalent Cr, whereas the resulting change depends on the type of modified adsorbent. The images showed that, there was no irregularity or destruction on the adsorbent's exterior facets before applying the remotion process, and not many pores and cavities were present on the adsorbents' exterior surface. However, the process caused more pores and cavities and also been associated with the adsorbent's surface destruction. The creation of significant irregularities has caused the surface deformation of the adsorbents.

Hence in acid-modified adsorbents, the change and destruction of surfaces after adsorption of hexavalent Cr

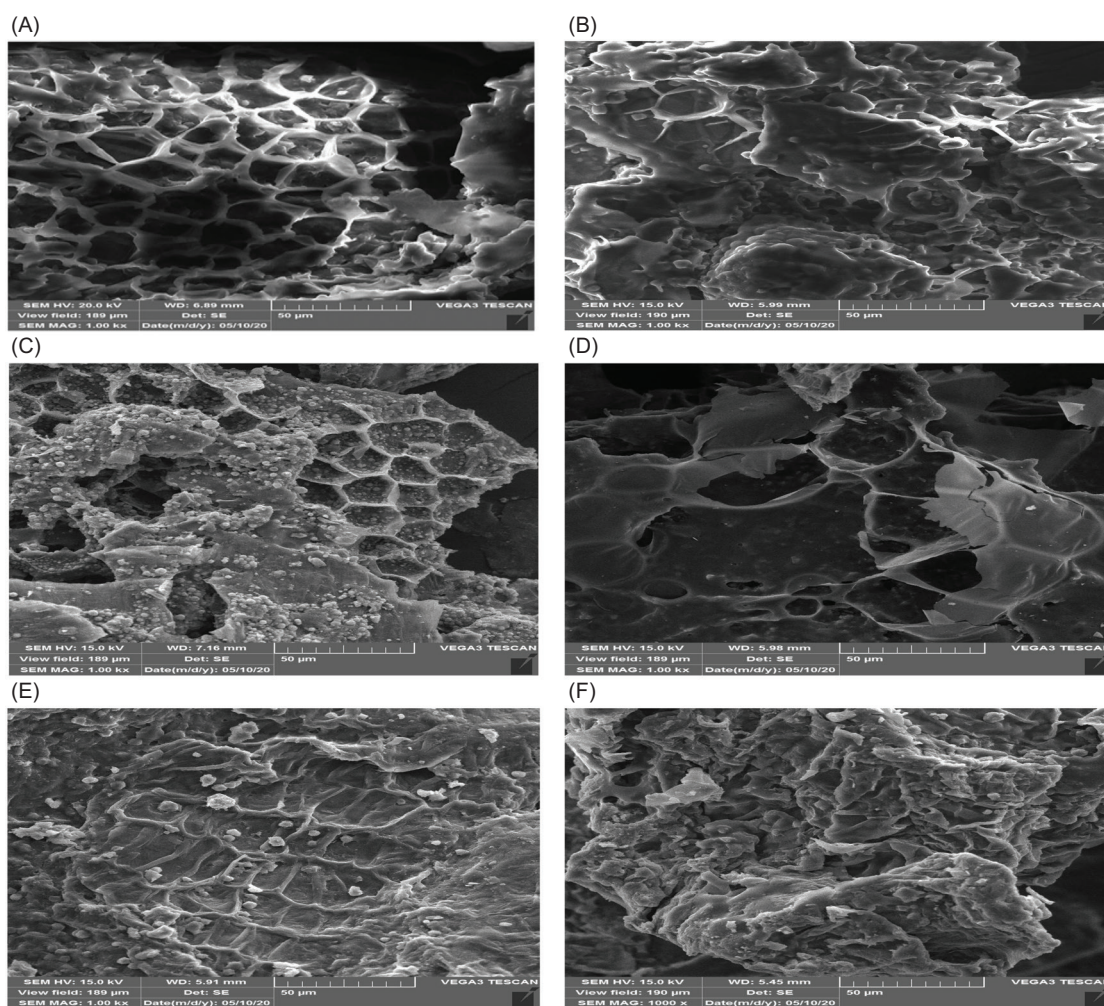


Figure 2. SEM images for modified rice bran before and after adsorption for (A, B) acidic rice bran, (C, D) biochar rice bran, and (E, F) alkaline rice bran.

was more than biochar and alkaline-modified adsorbents. This issue has a direct relationship between the appearance of adsorbents and their irregularity after the adsorption of hexavalent Cr with increasing porosity and thus increasing the specific surface area and cation exchange capacity, which as a result, increases the adsorption rate. The honeycomb sponge structure visible in all three types of modified rice bran adsorbents before adsorption refers to the successful adsorption of Cr (IV) by adsorbents. The lower destruction of the surface means that the adsorbent has fewer pores and consequently has a lower metal adsorption efficiency.

