Equilibrium studies for copper removal from aqueous solution using nanoadsorbent synthesized from rice husk

Mandeep Kaur¹ · Praveen Sharma¹ · Santosh Kumari²

© Springer Nature Switzerland AG 2019

Abstract

Nanomaterials have gained utmost attention in the field of science and technology due to magnetic, catalytic, thermal and adsorption properties. This study reports the incisiveness of preparation and characterization of nanoadsorbent synthesized from rice husk an agricultural waste by chemo-mechanical method and its ease in the removal of copper from aqueous solution. Nanoadsorbent was individuated by different techniques viz. Force-emission scanning electron microscopy, Fourier Transform Infrared spectroscopy technique and Atomic force microscopy. Adsorbent to metal interaction by adsorption process was accomplished in batch mode to optimize different parameters viz., pH, adsorbent dose, contact time, metal ion concentration, temperature. Thermodynamic parameters Gibb's free energy change, enthalpy change and entropy change implied that Cu (II) adsorption is spontaneous and endothermic. The experimental data of Cu (II) adsorption rate was well accounted by pseudo second order kinetic model with R^2 value 0.998. The adsorption of copper on the nanoadsorbent surface was modeled with Freundlich, Langmuir and Temkin isotherm models with R^2 values 0.993, 0.968 and 0.960 respectively. The results confided that Cu (II) is substantially adsorbed on the nanoadsorbent and turned up to be economically viable approach for copper removal from aqueous solution.

Keywords Rice husk · Nanoadsorbent · Copper · Adsorption · Kinetics · Isotherm models

1 Introduction

Accelerated industrialization, swift expansion in urbanization and commercialization has generated critical environmental problems like urban runoff and wastewater discharge that hassle upon aquatic component of environment [36]. All mess is due to metal-laden wastewater and thus heavy metal contamination is a severe annoyance [13]. Therefore, an emerging sustainable nanomaterial i.e. nanocellulose that unites vigor and flexibility with a high surface area has been examined as potential adsorbent for wastewater treatment and environmental remediation [28]. As heavy metals are persistent in nature therefore they deteriorate the environmental eminence. Some of the heavy metals like copper, zinc, lead, mercury,

cadmium, chromium etc. are repeatedly spotted in industrial wastewaters [43]. Copper is the third most metal used worldwide [38]. As a micronutrient copper is very essential for the development and growth of animals and plants but once dispersed in the biosphere it cannot be retrieved [14]. Excessive exposure to copper leads to Wilson disease in humans and causes cellular damage. Hemolysis, hepatotoxic and nephrotoxic effects also occur due to panoptical intake of copper. The copper level in environment is also elevated due to its emission from various industries as well as natural and other man-made sources [48]. Mining and production processes, fertilizer, pulp and paper, paper and paper board mills liberate copper ions which get distributed in water streams and causes contamination of drinking water [1, 9, 22, 53].

✉ Mandeep Kaur, mandeepkaur76@gmail.com; Praveen Sharma, ps.enbt@gmail.com; Santosh Kumari, kaushdbs@gmail.com |

¹Department of Environmental Science and Engineering, Guru Jambheshwar University of Science and Technology, Hisar, Haryana 125001, India. ²Department of Bio and Nano Technology, Guru Jambheshwar University of Science and Technology, Hisar, Haryana 125001, India.

The metal contaminated wastewater is generally treated by adopting different traditional and advanced technologies such as ion-exchange, reverse osmosis, chemical precipitation, electrodialysis, oxidation–reduction, solvent extraction [42]. Researchers are in a hunt to replace such costly wastewater treatment methods by cheaper and economical technologies and adsorption is the most suitable contender [46] because of its versatility and easy operation [10, 41]. Various adsorbents have been used for removing metals from metal-laden wastewater such as activated carbon, zeolites [35], naturally occurring materials and agricultural waste materials [20, 27]. Recently scientists have explored novel and brainstorming approach as nanocellulose [34] from agricultural waste to be used as nanoadsorbent with prominent adsorption capacity which is due to altered and intensified surface area and more active sites for interaction with metallic species [11, 49]. In present study rice husk has been used to synthesize nanoadsorbent conferred properties like abundance, renewability and biodegradability [6] which has tremendous potential to mitigate environmental obstacles related to heavy metals.

2 Experiments

2.1 Materials and reagents

All the chemicals used were of AR grade. NaOH (pellets) and H_2SO_4 were incurred from SD Fine Chem. Ltd., Mumbai. NaClO_2 and copper nitrate were obtained from CDH.

