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Adsorption efficacy of *Carissa opaca* roots residual biomass for the removal of copper from contaminated water

Hina Abid, Alia Amanat, Dildar Ahmed and Tariq Qamar*

Department of Chemistry, Faculty of Natural Sciences, Forman Christian College (A Chartered University), Ferozepur Road Lahore 54600, Pakistan
*Corresponding author's E. mail: tariqqamar@fccollege.edu.pk

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ABSTRACT

Waste material of different types coming from industries seriously affects the environment and contaminates water, soil, and air. The heavy metals effluents from industries constitute one of the most hazardous type of pollutants and the removal of these metals from the ecosystem is highly desirable to ensure the sustainability of environment. In the present study, residual biomass produced from roots of *Carissa opaca* upon extraction of bioactive compounds was used as a biosorbent to eliminate copper (Cu^{2+}) ions from wastewater. The effect of different parameters such as contact time, pH, and initial concentration has been studied and maximum adsorption was observed for 10 ppm copper ions at contact time 120 minutes and pH 5. Adsorption isotherm studies reveal the good fitting of Langmuir adsorption isotherms than others and the adsorption efficiency of bio sorbent follows the pseudo-second order kinetic model. Conclusively *Carissa opaca* proved as a good biosorbent for the removal of copper ions from the contaminated water.

Capsule Summary: The *Carissa opaca* roots was used as an adsorbent for the removal of copper ions and at optimum conditions of process variable, *C. opaca* roots biomass showed promising adsorption efficiency, which could be employed for the remediation of copper ions from the effluents.

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INTRODUCTION

Water pollution is among the major environmental issues that humanity faces today, and its ascending trend is mainly due to the industrial effluents containing toxic and hazardous contaminants such as heavy metals, dyes, phenols, and pesticides (Aslam et al., 2018; Qamar et al., 2015; Sun et al., 2019). The continuous releases of these pollutants not only contaminate the surface water but also disturb the ground water through seepage. Removal of the heavy metals from soil and water is imperative due their widespread occurrence in the environment, non-degradability, and highly toxic impacts on living beings (Sakhi et al., 2018; Ruthiraan et al., 2019).

Heavy metals are the metals having specific weight usually rages from 63 to 200 g/mol with high specific gravity and their density lies between 3.5 and 7 g cm^{-3} (Shanab et al., 2012). Among heavy metals, copper has received considerable attention because of its toxicity, incremental accumulation in the food chain, persistence in the ecosystem, its wide spread existence and its possible introduction into the water system from various industrial activities such as during the manufacturing of metal plating, batteries, fertilizers, tanneries, paper, manning, and pesticides (Yu et al., 2000). The continuous intake of copper more than its permissible limit by human beings leads to necrotic changes in the liver and kidney, mucosal irritation, widespread capillary damage, depression, weakness, lethargy, anorexia, gastrointestinal irritation and lung cancer (Manzoor et al., 2013; Mebrahtu et al., 2011). Therefore, the presence of copper in the water is among potential risks and its remediation is equally important. Adsorption is an important phenomenon that is used for removal of toxic material from water. As the literature shows, numerous materials have been studied for this purpose (El-Said et al., 2012). They include biomass of pomegranate, rice husk, straw, fly ash, bamboo dust, coconut shell, coal sawdust, babhul bark, rice husk ash, boiler bottom ash, wood coal, corncob carbon, coconut oil cake, pngamia pinnata bark, canjan husk and borussus bark, peel of orange and banana have been investigated for the decontamination of water and response was promising (Renge et al., 2012).

However, still breakthrough is needed and in the present study, an effort has been made to use *C. opaca* roots biomass for the abatement of copper from the contaminated water. *C. opaca* is a medicinal shrub, native to tropical and subtropical regions of Asia, Africa and Australia. The various species of genus Carissa are cultivated as ornamental plants in America. The evergreen shrubs are 2–10-meter-tall, with white fragrant flower and red colored fruit (Patel, 2013). When bioactive natural products are extracted from roots of this plant, a biomass is left behind. The objective of this study was to explore that biomass for its ability to adsorb copper from water.