Comparing the modification methods for Cr (VI) adsorption efficacy

Acid, biochar, and alkali modifications were applied to rice bran, and their efficacies were assessed by Cr (VI) removal measurements. The average Cr (VI) removal efficiencies for the acid, biochar, and alkali modified rice bran were 85.1%, 82.64%, and 76.1%, respectively. Pretreatment of rice bran by sodium hydroxide significantly decreased Cr (VI) removal efficiency. Zhang *et al.* (2018) stated that this was because of the destruction of the fiber structure by alkali modification that easily dissolves lignin (as a component of rice bran). In contrast, pretreatment of rice bran by hydrochloric acid increased the Cr (VI) elimination efficacy. Probably because of the removal of soluble organic compounds and a noticeable increase in the efficiency of metal adsorption (Acharya *et al.*, 2018). Conversion of rice bran to biochar was approximately as effective as acid rice bran in Cr (VI) removal efficiency. Table 1 compares the effects of

adsorbent type, different pH's, contact duration, initial Cr (VI) concentrations and dosages of the adsorbent, and their interactions on the adsorption efficiency. The difference in these variables brought about different adsorption efficiency performances. Only the effects which were attested to be statistically significant were included.

pHs of 2, 4, and 6 were used for exploring the possible effect of the pH on the polluted solution. Decreasing the pH showed increased efficacy of Cr (VI) removal using modified rice bran as the adsorbent whereas, pH values to greater than 4 declined the removal efficacy. This outcome agreed with the studies of Saha and Orvig (2010), Hosseini *et al.* (2013), and Fu *et al.* (2018). It can be because, in acidic pH, H⁺ ions neutralize or protonate the negative charges on the adsorbent's exterior surface and effectively increases the attraction of Cr species by electrostatic sorption (Chen *et al.*, 2015).

The possible impacts of adsorbent's doses checking were performed using the doses of 0.5, 1, and 2 g/L. Higher doses fastened the removal of Cr (VI) as a contaminant. In fact, by increasing the adsorbent weight, the available sites for accomplishing the adsorption process could be improved, and consequently, the efficiency of natural adsorbents increased for contaminants adsorption. In other words, by increasing the adsorbent weight, the accessibility of Cr (VI) to adsorption points was enhanced. These outcomes were in line with the studies of Shakya *et al.* (2019) and Zhang *et al.* (2011).

An inverse relationship was found between the Cr (VI) concentration and adsorption efficacy. The findings suggested that by raising the concentration of Cr (VI) from

Table 1. Comparing the effects of adsorbent type, different pH's, contact durations, initial Cr (VI) concentrations and dosages, and their interactions on the adsorption efficiency.

P value	F-value	Mean square	Df	Sources of change
<.0001	3657.53	6556.03**	2	Adsorbent type
<.0001	8436.81	16045.03**	2	pH
<.0001	190.29	361.90**	3	Time
<.0001	137.39	261.28**	2	Adsorbent weight
<.0001	1316.15	2503.11**	2	Concentration
<.0001	177.70	337.94**	5	Adsorbent type-pH
0.0020	4.29	8.15**	4	Adsorbent type-adsorbent weight
<.0001	106.64	202.80**	4	Adsorbent type-concentration
0.0088	2.72	5.16**	7	Time-p
0.0096	3.37	6.41**	4	pH-adsorbent weight
0.0206	2.92	5.55**	4	pH-concentration
0.0002	4.54	8.62**	6	Time-adsorbent weight
<.0001	8.49	16.41**	6	Concentration-time
0.0220	2.88	5.48*	4	Adsorbent weight-concentration

50 to 200 mg/L, the percentage of Cr (VI) remotion using the acid, alkali, and biochar modified rice bran adsorbents decreased from 87.24% to 81.74%, 85.34% to 77.85%, and 77.41% to 74.62%, respectively. Indicating that adsorption can be strongly related to the initial concentration (Kermani *et al.*, 2006), probably because the adsorbents have limited and specified adsorption sites. So at low concentrations, more adsorption sites are available on the adsorbent surface, causing the rapid contaminant adsorption and noticeably increased removal efficiency because of the possibility of collision and contact between the adsorbate and the adsorbent (Wu and Yu, 2006; Sarin and Pant, 2006).