2.2 Preparation of nanocellulose

The nanocellulose was prepared by chemo-mechanical method as reported earlier by [29]. Rice husk collected from local storage area was immersed in water and washed to take away extra dirt. The material was ground, sieved and subjected to alkali treatment with 4 wt% NaOH (pulp to alkali ratio—1:10 g mL^{-1}) at 80 °C for 1 h to remove non-cellulosic components. The mixture was filtered and washed with distilled water. After alkali treatment rice husk was treated with 5 wt% NaClO_2 (pulp to chemical ratio—1:15 g mL^{-1}) at 80 °C for 2 h for delignification of the native material. The mixture was allowed to cool and was filtered using distilled water. The process was repeated four to five times until the products become white. Further hydrolysis was performed (pulp to acid ratio—1:10 g mL^{-1}) with 50 wt% H_2SO_4 at 45 °C for 60 min. Centrifugation at 9000 rpm was done until pH become 4–6 to remove acidic solution followed by ultrasonication for 60 min and magnetic stirring for 180 min.

2.3 Chemical characterization

Field emission scanning electron microscopy (FE-SEM) was applied for analyzing surface morphology of rice husk. The sample was also investigated by Atomic force microscopy (AFM) using a NT-MDTs Solver PRO atomic force microscope. Fourier transform infrared (FTIR) spectroscopy was done with wavelength range 400–4000 cm^{-1} using a Perkin-Elmer FTIR spectrophotometer.

2.4 Adsorption experiments

The batch mode experiments were executed to study the removal of Cu (II) from aqueous solution using 50 mL of copper nitrate solution of desired concentration (50 mg L^{-1}). All adsorption experiments were conducted at 27 ± 1 °C in Erlenmeyer flask at 180 rpm stirring speed in orbital shaker under suitable conditions (Scigenics Biotech ORBITEK, India).

The known dosage of prepared nanoadsorbent (0.1–1.0 g) was added and pH was varied from 2 to 10. At pre-settled pH and adequate adsorbent dosage the mixture was agitated for 180 min on a mechanical shaker. Thereafter the suspension was allowed to settle down. The metal ion solution with residual adsorbent was filtered and metal ion estimation was performed using atomic absorption spectrophotometer (Shimadzu 6300, Japan). The percentage removal of Cu (II) was calculated by equations as under:

$$(\%)R = \left(\frac{C_i - C_e}{C_i} \right) \times 100 \quad (1)$$

$$q_e = \frac{C_i - C_e}{m} \times V \quad (2)$$

where C_i is initial and C_e is final concentration, V (L) is copper solution volume, m (g) is the mass of adsorbent and q_e (mg g^{-1}) is the amount of copper adsorbed per unit of the adsorbent at equilibrium.

3 Results and discussion

3.1 Characterization

The surface morphology of nanocellulose of rice husk before adsorption and after adsorption was determined at an accelerating voltage of 5 kV. It can be observed from FE-SEM micrograph (Fig. 1a) that surface of nanocellulose show irregularities and after adsorption (Fig. 1b) there were clusters or agglomerations of copper on the

Fig. 1 **a** FESEM image of nanocellulose synthesized from rice husk. **b** FESEM image of copper adsorbed nanoadsorbent synthesized from rice husk

Fig. 2 AFM image of nanoadsorbent synthesized from rice husk

nanoasdsorbent (nanocellulose synthesized from rice husk) surface confirming the adsorption of copper. Size measurement of nanocellulose was settled by AFM image (Fig. 2) which illustrated a three-dimensional view of the surface structure of nanocellulose with presence of spherical attracters obtained by acid hydrolysis. Similar observations were reported by [23]. The incurred nanocellulose from this study has particle size of 76.77 nm.

Fourier transform infrared spectroscopy technique (Fig. 3) effectively exhibited the attachment of different functional groups on the surface of nanocellulose. A large absorption band near $3400\text{--}3440\text{ cm}^{-1}$ corresponds to free O–H stretching quivering of hydroxyl groups in cellulose. The peak observed near $2900\text{--}2930\text{ cm}^{-1}$ is consorted with C–H stretching vibrations. The closer peak at 1640 cm^{-1} is ascribed to O–H turning of the adsorbed water [37]. The band at 1165 cm^{-1} is imputed to stretching of C–C ring, C–O–C glycosidic ether linkages and presence of sulfonates. The absorbance peak at 1373 cm^{-1} is due to aromatic rings of polysaccharides that suggest the presence of saccharide. The peak at 1054 cm^{-1} is attributed to the glycosidic linkage among glucose molecules in cellulose, the C–O–C stretching, O–H bending vibration and C–H deformation vibration. The peak at 1029 cm^{-1} is assigned to ether linkage (C–O–C) from lignin or hemicellulose [47]. The peak at 892 cm^{-1} is due to stretching vibration in C–O–C linkage related to pyranose ring [2].