MATERIAL AND METHODS

Chemicals and reagents

The chemicals used in the study were of analytical grade. Hydrochloric acid and sodium hydroxide (Daejung, Korea)

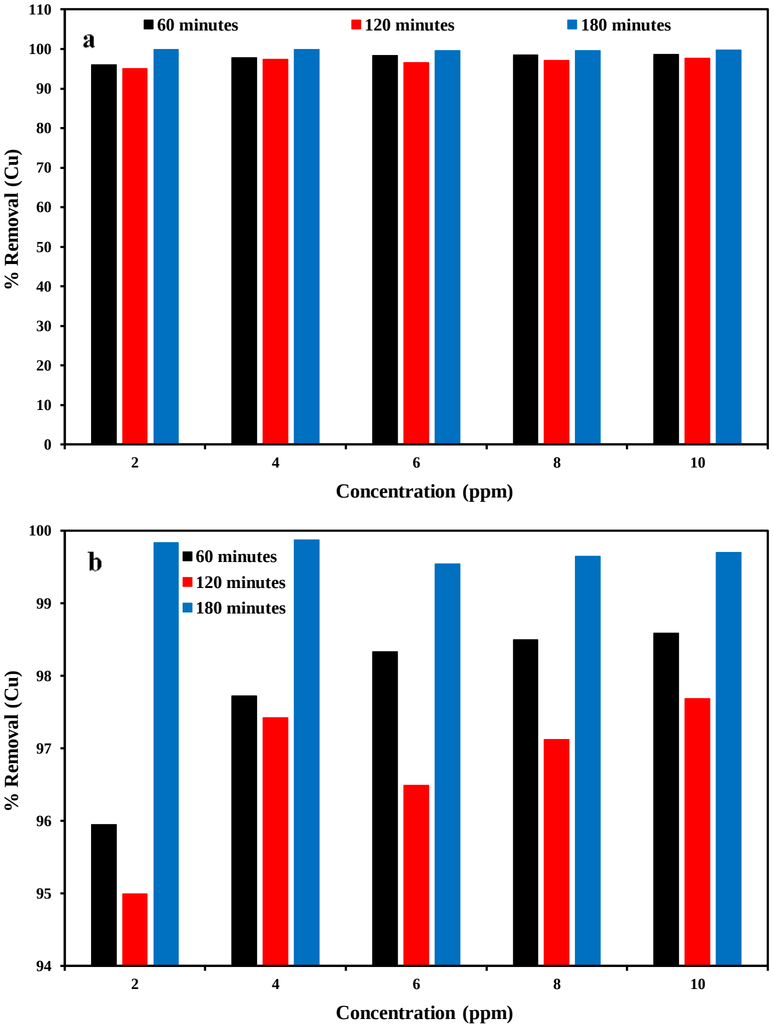

Fig. 1: Adsorption capacity of *Carissa opaca* root biomass for copper ions (a) effect of initial metal ion concentrations and contact times and (b) exploded view of the a.

were used to maintain pH of the metal ion solutions. Distilled water was used to prepare standardized solutions of the metal salts. Copper (II) sulfate pentahydrate (Sigma-Aldrich, Germany) was used to prepare solutions of copper (II) ions.

Biomass collection and preparation

Carissa opaca roots were collected from the hilly area of Abbottabad, Pakistan, washed with distilled water and dried in shade for 2 weeks before grinding to obtain a powder. The powder was extracted with methanol by cold maceration for 15 days. The methanolic extract was filtered and the residual biomass was collected, dried and stored in a beaker covered with aluminum foil for the present study. The adsorbate was prepared by dissolving 3.929 g of $CuSO_4.5H_2O$ in distilled water. The resulting solution had 1000 ppm Cu^{2+} ions and marked as stock solution. A series of adsorbate dilutions with varying concentrations (2, 4, 6, 8 and 10 ppm) of Cu^{2+} ions were prepared from the stock solution (Annadurai et al., 2003; Bulut, 2007; Ngah and Hanafiah, 2008).