The rate of Cr (VI) remotion for all the modified adsorbents was directly related to contact time. Increasing the contact time from 20 to 100 minutes led to the augment of Cr (VI) exclusion efficacy because the abundance of empty adsorption sites in the first 20 minutes aided in more than 80% of Cr (VI) removal. In line with Entezari *et al.* (2016), not much change in the amount of adsorption after 100 minutes was noted (for the optimized condition, the removal efficiency of the adsorbents was also investigated, for four contact times more than 100 minutes). Figure 3 depicts the interactive effects of the study's variables on the Cr (IV) removal schematically.

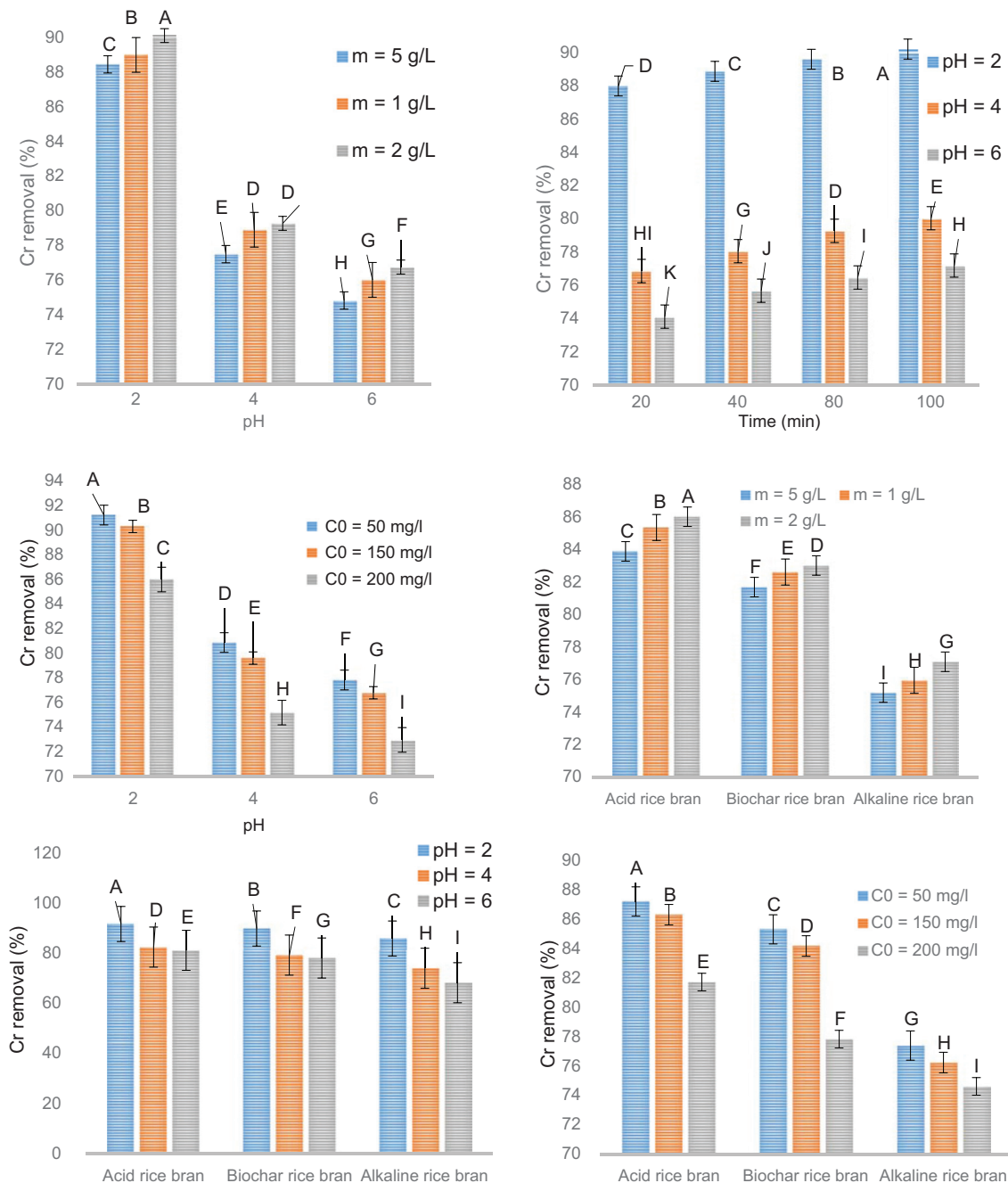


Figure 3. The impacts of the study's variables and their interactions on the Cr (IV) removal.

Table 2. Experimental results at optimum conditions for modified and unmodified adsorbents.