3.2 Batch mode study

3.2.1 Effect of pH

In adsorption experiments, pH is one of the most important operational parameters which determine nature of the metal ion, charge on the surface of adsorbent and degree of ionization of different pollutants [58]. pH of the medium has significant effect on the adsorption of metal ions partially due to hydrogen ion being itself is a strong contending adsorbate and partially due to the chemical speciation of the metal ions. The effect of pH was studied by varying the pH from 2 to 10 (2, 4, 6, 8 and 10) using 0.5 g/50 mL of adsorbent dose at 50 mg L^{-1} metal ion concentration at $27 \pm 1^\circ\text{C}$ in 250 mL Erlenmeyer flasks kept on magnetic stirrer at 180 rpm for 90 min. The results showed that the percent removal of Cu (II) increased from 69 to 91% with increase in pH from 2 to 8 (Fig. 4). The maximum removal was achieved at pH 8 and remained constant after that. It can be explained by the fact that greater number of precipitates of $\text{Cu}(\text{OH})_2$ were exhibited at higher pH [25]. Further precipitation carryover of metal ions with increased pH may lead to increase in adsorption. Similar fact was also given by [57] that with increase in pH above 6–8 the copper removal is much influenced by precipitation than adsorption. It can be due to the fact that van der Waals forces of attraction aids in binding of metal ions with nanocellulose and can also be due to ion exchange process between negatively charged OH^- and COO^- groups of nanocellulose and metallic cations [26]. Other fact suggests that at lower pH, lesser sites were available for metal adsorption which is due to protonation of the functional groups. While at higher pH negative

Fig. 3 FTIR spectra of acid hydrolysed rice husk

Fig. 4 Effect of pH on Cu (II) removal

Fig. 5 Variation of pH for Cu (II) precipitation

charge on the surface of nanoadsorbent increased due to deprotonation of metal binding sites resulting in higher adsorption capacity [33]. To explore the pH range at which metal ions got precipitated, the experiment was carried out in which five flasks each with 50 mg L^{-1} copper nitrate solution were taken. pH 2, 4, 6, 8 and 10 was maintained in each flask and shaken thoroughly for 30 min. Then mixture was subjected to centrifugation for 10 min and filtered out. Finally concentration of solution in each flask was determined to find out the variation of pH. It was observed from

Fig. 5 that concentration decreased from 50 mg L^{-1} at pH 8 where the precipitation occurred resulting in increased removal of Cu (II). It can be due to change in copper speciation. Copper form free metal cations, diverse soluble complexes and precipitates or insoluble particles while interacting in water. Copper exist as Cu^{2+} , $\text{Cu}(\text{OH})^+$, $\text{Cu}_2(\text{OH})_2^{2+}$ and $\text{Cu}(\text{OH})_2$ at pH 6–8 and are easily adsorbed on the negatively charged surface of nanoadsorbent. Similar results were reported by [32].

3.2.2 Effect of adsorbent dose

The dose was varied from 0.1 to 0.7 g/50 mL to study the removal of Cu (II) keeping other variables constant. With varying dose there was an increase in percent removal from 75 to 97% and maximum removal was attained with 0.5 g dose (Fig. 6). However no significant increase was observed on further increment in the dose. This outcome may be due to the fact that with increase in nanoadsorbent dose the surface area has increased. Due to this availability of surface active sites for adsorption has increased [26]. At same conditions, the adsorption capacity showed a reverse trend i.e. with increase in adsorbent dose from 0.1 to 0.7 g/50 mL the adsorption capacity decreased from 18.79 to 4.88 mg g⁻¹ shown in Fig. 7. It can be due to the fact that surface active sites get overlapped because of excessive crowding of adsorbent molecules [8].

3.2.3 Effect of contact time

To investigate the equilibrium time for the percent removal of Cu (II) the effect of contact time was studied. The experiments were conducted at different contact times varying from 10 to 80 min. The metal removal increased from 74.7 to 91.78% up to 50 min (Fig. 8). An equilibrium was attained at 50 min. Initially the adsorption rate was faster due to (1) van der waal forces of attraction between adsorbent and adsorbate (2) vacant surface binding sites were available for adsorption. But with increase in time, repulsive forces within solutes of solid and bulk phase squashed the sorption rate and later equilibrium was achieved. Subsequently, the leftover empty binding sites no longer adhered with the metals ions [19]. The obtained results were used to determine the kinetics of metal adsorption through kinetic models.