Adsorption studies

For adsorption study, the experimental work is categorized into two phases. In the first phase, a flask containing 0.2 g of adsorbent (*C. opaca* root residual biomass) and 50 mL 2 ppm Cu^{2+} ion solution was shaken at 300 rpm for 60 minutes using an orbital shaker at room temperature. The mixture was filtered under gravity with filter paper and the filtrate was evaluated on an atomic absorption spectrophotometer (AAS) for the determination of un-adsorbed copper ions. The same experiment was performed by varying the contact time, i.e., 120 and 180 minutes. Moreover, the similar adsorption studies were conducted with other adsorbate dilutions, i.e., 4, 6, 8 and 10 ppm for 60, 120 and 180 minutes contact times. During the second phase of experiment, the effect of pH (4, 5 and 10) was investigated under the similar experimental conditions except the contact time, which was kept constant at 180 minutes due to experimental results of phase I. all the experiments were conducted in triplicate and data thus obtained was averaged.

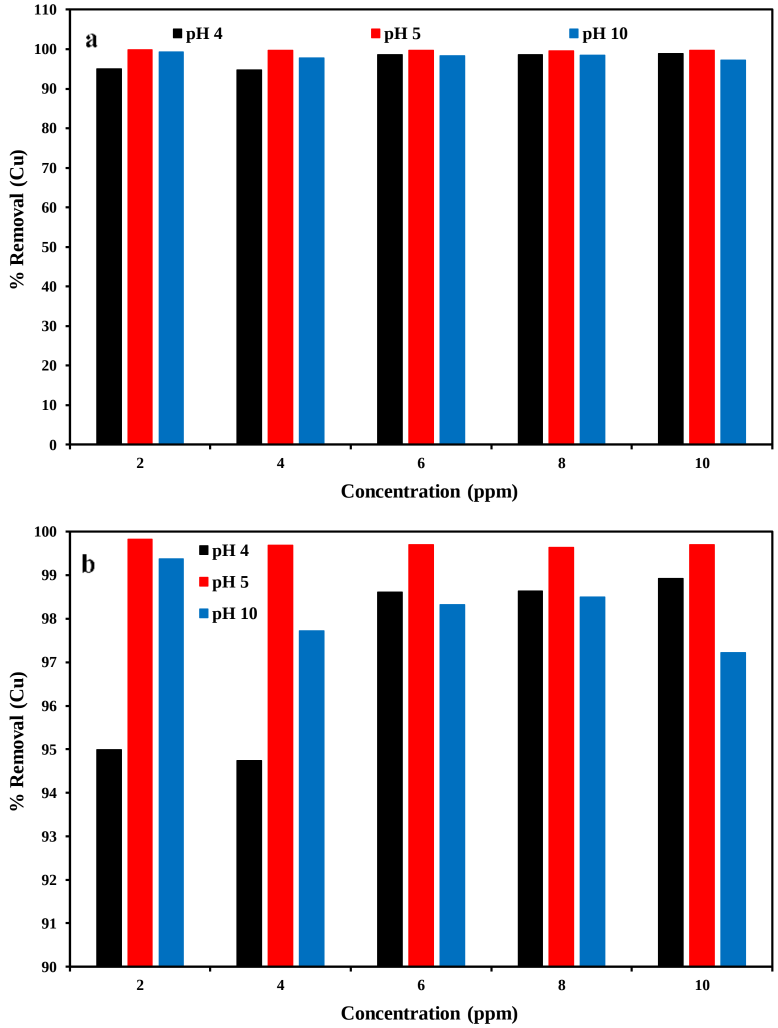

Fig. 2: Adsorption capacity of *Carissa opaca* root biomass for copper at (a) effect of initial metal ion concentrations and pH and (b) exploded view of (a).