Adsorbent type	pH	Adsorbent dose (g/L)	Concentration (mg/L)	Contact time (min)	Removal (%)	SD	Significance (two-tailed)
Acid rice bran	2	2	50	100	94.502	8.7654	0.0000*
Alkali rice bran	2	2	50	100	88.601	6.0094	0.0398*
Biochar rice bran	2	2	50	100	94.275	7.9985	0.0000*
Unmodified rice bran	2	2	50	100	90.180	7.4536	0.0001*

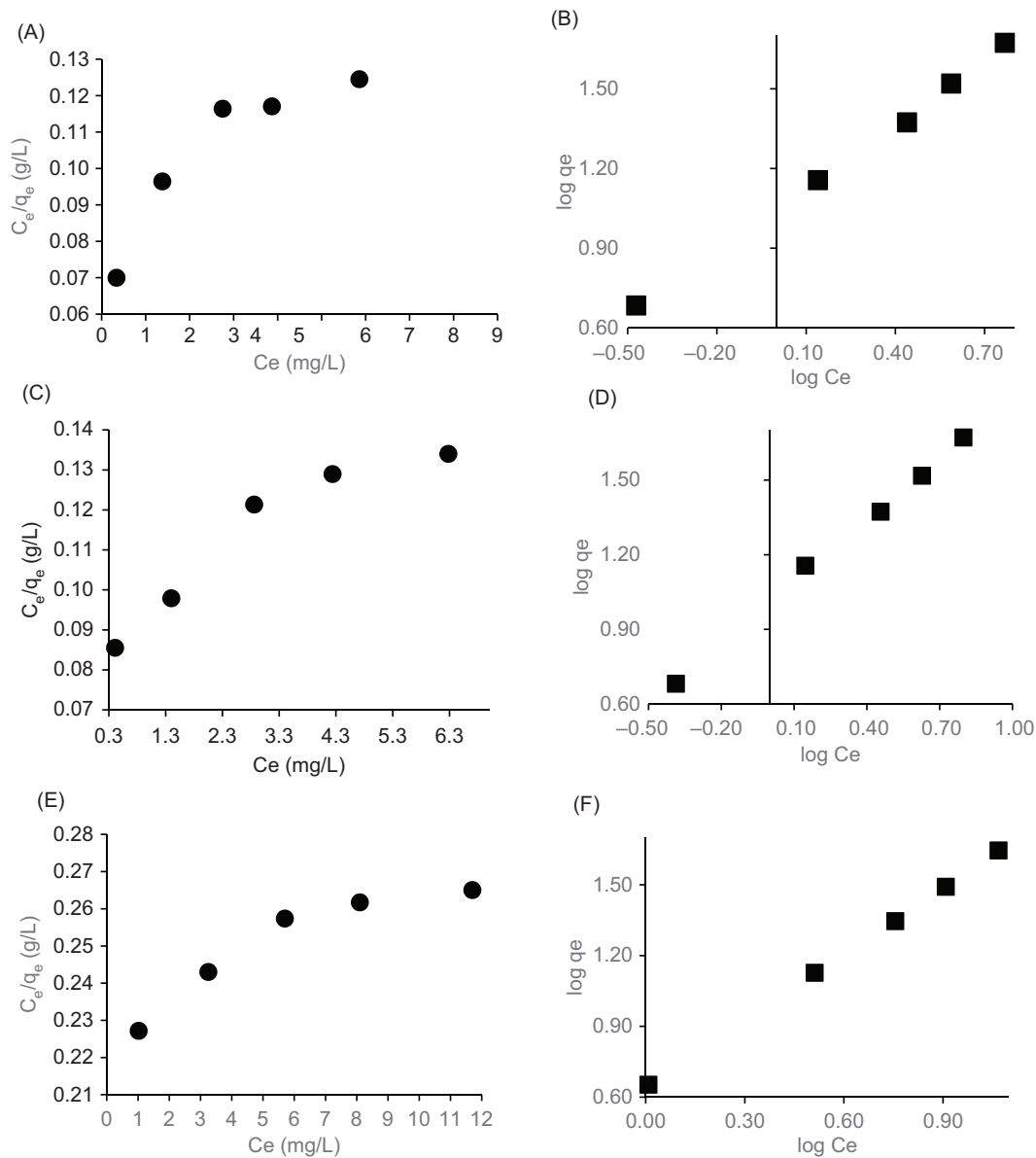


Figure 4. (A, C, E) Langmuir and (B, D, F) Freundlich isotherm models for Cr (VI) removal by acidic, biochar, and alkaline rice bran, respectively. ●, Langmuir; ■, Freundlich.