Fig. 6 Effect of adsorbent dose on Cu (II) removal

Fig. 7 Effect of adsorbent dose on adsorption capacity of Cu (II)

3.2.4 Effect of metal ion concentration

The effect of initial metal ion concentration on the percent removal of Cu (II) was carried out with metal ion concentration ranging from 20 to 100 mg L⁻¹. Other parameters viz. adsorbent dose 0.5 g, pH 8 and contact time 60 min were kept constant. The maximum removal was observed at low initial metal ion concentration i.e. 20 mg L⁻¹ due to large number of active sites available on the adsorbent surface. Figure 9 clearly depicts that Cu (II) removal decreased from 75.9 to 64.55% with increase in concentration of metal ions due to saturation of surface active sites with copper ions. Similar results were reported by [7].

3.2.5 Effect of temperature

The effect of temperature on percent removal of Cu (II) was investigated at different temperatures varying from 20 to 80 °C. The percent removal of copper increased from 73.6 to 88% with rise in temperature due to increase in solubility (Fig. 10) indicating endothermic nature of the process. As temperature increased, molecular vibrations begin to terminate intrinsic bonds of water molecules on

Fig. 8 Effect of contact time on Cu (II) removal

Fig. 9 Effect of initial metal ion concentration on Cu (II) removal

Fig. 10 Effect of temperature on Cu (II) removal

the surface of nanoadsorbent due to the heat energy and liberate number of active sites as hydrogen ions on the surface of adsorbent and pH decelerate. It may be attributed that increased motivity and distribution of copper ions in solution due to increase in temperature might have raised the surface active sites of nanoadsorbent [15]. Although, the rate of adsorption increased with increase in temperature, but all the adsorption experiments were carried out at room temperature.

3.3 Adsorption isotherm models

Adsorption isotherm models set forth the adsorbate distribution related to the heterogeneous or homogeneous property of the adsorbent. Adsorption data was stated by linear form of Langmuir, Freundlich and Temkin equations [50].

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad (3)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

$$q_e = B \ln K_T + B \ln C_e \quad (5)$$

Langmuir adsorption model assume monolayer distribution of metal at a specific homogeneous site within the adsorbent surface [31]. The $q_{\max}$ is the maximum monolayer adsorption capacity (mg g^{-1}), b is the Langmuir constant (L mg^{-1}). Linear plot was obtained between C_e/q_e versus C_e to calculate adsorption parameters. The parameter values and correlation coefficients are presented in Table 1.

Freundlich model is often applied on non-ideal adsorption for that adsorbent surface is heterogeneous and multilayer adsorption is assumed [18]. K_f (L mg^{-1}) is Freundlich equilibrium constant and n is empirical constant. The linear plot between $\log q_e$ versus $\log C_e$ gives the value of K_f and n . For favourable adsorption the value of n should lie in between 1 and 10 [40]. The Freundlich parameter values and correlation coefficients are presented in Table 1.

Temkin and Pyzhev model assume that there is uniform distribution of heterogeneous binding sites [54]. It also assumes that decline in the heat adsorption is linear rather than logarithmic. $B = RT/b$, R ($8.314 \text{ J mol}^{-1} \text{ K}$) is gas constant, b (J mol^{-1}) Temkin constant is linked with heat of adsorption and K_T (Lg^{-1}) is Temkin equilibrium binding constant. The graph between q_e and $\ln C_e$ gives the values of K_T and B .

The correlation coefficient and parameter values for all the three isotherm models are presented in Table 1. The correlation coefficient (R^2) values for Freundlich, Langmuir and Temkin models indicated the adequate equipping of data for adsorption with R^2 values 0.993, 0.9686 and 0.9602 respectively. However, Freundlich model has higher value of correlation coefficient R^2 0.993 than other models which correlate to the multilayer adsorption on heterogeneous active sites of adsorbent and model is in good agreement with Cu (II) adsorption. When compared

Table 1 Parameters for copper adsorption onto nanocellulose through adsorption models