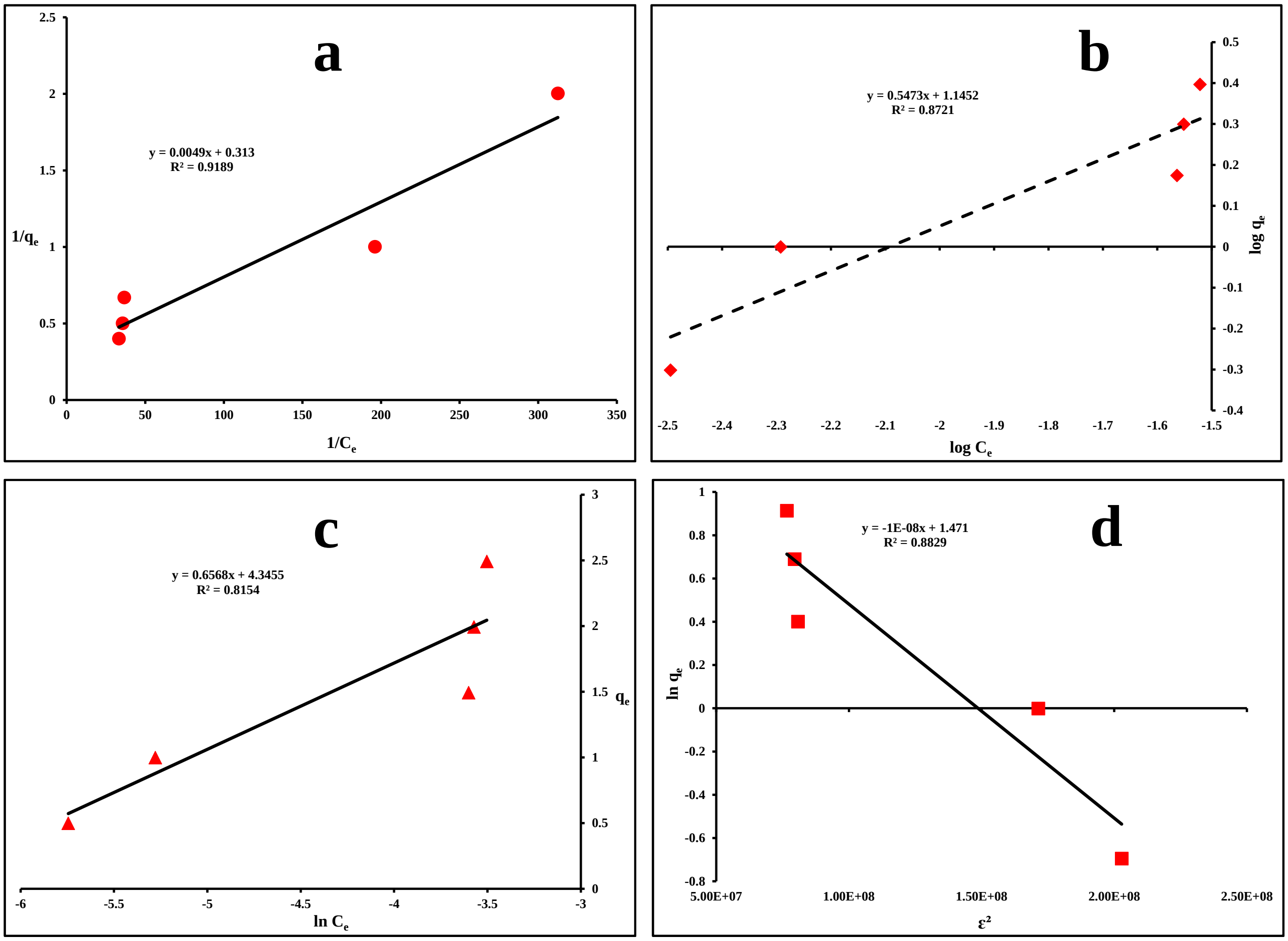

Fig. 3: Comparison of (a) Langmuir (b) Freundlich (c) Temkin and (d) Dubinin-Radushkevich isotherms