After optimizing the test conditions for different parameters, the best removal efficacy conditions recorded were at a pH of 2, dosage of 2 g/L, the concentration of 50 mg/L, and during 100 minutes of contact for acid, alkaline, and biochar modified and unmodified rice bran (94.5, 88.6, 94.27, and 90.18%, respectively; Table 2).

Isotherm and kinetic analyses

The reaction between the contaminant and the adsorbent is pronounced by adsorption isotherms (Seidmohammadi *et al.*, 2019). As Figure 4 depicts, under optimum condition, the R^2 values for the Cr (VI) adsorption by

modified adsorbents (acidic, alkali, and biochar rice bran) for Freundlich isotherm were 0.99, which were greater than those obtained for the Langmuir model consistent with the results of the Zhang *et al.* (2011), Asgari *et al.* (2015), and Nata *et al.* (2020). The R^2 values estimated for the Langmuir model were 0.79, 0.88, and 0.85 for acidic, biochar, and alkali rice bran, respectively. For describing the kinetics of the adsorption, the pseudo-first-order Equation (3) was,

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (3)$$

The obtained R^2 values (0.88, 0.94, and 0.89 for acidic, biochar, and alkali rice bran, respectively) were not

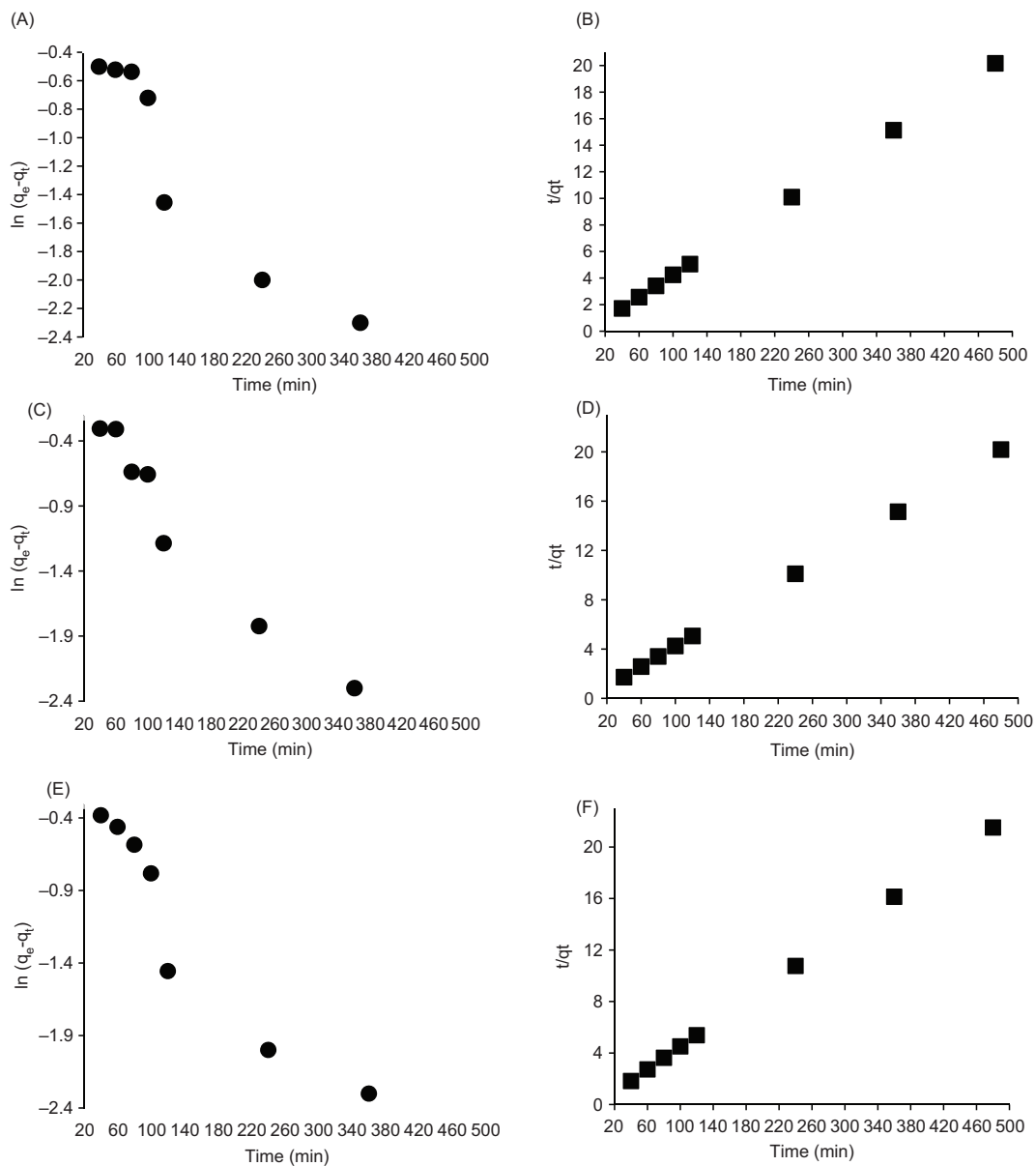


Figure 5. (A, C, E) Pseudo-first- and (B, D, F) pseudo-second-kinetic models for Cr (VI) removal by acidic, biochar, and alkaline rice bran, respectively. •, pseudo-first; ■, pseudo-second kinetic model.

acceptable. Consequently, the pseudo-second-order Equation (4) was tried (Georgieva *et al.*, 2015).

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

R² values for the pseudo-second-order kinetic model for the acidic alkaline and biochar rice bran were 1.0, 1.0, and 1.0, respectively. As discernible in Figure 5, the R² values were high enough and in agreement with the results of Bhatti *et al.* (2017). The pseudo-second-order kinetics could also elucidate different factors like liquid components penetration, adsorption, and internal penetration of particles.

Conclusion