Isotherm model	Parameters	Values
Freundlich	K_f (mg g^{-1})	0.495
	$1/n$	0.7159
	R^2	0.993
Langmuir	$q_{\max}$ (mg g^{-1})	13.003
	b (L mg^{-1})	0.025
	R^2	0.9686
	R_L	0.444
Temkin	C_0	50
	B	2.4501
	K_T (L g^{-1})	0.316
	R^2	0.9602

Table 2 Comparative study of adsorption capacity of different adsorbents for Cu (II) removal

Adsorbent	$q_{\max}$ (mg g ⁻¹)	References
Activated carbon from cassava peels	8	[44]
Nanoporous activated neem bark	21.23	[39]
Sunflower hulls	57.14	[56]
Orange peel	4.64	[16]
Potato peel	0.3877	[3]
Olive stone	3.19×10^{-5}	[17]
Rice shell (raw)	17.42	[4]
Barley starw	4.6	[45]
Pomelo peel	21.1	[52]
Rice husk	13.003	Present study

further the higher adsorption capacity for Cu (II) adsorption for Langmuir isotherm model was 13.003 mg g⁻¹ corresponding to the monolayer adsorption on homogeneous active sites which was also supported by [5, 12] to describe adsorption capacity of nano magnetic wheat straw. Table 2 enumerates the comparison of adsorption capacity of nanoadsorbent with other studied adsorbents.

3.4 Kinetic study

Rate mechanism of adsorption of Cu (II) by nanoadsorbent was determined using pseudo first order [30], pseudo second order [24] and intraparticle diffusion [55].

$$\log q_e - q_t = \log q_e - \left(\frac{k_1}{2.303} \right) t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

$$q_t = E_{id} t^{1/2} + E_T \quad (8)$$

In Langergran pseudo first order equation, q_e (mg g⁻¹) is adsorption capacity per unit weight at equilibrium, q_t (mg g⁻¹) is adsorption capacity per unit weight at any time t and k_1 (min⁻¹) is kinetic rate constant. The values of k_1 and q_e were determined from plots of $\log (q_e - q_t)$ versus t . Correlation coefficient R^2 was calculated with low value which showed that this model is not fit for the data (Table 3).

In pseudo second order equation, k_2 (mg g⁻¹ min⁻¹) is rate constant for pseudo-second order reaction. Slope and intercept of the plot gives values of k_2 and q_e . Experimental data with both kinetic equations showed that the value of R^2 (0.8748) for pseudo first order was less in comparison to value of R^2 value (0.9988) for pseudo second order (Table 3).

Table 3 Parameters for copper adsorption onto nanocellulose through kinetic models

Kinetic model	Parameters	Values
Pseudo-first order	q_e (mg g ⁻¹) (cal)	1.642
	k_1 (min ⁻¹)	0.0529
	R^2	0.8748
Pseudo-second order	q_e (mg g ⁻¹) (cal)	4.803
	k_2 (g mg ⁻¹ min)	0.055
	R^2	0.9988
Intraparticle diffusion	k_{id} (mg g ⁻¹ min)	0.159
	C_T	3.2773
	R^2	0.9075

The diffusion mechanism of adsorbed copper was determined by intraparticle diffusion transport in which adsorption rate is found out by adsorbate transfer rate from the bulk solution to the site of adsorption [55] and uptake changes proportionally with square root of time [51]. q_t (mg g⁻¹) is metal uptake, k_{id} (mg m⁻¹ min^{-1/2}) is rate constant for intraparticle diffusion and constant C_T depicts the thickness of the boundary layer. Plot of q_t and $t^{1/2}$ gives values of k_{id} and C_T . For ($C_T \neq 0$), i.e. if plot does not pass through the origin then the intraparticle diffusion is the only rate verifying step. The values obtained for R^2 and C_T presents (Table 3) that intraparticle diffusion is not significant for adsorption of copper in this study and may be controlled by film diffusion or some other mechanism.

3.5 Thermodynamic study

To evaluate the feasibility of adsorption the thermodynamic properties of Cu (II) onto nanoadsorbent were studied. Temperature was varied from 20 to 80 °C and other variables were kept constant. Three thermodynamic parameters were studied (1) Gibb's free energy change (ΔG°), (2) enthalpy change (ΔH°) and (3) entropy change (ΔS°). The Gibb's free energy was calculated by Vent Hoff's equation

$$\Delta G^\circ = -RT \ln K_d \quad (9)$$

where R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), K_d is the equilibrium constant and T is the temperature (K)

$$K_d = \frac{C_a}{C_e} \quad (10)$$

where C_a is the amount of copper adsorbed at equilibrium. C_e is the concentration of copper in the solution at equilibrium. The Gibb's free energy change, enthalpy change and entropy change are determined by equation given below.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

ΔH° and ΔS° values are given by slope and intercept of plots between $\log q_e/C_e$ and $1/T$. The positive value of ΔH° 12.55 kJ mol⁻¹ for copper adsorption indicates the endothermic nature of the adsorption process. The positive value of ΔS° 9.67 kJ mol⁻¹ corresponds to increase in the degree of freedom of adsorption of copper. Negative value of ΔG° - 2.88 kJ mol⁻¹ confirmed the feasibility and spontaneity of adsorption process [21]. The physical adsorption was confirmed by values of thermodynamic parameters.