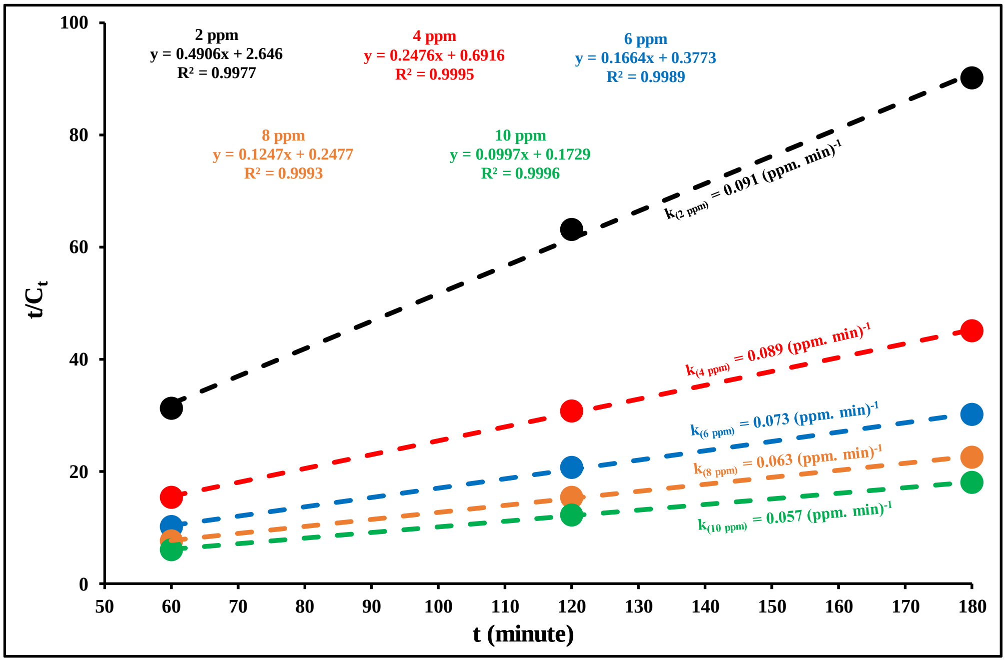

Fig. 4. Comparison of pseudo-second order kinetic model for the adsorption of copper on *Carissa opaca* root biomass

The pH of a given dilution of the metal solution was adjusted with 1 M solution of HCl and NaOH. The concentration of the metal ion adsorbed by the biomass in each contact time (C_t), was calculated with the help of the following Eq. 1.

$$C_t = C_i - C_e \tag{1}$$

Where, C_i is the initial concentration of the metal, while C_e is its equilibrium concentration after the adsorption has taken place. The adsorption capacity (q) of the biomass for the metal, the following Eq. 2.

$$q = \frac{V(C_i - C_e)}{W} \tag{2}$$

Where, q is adsorption capacity, V is volume of the metal ion solution and W is mass of the biomass used. The percentage adsorption or removal of Cu^{2+} was calculated using Eq. 3.

$$\text{Removal (\%)} = \frac{(C_i - C_e)}{C_i} \times 100 \tag{3}$$

RESULTS AND DISCUSSION

The comparison of different concentration of copper ion and contact times on the adsorption of metal ion on the surface of *C. opaca* root biomass is presented in Figure 1. The exploded view in Figure 1 shows that both metal ion concentration and contact time are important parameters to investigate and it is observed that both parameters have significant effect upon the removal of copper ion from the contaminated water and it is recommended that 180 minutes contact time is the optimum time for the removal of copper ions of various concentrations such as 2 to 10 ppm while using *C. opaca* root biomass as an adsorbent.

Effect of pH upon the adsorption of copper ion was also investigated and it is observed that pH has an important role in adsorption of metal ions and as shown in Figure 2, pH 5 is observed the optimum pH for the maximum adsorption of copper on the surface of *C. opaca* root biomass.

The removal of copper increased with the increase in metal ion concentration. The phenomenon of biosorption is complicated involving various factors. Many theories have been propounded to explain the biosorption process. The two most important isotherm models used for this purpose are Langmuir and Freundlich models. According to the Langmuir model, biosorption process occurs only at the very first layer of adsorbent. The model determines the maximum adsorption capacity (q_{max}). The model is based on the assumptions that all the adsorption sites are energetically identical, adsorption occurs on a structurally homogeneous adsorbent and intermolecular forces decrease rapidly with the distance from the adsorption surface (Manzoor et al., 2013). The linear form of the Langmuir isotherm model is presented in Eq. 4.

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} K_L + \frac{Ce}{q_{max}} \tag{4}$$

Where, q_e is metal ion quantity adsorbed in mg/g, C_e is the equilibrium concentration of metal ion, q_{max} represents maximum adsorption capacity and K_L is the Langmuir constant.

In contrast to the Langmuir model, the Freundlich model assumes that the biosorption process occurs at many layers of adsorbent. This model can be used to describe the sorption on heterogeneous surfaces and multilayers (Ewecharoen et al., 2008). the linearized from of this model is shown in Eq. 5.

$$log q_e = \frac{1}{n} * \log C_e + \log K \tag{5}$$

Where, *1/n* and *k* are Freundlich constants. The value of n in the range 1–10 is another standard to assess the good adsorbent–adsorbate interaction (Kumar et al., 2012). The magnitude of the exponent, 1/n gives an indication of the favorability of adsorption. The values of n > 1 represent favorable adsorption condition (Pandey et al., 2011). The graphs of Langmuir and Freundlich isotherms are given in Figure 3 and Table 1, showing the comparison of both isotherm parameters. It is considered that the stronger binding sites are occupied first, and that the binding strength decreases with increasing degree of site occupation (Srividya and Mohanty, 2009). From the obtained value of *K, R^2* and q_{max}, it is concluded the Langmuir model better explained the phenomena of biosorption as compared to Freundlich model.