The treatment of wastewater or polluted seems imperative considering the urgent problem of limited water resources. Consequently, many researchers have focused on the possibility of wastewater reuse for agricultural intentions. Wastewater treatment is a process that aims to reduce the concentration of pollutants in wastewater to the level allowed by current regulations. Ofman *et al.* (2017) showed that the quality of the treated wastewater was very similar to the freshwater for irrigation purposes, and healthy crops could also be the outcomes of treated, desalinated wastewater. Among different methods of treatment, adsorption has become very common because of its efficacy and low cost, particularly in the employment of natural, organic absorbents (Bhatti *et al.*, 2017).

This study examined the Cr (VI) removal from solutions by adsorption process in the presence of modified rice bran under various circumstances for optimizing the efficiency of the process. The outcomes showed that decreasing Cr (VI) concentration and pH; and increasing the adsorbent dosage led to the enhancement of the Cr (VI) removal efficacy. The best efficacy was observed (more than 94%) at the following optimum parameters: pH of 2, the adsorbent dose of 2.0 g/L, the contact duration of 100 minutes, the Cr (VI) concentration of 50 mg/L, and acidic rice bran adsorbent. The adsorption kinetics was satisfactorily suited to the pseudo-second-order equations, whereas the Freundlich isotherm model explained the equilibrium adsorption process soundly.

Our findings imply that the chemically modified rice bran prominently performance in the remediation of the wastewater containing Cr (VI). Considering the freshwater shortage, treating the polluted water and reusing it seems imperative instead of decreasing the number of crops or taking the risk of irrigating the crops with contaminated water. Similar studies need to focus on the economic benefits of wastewater treatment, adsorbing other contaminants from the polluted water, or examining other organic absorbents

for the treatment process. These may provide further insights into overcoming the challenge of water resources shortages and pave the way for the treated wastewater reuse for industrial, agricultural, and environmental purposes.