4 Conclusion

The present study centred on the application of nanocellulose synthesized from rice husk by chemo-mechanical method and its potential as nanoadsorbent for Cu (II) adsorption from aqueous solution. The surface properties of nanoadsorbent were confirmed by FESEM which showed that copper has been adsorbed onto the nanocellulose. The metal adsorption is highly dependent on pH, adsorbent dose and temperature. The experimental data was analyzed with Freundlich, Langmuir and Temkin isotherm models and Pseudo-second order is the best fitted kinetic model with adsorption capacity 4.803 mg g⁻¹. Pseudo-second order is best fitted model with adsorption capacity 4.803 mg g⁻¹. Intra-particle diffusion is non-significant for the study. Thermodynamic study confirmed that Cu (II) adsorption process is spontaneous and feasible. Therefore, it can be concluded that synthesized nanoadsorbent can be beneficial for heavy metal removal.

Acknowledgements We gratefully acknowledge the UGC-BSR, UGC-SAP, CIRCOT-Mumbai for AFM, Punjab University Chandigarh for SEM and Central University Bathinda for FE-SEM.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Akar ST, Akar T, Kaynak Z, Anilan B, Cabuk A, Tabak O, Demir TA, Gedikbey T (2009) Removal of copper (II) ions from synthetic solution and real wastewater by the combined action of dried *Trametes versicolor* cells and montmorillonite. *Hydrometallurgy* 97:98–104
- Alemдар A, Sain M (2008) Isolation and characterization of nanofibers from agricultural residues—wheat straw and soy hulls. *Biores Technol* 99:1664–1671
- Aman T, Kazi AA, Sabri MU, Bano Q (2008) Potato peels as solid waste for the removal of heavy metal copper (II) from waste water/industrial effluent. *Colloids Surf B Biointerfaces* 63:116–121
- Aydin H, Bulut Y, Yerlikaya Ç (2008) Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents. *J Environ Manag* 87:37–45
- Azizi Haghighat Z, Ameri E (2016) Synthesis and characterization of nano magnetic wheat straw for lead adsorption. *Desalin Water Treat* 57:9813–9823
- Azizi Samir MAS, Alloin F, Dufresne A (2005) Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromol* 6:612–626
- Bagbi Y, Sarswat A, Mohan D, Pandey A, Solanki PR (2016) Lead (Pb²⁺) adsorption by monodispersed magnetite nanoparticles: surface analysis and effects of solution chemistry. *J Environ Chem Eng* 4:4237–4247
- Bansal M, Garg U, Singh D, Garg VK (2009) Removal of Cr(VI) from aqueous solutions using pre-consumer processing agricultural waste: a case study of rice husk. *J Hazard Mater* 162:312–320
- Bilal M, Shah JA, Ashfaq T, Gardazi SMH, Tahir AA, Pervez A, Haroon H, Mahmood Q (2013) Waste biomass adsorbents for copper removal from industrial wastewater—a review. *J Hazard Mater* 263:322–333
- Burakov AE, Galunin EV, Burakova IV, Kucherova AE, Agarwal S, Tkachev AG, Gupta VK (2018) Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: a review. *Ecotox Environ Saf* 148:702–712
- Colvin VL (2013) The potential environmental impact of engineered nanomaterials. *Nat Biotechnol* 21:1166–1171
- Cheraghi E, Ameri E, Moheb A (2015) Adsorption of cadmium ions from aqueous solutions using sesame as a low-cost biosorbent: kinetics and equilibrium studies. *Int J Environ Sci Technol* 12:2579–2592
- Cheraghi E, Ameri E, Moheb A (2016) Continuous biosorption of Cd (II) ions from aqueous solutions by sesame waste: thermodynamics and fixed-bed column studies. *Desalin Water Treat* 57:6936–6949
- Demirbas A (2008) Heavy metal adsorption onto agro-based waste materials: a review. *J Hazard Mater* 157:220–229
- Fan T, Liu Y, Feng B, Zeng G, Yang C, Zhou M, Wang X (2008) Biosorption of cadmium (II), zinc (II) and lead (II) by *penicillium simplicissimum*: isotherms, kinetics and thermodynamics. *J Hazard Mater* 160:655–661
- Feng N, Guo X, Liang S (2009) Adsorption study of copper (II) by chemically modified orange peel. *J Hazard Mater* 164:1286–1292
- Fiol N, Villaescusa I, Martínez M, Miralles N, Poch J, Serarols J (2006) Sorption of Pb(II), Ni (II), Cu (II) and Cd (II) from aqueous solution by olive stone waste. *Sep Purif Technol* 50:132–140
- Freundlich HMF (1906) Over the adsorption in solution. *J Phys Chem* 57:385–471
- Ge H, Huang H, Xu M, Chen Q (2016) Cellulose/poly (ethylene imine) composites as efficient and reusable adsorbents for heavy metal ions. *Cellulose* 23:2527–2537
- Guo H, Zhang S, Kou Z, Zhai S, Ma W, Yang Y (2015) Removal of cadmium (II) from aqueous solutions by chemically modified maize straw. *Carbohydr Polym* 115:177–185
- Guo S, Jiao P, Dan Z, Duan N, Chen G, Zhang J (2017) Preparation of L-arginine modified magnetic adsorbent by one-step method for removal of Zn (II) and Cd (II) from aqueous solution. *Chem Eng J* 317:999–1011
- Gupta VK (1998) Equilibrium uptake, sorption dynamics, process development, and column operations for the removal of copper and nickel from aqueous solution and wastewater using activated slag, a low-cost adsorbent. *Ind Eng Chem Res* 37:192–202
- Haafiz MM, Eichhorn SJ, Hassan A, Jawaid M (2013) Isolation and characterization of microcrystalline cellulose from oil palm biomass residue. *Carbohydr Polym* 93:628–634
- Ho YS, Ng JCY, McKay G (2000) Kinetics of pollutant sorption by biosorbents. *Sep Purif Method* 29:189–232