Temkin isotherm elaborately explains adsorbent–adsorbate interactions. By ignoring the extreme value at lower and higher side, Temkin isotherm heat of adsorption of molecules in a layer decrease linearly (Aharoni and Ungarish, 1977; Temkin, 1940). There is consistent distribution of binding energy can be plotted by considering maximum binding energy of sorbed q_e against *lnCe*. Constants are calculated by intercept and slope. The model is depicted in Eq. 6 (Temkin, 1940).

$$log qe = \frac{RT}{b\gamma} lnA\gamma + \left(\frac{RT}{b}\right) \ln Ce \tag{6}$$

Where, b_T = Temkin isotherm constant R= universal gas constant (8.314J/mol/K) T= Temperature at 298K. B = Constant related to heat of sorption (J/mol).

Dubinin–Radu shkevich isotherm explains the relationship between adsorption mechanism and Gaussian energy distribution for heterogeneous surface (Günay et al., 2007; Dąbrowski, 2001). This model is successfully suitable for intermediate range of concentrations data and high solute activities (Eq. 7).

$$ln q_e = ln(q_s) - K_{ad} \in^2 \tag{7}$$

Where, q_e, q_s ε, K_{ad}, are as, q_e = amount of adsorbate in the adsorbent at equilibrium(mg/g); qs = theoretical isotherm

Table 1: Parameters obtained from various adsorption isotherms

Langmuir Isotherm				Freundlich Isotherm			
q_{max} (mg/g)	k_L (L/mg)	R^2		1/n	N (mg/g)	K_f (mg/g)	R^2
3.19	63.87	0.92		0.55	1.82	3.14	0.87
Temkin Isotherm				**Dubinin-Radushkevich Isotherm**			
A_T (L/mg)	b_T	B	R^2	q_s (mg/g)	K_{ad} (mol^2/J^2)	E (KJ/mol)	R^2
723.43	3753.89	0.66	0.82	4.35	1×10^{-8}	7.07	0.88

saturation capacity (mg/g); K_{ad} = Dubinin–Radushkevich isotherm constant (mol^2/kJ^2) and ε = Dubinin–Radushkevich isotherm constant. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms are plotted below in Figure 3 and their respective constants are presented in Table 1. According to the results, it is evident from the isotherms that the adsorption of copper ion on the surface of *C. opaca* root biomass follows the Langmuir adsorption isotherms. Moreover, Figure 4 shows that the adsorption of copper obeys the second order kinetics and the rate of adsorption decreases as the as the concentration of adsorbate increases which varies from 0.091 to 0.057 (ppm. min)$^{-1}$.

CONCLUSIONS

In this study, *C. opaca* root biomass showed excellent adsorption capacity for the removal of copper ions from polluted water. The adsorption of copper is pH dependent, and the maximum adsorption was obtained at pH 5. This adsorption data fitted well in Langmuir adsorption model as compared to Freundlich, Temkin, and Dubinin-Radushkevich isotherms, and the rate of adsorption of copper upon the surface of *C. opaca* root biomass obeyed pseudo-second order kinetics.

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REFERENCES

Aharoni, C., Ungarish, M., 1977. Kinetics of activated chemisorption. Part 2. Theoretical models. Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases 73, 456-464.

Annadurai, G., Juang, R.S., Lee, D.J., 2003. Adsorption of heavy metals from water using banana and orange peels. Water Science and Technology 47(1), 185-190.

Aslam, M., Qamar, M. T., Ali, S., Rehman, A. U., Soomro, M. T., Ahmed, I., Hameed, A., 2018. Evaluation of SnO_2 for sunlight photocatalytic decontamination of water. Journal of Environmental Management 217, 805-814.

Bulut, Y., 2007. Removal of heavy metals from aqueous solution by sawdust adsorption. Journal of Environmental Sciences 19(2), 160-166.