References

- Acharya, J., Kumar, U. and Rafi, PM., 2018. Removal of heavy metal ions from wastewater by chemically modified agricultural waste material as potential adsorbent-a review. *International Journal of Current Engineering and Technology* 8(3): 526–530. <https://doi.org/10.14741/ijcet/v.8.3.6>
- Alavi, S., Shamshiri, S., Pariz, Z., Dargahi, A., Mohamadi, M., Fathi, S., et al. 2016. Evaluating the palm leaves efficiency as a natural adsorbent for removing cadmium from aqueous solutions: isotherm adsorption study. *International Journal of Pharmacy and Technology* 8: 13919–13929. <https://doi.org/10.23.305656370>
- Almasi, A., Dargahi, A., Ahagh, M., Janjani, H., Mohammadi, M. and Tabandeh, L., 2016. Efficiency of a constructed wetland in controlling organic pollutants, nitrogen, and heavy metals from sewage. *Journal of chemical and pharmaceutical sciences* 9: 2924–2928.
- Asgari, G., Dargahi, A. and Mobarakian, SA., 2015. Equilibrium and synthetic equations for index removal of methylene blue using activated carbon from oak fruit bark. *Journal of Mazandaran University of Medical Sciences* 24: 172–187.
- Bansal, M., Garg, U., Diwan, S. and Garg, VK., 2009. Removal of Cr (VI) from aqueous solutions using pre-consumer processing agricultural waste: a case study of rice husk. *Journal of Hazardous Materials* 16: 312–320. <http://doi.org/10.1016/j.jhazmat.2008.05.037>
- Bhatti, HN., Jabeen, A., Iqbal, M., Noreen, D. Noreen S and Naseem, Z., 2017. Adsorptive behavior of rice bran-based composites for malachite green dye: isotherm, kinetic and thermodynamic studies, *Journal of molecular liquids* 23(7): 322–333. <http://dx.doi.org/10.1016%2Fj.molliq.2017.04.033>
- Butt, H. Graf, K. and Kappl, M. 2003. *Physics and chemistry of interfaces*. Wiley Publications.
- Chen, C., Zhao, P., Li, Z. and Tong, Z. 2015. Adsorption behavior of chromium (VI) on activated carbon from eucalyptus sawdust prepared by microwave-assisted activation with ZnCl₂. *Water Treatment* 57, 12572–12584. <https://doi.org/10.1080/19443994.2015.1049960>
- Claoston, N., Samsuri, A., W., Husni, MH., and Amran, MS., 2014. Effects of pyrolysis temperature on the physicochemical properties of empty fruit bunch and rice husk biochars. *Waste management and research* 32: 331–342. <https://doi.org/10.1177/0734242X14525822>
- Dargahi, A., Golestanifar, H., Darvishi, P. and Karam, A., 2015. An investigation and comparison of removing heavy metals (lead and chromium) from aqueous solutions using magnesium oxide nanoparticles. *Polish Journal of Environmental studies* 25(2): 557–563. <https://doi.org/10.15244/pjoes/60281>
- Elhami, S. and Bahadori, A. 2015. Using modified sawdust for removal of chromium (VI) from aqueous solutions. *Biological Forum* 7(2): 47–51.