25. Hoslett J, Ghazal H, Ahmad D, Jouhara H (2019) Removal of copper ions from aqueous solution using low temperature biochar derived from the pyrolysis of municipal solid waste. *Sci Total Environ* 673:777–789
26. Ibrahim MNM, Wan Ngah WS, Norliyana MS, Wan Daud WR, Rafatullah M, Sulaiman O, Hashim R (2010) A novel agricultural waste adsorbent for the removal of lead (II) ions from aqueous solutions. *J Hazard Mater* 182:377–385
27. Jamshaid A, Hamid A, Muhammad N, Naseer A, Ghauri M, Iqbal J, Rafiq S, Shah NS (2017) Cellulose-based materials for the removal of heavy metals from wastewater—an overview. *Chem Biol Eng Rev* 4:240–256
28. Kaur M, Sharma P, Kumari S (2017) Extraction preparation and characterization: nanocellulose. *Int J Sci Res* 6:1881–1886
29. Kaur M, Kumari S, Sharma P (2018) Chemically modified nanocellulose from rice husk: synthesis and characterisation. *Adv Res* 13:1–11
30. Lagergren S (1898) Zur theorie der sogenannten adsorption gelöster stoffe. *Kung Sven Vetén Hand* 24:1–39
31. Langmuir I (1916) The constitution and fundamental properties of solids and liquid. *J Am Chem Soc* 38:221–2295
32. Li J, Hu J, Sheng G, Zhao G, Huang Q (2009) Effect of pH, ionic strength, foreign ions and temperature on the adsorption of Cu (II) from aqueous solution to GMZ bentonite. *Colloids Surf A* 349:195–201
33. Li N, Zhang L, Chen Y, Tian Y, Wang H (2011) Adsorption behavior of Cu (II) onto titanate nanofibers prepared by alkali treatment. *J Hazard Mater* 189:265–272
34. Mahfoudhi N, Boufi S (2017) Nanocellulose as a novel nanostructured adsorbent for environmental remediation: a review. *Cellulose* 24:1171–1197
35. Malamis S, Katsou E (2013) A review on zinc and nickel adsorption on natural and modified zeolite, bentonite and vermiculite: examination of process parameters, kinetics and isotherms. *J Hazard Mater* 252:428–446
36. Malucelli LC, Lacerda LG, Dziedzic M, da Silva Carvalho Filho MA (2017) Preparation, properties and future perspectives of nanocrystals from agro-industrial residues: a review of recent research. *Rev Environ Sci Bio/Technol* 16:131–145
37. Mandal A, Chakrabarty D (2011) Isolation of nanocellulose from waste sugarcane bagasse (SCB) and its characterization. *Carbohydr Poly* 86:1291–1299
38. Mautner A, Maples HA, Sehaqui H, Zimmermann T, Perez de Larraya U, Mathew AP, Lai CY, Li K, Bismarck A (2016) Nitrate removal from water using a nanopaper ion-exchanger. *Environ Sci Water Res Technol* 2:117–124
39. Maheshwari U, Mathesan B, Gupta S (2015) Efficient adsorbent for simultaneous removal of Cu (II), Zn (II) and Cr(VI): kinetic, thermodynamics and mass transfer mechanism. *Process Saf Environ Prot* 98:198–210
40. Mishra SP, Tiwari D, Dubey RS, Mishra M (1998) Biosorptive behaviour of casein for Zn^{2+} , Hg^{2+} and Cr^{3+} : effects of physico-chemical treatments. *Biores Technol* 63:1–5