Dąbrowski, A., 2001. Adsorption—from theory to practice. Advances in Colloid and Interface Science 93(1-3), 135-224.

El-Said, A.G., Badawy, N.A., Garamon, S.E., 2010. Adsorption of cadmium (II) and mercury (II) onto natural adsorbent rice husk ash (RHA) from aqueous solutions: study in single and binary system. International Journal of Chemistry 6(12), 400-409.

Ewecharoen, A., Thiravetyan, P., Nakbanpote, W., 2008. Comparison of nickel adsorption from electroplating rinse water by coir pith and modified coir pith. Chemical Engineering Journal 137(2), 181-188.

Günay, A., Arslankaya, E., Tosun, I., 2007. Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics. Journal of Hazardous Materials 146(1-2), 362-371.

Kumar, A.S.K., Ramachandran, R., Kalidhasan, S., Rajesh, V., Rajesh, N., 2012. Potential application of dodecylamine modified sodium montmorillonite as an effective adsorbent for hexavalent chromium. Chemical Engineering Journal 211, 396-405.

Manzoor, Q., Nadeem, R., Iqbal, M., Saeed, R., Ansari, T.M., 2013. Organic acids pretreatment effect on Rosa bourbonia phyto-biomass for removal of Pb (II) and Cu (II) from aqueous media. Bioresource technology 132, 446-452.

Mebrahtu, G., Zerabruk, S., 2011. Concentration of heavy metals in drinking water from urban areas of the Tigray. Momona Ethiopian Journal of Science 3, 105–121.

Ngah, W.W., Hanafiah, M.M., 2008. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. Bioresource Technology 99(10), 3935-3948.

Pandey, S., Mishra, S.B., 2011. Organic–inorganic hybrid of chitosan/organoclay bionanocomposites for hexavalent chromium uptake. Journal of Colloid and Interface Science 361(2), 509-520.

Patel, S., 2013. Food, pharmaceutical and industrial potential of Carissa genus: an overview. Reviews in Environmental Science and Bio/Technology 12(3), 201-208.

Qamar, M.T., Aslam, M., Ismail, I.M., Salah, N., Hameed, A., 2015. Synthesis, characterization, and sunlight mediated photocatalytic activity of CuO coated ZnO for the removal of nitrophenols. ACS Applied Materials Interfaces 7, 8757-8769.

Renge, V.C., Khedkar, S.V., Pande, S.V., 2012. Removal of heavy metals from wastewater using low-cost adsorbents: a review. 1Scientific Reviews and Chemical Communications 2(4), 580-584.

Ruthiraan, M., Mubarak, N.M., Abdullah, E.C., Khalid, M., Nizamuddin, S., Walvekar, R., Karri, R.R., 2019. An overview of magnetic material: preparation and adsorption removal of heavy metals from wastewater. Magnetic Nanostructures 131-159.

Sakhi, D., Rakhila, Y., Elmchaouri, A., Abouri, M., Souabi, S., & Jada, A. (2018, July). Optimization of coagulation flocculation process for the removal of heavy metals from real textile wastewater. In International Conference on Advanced Intelligent Systems for Sustainable Development (pp. 257-266). Springer, Cham.

Shanab, S., Essa, A., Shalaby, E., 2012. Bioremoval capacity of three heavy metals by some microalgae species (Egyptian Isolates). Plant Signaling and Behavior, 7(3), 392-399.

Srividya, K., Mohanty, K., 2009. Biosorption of hexavalent chromium from aqueous solutions by Catla catla scales: equilibrium and kinetics studies. Chemical Engineering Journal 155(3), 666-673.

Sun, Y., Shah, K. J., Sun, W., Zheng, H., 2019. Performance evaluation of chitosan-based flocculants with good pH resistance and high heavy metals removal capacity. Separation and Purification Technology 215, 208-216.

Temkin, M., 1940. Kinetics of ammonia synthesis on promoted iron catalysts. Acta Physiochim URSS 12, 327-356.

Yu, B., Zhang, Y., Shukla, A., Shukla, S. S., Dorris, K.L., 2000. The removal of heavy metal from aqueous solutions by sawdust adsorption—removal of copper. Journal of Hazardous Materials, 80(1-3), 33-42.

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