- Entezari, A., Khosravi, R., Arghavan, F., Taghizadeh, A., Khodadadi, M. and Eslami, H., 2016. Investigation of hexavalent chromium removal from aqueous solution using granular and powdered activated carbon produced from peganum harmala seed. *Journal of Rafsanjan University of Medical Sciences* 15: 645–656.
- Esfahani, AR., Zhang, Z., Sip, YL., Zhai, L. and Sadmani A., 2020. Removal of heavy metals from water using electrospun poly-electrolyte complex fiber mats. *Journal of Water Process Engineering* 37: 101–138.
- Fu, W., & Huang, Z., 2018 Magnetic dithiocarbamate functionalized reduced graphene oxide for the removal of Cu (II), Cd (II), Pb (II), and Hg (II) ions from aqueous solution. Synthesis, adsorption, and regeneration. *Chemosphere* 20: 449–456. <https://doi.org/10.1016/j.chemosphere.2018.06.087>
- Georgieva, VG., Tavlieva, MP., Genieva, SD. and Vlaev, LT. 2015. Adsorption kinetics of Cr (VI) ions from aqueous solutions onto black rice husk ash. *Journal of Molecular Liquids* 20: 219–226. <https://doi.org/10.1016/j.molliq.2015.04.047>
- He, Z., Liang, R., Zhou, C., Yan, G. and Wu, L., 2020. Carbon quantum dots (CQDs)/noble metal co-decorated MIL-53 (Fe) as difunctional photocatalysts for the simultaneous removal of Cr (VI) and dyes. *Separation and Purification Technology* 13:117–125. <https://doi.org/10.1016/j.seppur.2020.117725>
- Hosseini, SM., Farrokhiyan, FA., Babaei, AA. and Heidarzadeh, F. 2013. Removal of Cu (II) from aqueous solution by modified tea waste with magnetic nanoparticles. *Journal of Water and Wastewater* 24(4): 112–119. <https://doi.org/10.1021/je1012873>
- Kermani, M., Pourmoghaddas, H., Bina, B. and Khazaei, Z., 2006. Removal of phenol from aqueous solutions by rice husk ash and activated carbon. *Pakistanian Journal of Biological Sciences* 9: 1905–1910. <https://doi.org/10.3923/pjbs.2006.1905.1910>
- Kim, K.H., Kim, J.Y., Cho, TS. and Choi, J.W. 2012. Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine (*Pinus rigida*). *Bioresource technology* 11(8): 158–162. <https://doi.org/10.1016/j.biortech.2012.04.094>
- Langeroodi, NS., Tahery, F. and Mehrani, S. 2015. Thermodynamic and kinetic investigation of citric acid adsorption by rice bran. *Nova Biologica Reperta* 2: 166–175. <https://doi.org/10.21859/acadpub.nbr.2.3.166>
- Montanher, S., Oliveira, E. and Rollemberg, M., 2005. Removal of metal ions from aqueous solutions by sorption onto rice bran. *Journal of Hazardous Materials* 17: 207–211. <https://doi.org/10.1016/j.jhazmat.2004.09.015>
- Munyengabe, A., Zvinowanda, C., Zvimba, JN. and Ramontja, J., 2020. Innovative oxidation and kinetic studies of ferrous ion by sodium ferrate (VI) and simultaneous removal of metals from a synthetic acid mine drainage. *Physics and Chemistry of the Earth* 56: 102–132. <https://doi.org/10.1016/j.pce.2020.102932>
- Nata, IE., Wicakso, DR., Mirwan, A., Irawan, C. and Ramadhani, D., 2020. Selective adsorption of Pb (II) ion on amine-rich functionalized rice husk magnetic nanoparticle biocomposites in aqueous solution. *Journal of Environmental Chemical Engineering* 8: 114–133. <https://doi.org/10.1016/j.jece.2020.104339>
- Ofman, P., Puchlik, M., Simson, G., Krasowska, M. and Struk-Sokolowska, J. 2017. Impact assessment of treated wastewater on water quality of the receiver using the Wilcoxon test. *Web of Conferences* 17:56–64. <https://doi.org/10.1051/e3sconf/20172200127>
- Saha, B. and Orvig, C., 2010. Biosorbents for hexavalent chromium elimination from industrial and municipal effluents. *Coordination Chemical Review* 25: 2959–2972. <https://doi.org/10.1016/j.ccr.2010.06.005>
- Sarin, V. and Pant, K., 2006. Removal of chromium from industrial waste by using eucalyptus bark. *Bioresource Technology* 97: 15–20. <https://doi.org/10.1016/j.biortech.2005.02.010>
- Seidmohammadi, A., Asgari, G., Dargahi, A., Leili, M., Vaziri, Y., Hayati, B., et al. 2019. Comparative study for the removal of methylene blue dye from aqueous solution by novel activated carbon based adsorbents. *Progress in Color, Colorants and Coatings* 12: 133–144.
- Shakya, A., Nunez-Delgado, A. and Agarwal, TJ., 2019. Biochar synthesis from sweet lime peel for hexavalent chromium remediation from aqueous solution. *Journal of Environmental Management* 25: 1095–1111. <https://doi.org/10.1016/j.jenvman.2019.109570>
- Singh R, Mishra V. and Singh RP, 2011. Synthesis, characterization and role of zero-valent iron nanoparticle in removal of hexavalent chromium from chromium-spiked soil. *Journal of Nanoparticle Research* 13: 4063–4073. <https://doi.org/10.1007/s11051-011-0350-y>
- Soltani, F., Shamohamady, N. and Radfar, D. 2012. Chromium removal from aqueous solution by rice stem the environment for sustainable development. The first national conference on strategies to achieve sustainable development, Tehran.
- Tahir, N. Bhatti, H. N. Iqbal, M. and Noreen, S. 2017. Biopolymers composites with peanut hull waste biomass and application for Crystal Violet adsorption. *International Journal of Biological Macromolecules* 94: 210–220. <https://doi.org/10.1016/j.ijbiomac.2016.10.013>
- Wang, Z. and He, Z., 2020. Frontier review on metal removal in bio-electrochemical systems: mechanisms, performance, and perspectives. *Journal of Hazardous Materials Letters* 56: 100–112. <https://doi.org/10.1016/j.hazl.2020.100002>
- Wannghah, WS. and Hanafiah, MA., 2008. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. *Bioresour Technology* 99: 3935–3948. <https://doi.org/10.1016/j.biortech.2007.06.011>
- Wu, J. and Yu, Q., 2006. Biosorption of 2, 4-dichlorophenol from aqueous solution by *Phanerochaete chrysosporium* biomass: isotherms, kinetics and thermodynamics. *Journal of hazardous materials* 13: 498–508. <https://doi.org/10.1016/j.jhazmat.2006.02.026>
- Zhang, L., Song, X., Liu, X., Yang, L. and Pan, F., 2011. Studies on the removal of tetracycline by multi-walled carbon nanotubes. *Chemical engineering journal* 17:26–33. <https://doi.org/10.1515/ijcre-2019-0130>
- Zhang, X., Zhang L. and Li A., 2018. Eucalyptus sawdust derived bio-char generated by combining the hydrothermal carbonization and low concentration KOH modification for hexavalent chromium removal. *Journal of Environmental Management* 20: 989–998. <https://doi.org/10.1016/j.jenvman.2017.11.079>