41. Mittal A, Kurup L, Mittal J (2007) Freundlich and Langmuir adsorption isotherms and kinetics for the removal of Tartrazine from aqueous solutions using hen feathers. *J Hazard Mater* 146:243–248
42. Namasivayam C, Ranganathan K (1995) Removal of Cd (II) from wastewater by adsorption on waste Fe(III) Cr(III) hydroxide. *Wat Res* 29:1737–1744
43. Ngah WSW, Hanafiah MAKM (2008) Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. *Biores Technol* 99:3935–3948
44. Owamah HI (2014) Biosorptive removal of Pb(II) and Cu (II) from wastewater using activated carbon from cassava peels. *J Mater Cycles Waste Manag* 16:347–358
45. Pehlivan E, Altun T, Parlayici S (2012) Modified barley straw as a potential biosorbent for removal of copper ions from aqueous solution. *Food Chem* 135:2229–2234
46. Putro JN, Kurniawan A, Ismadji S, Ju Y (2017) Nanocellulose based biosorbents for wastewater treatment: study of isotherm, kinetic, thermodynamic and reusability. *Environ Nanotechnol Monit Manag* 8:134–149
47. Rosa MF, Medeiros ES, Malmonge JA, Gregorski KS, Wood DF, Mattoso LHC, Imam SH (2010) Cellulose nanowhiskers from coconut husk fibers: effect of preparation conditions on their thermal and morphological behavior. *Carbohydr Polym* 81:83–92
48. Saleh TA (2016) Nanocomposite of carbon nanotubes/silica nanoparticles and their use for adsorption of Pb(II): from surface properties to sorption mechanism. *Desalin Water Treat* 57:10730–10744
49. Savage N, Diallo MS (2005) Nanomaterials and water purification: opportunities and challenges. *J Nano Res* 7:331–342
50. Singh J, Kaur G (2013) Freundlich, Langmuir adsorption isotherms and kinetics for the removal of malachite green from aqueous solutions using agricultural waste rice straw. *Int J Environ Sci* 4:250–258
51. Suzuki M, Fujii T (1982) Concentration dependence of surface diffusion coefficient of propionic acid in activated carbon particles. *AIChE J* 28:380–385
52. Tasaso P (2014) Adsorption of copper using pomelo peel and depectinated pomelo peel. *J Clean Energy Technol* 2:154–157
53. Tregoni M, Valensin D, Toso L, Remelli M (2014) Copper chelators: chemical properties and bio-medical applications. *Curr Med Chem* 21:3785–3818
54. Temkin MJ, Pyzhev V (1940) Recent modifications to Langmuir isotherms. *Acta Physiochim USSR* 12:217–222
55. Weber WJ, Morris JC (1963) Kinetics of adsorption on carbon from solution. *J San Engg Div Am Soc Civ Engg* 89:31–60
56. Witek-Krowiak A (2012) Analysis of temperature-dependent biosorption of Cu^{2+} ions on sunflower hulls: kinetics, equilibrium and mechanism of the process. *Chem Eng J* 192:13–20
57. Wu Q, Chen J, Clark M, Yu Y (2014) Adsorption of copper to different biogenic oyster shell structures. *Appl Surf Sci* 311:264–272
58. Zhang X, Wang H, He L, Lu K, Sarmah A, Li J, Huang H (2013) Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. *Environ Sci Poll Res* 20:8472–8483

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.