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Kinetic, equilibrium, and thermodynamic studies for adsorptive removal of cobalt ions by rice husk from aqueous solution

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ABSTRACT

Herein, batch adsorptive removal of cobalt ions (Co(II)) from aqueous solution was studied at room temperature. Adsorption of cobalt ions onto rice husk (RH) was confirmed by utilizing Fourier transform infrared, scanning electron microscopy, and energy diffraction energy-dispersive X-ray analysis. The effect of contact time, mass of RH, initial concentration of cobalt ion solution, temperature, and pH on the percentage discharge of Co(II) was revealed. The nonlinear models such as pseudo-first-order model, pseudo-second-order model, intraparticle diffusion model, and Elovich model were utilized to study kinetics for adsorptive removal of cobalt ions (Co(II)) from aqueous solution. Results showed that experimental data fitted well to nonlinear pseudo-second-order kinetic model. Nonlinear isotherms such as Langmuir, Freundlich, and Dubinin–Radushkevivh (D–R) were used to reveal experimental data of cobalt ion adsorption onto RH. Results represented that experimental data fitted well to nonlinear isotherms. Adsorption thermodynamic study showed that adsorption of Co(II) onto RH was an endothermic and spontaneous process. Moreover, desorption of cobalt ions was also revealed. Therefore, RH could be utilized as a good adsorbent for the removal of Co(II) from aqueous solution at room temperature.

Keywords: Cobalt ion; Rice husk; Adsorption; Nonlinear isotherms; Endothermic process

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1. Introduction

Surface water polluted with heavy metals because of industrial wastewaters has been a problem for several countries in the world from the past few decades. The existence of heavy metals in aqueous environments has adverse effects on plant growth, human health, and animal habitat [1,2]. Cobalt is largely utilized in several industries including mining, metal-working, plating, pigments, electronics, and nuclear medicine [3]. In the human body, it is necessary for the synthesis of vitamin B12. However, high human exposure to cobalt can cause symptoms such as low blood pressure, nausea, vomiting, disorders of the nervous system, and paralysis [4]. According to the Environmental Bureau of Investigation (EBI) and Canadian Water Quality Guidelines (CWQG), the acceptable limits of cobalt in irrigation water and livestock watering are 0.05 and 1.0 mg/L, respectively [5,6]. Therefore, the removal of a nonacceptable amount of cobalt from water is necessary.

To date, various methods including precipitation, reverse osmosis, membrane electrolysis precipitation, ion-exchange, oxidation, and adsorption were utilized to discharge cobalt ions from huge volumes of aqueous solutions [7–10]. Adsorption is popular due to its simplicity, high efficiency, and cost-effectiveness in the discharge of metal ions from wastewater [11–15]. Several materials including iron oxide, nanomaterials, clay minerals, zeolites, coal, Mg/Al layered double hydroxides, chitosan, and carbon materials have been utilized as adsorbents [16–22]. Though, there are still some issues that bound their practical utilization such as these adsorbents are difficult to separate, their adsorption capacity is not enough, and so on [23]. Therefore, it is crucial to find new adsorbent. Currently, the application of agro-wastes as adsorbents is attracting great attention due to their presence in huge amounts, low price, presence of porous structure, and relatively high fixed carbon content.

One of the most important agricultural wastes is rice husk, which can be utilized as an adsorbent for the discharge of various kinds of pollutants particularly metal ions. Pakistan comes in the big producer of rice (5.2 million tons annually) and its husk which forms 20%–23% of the total rice grain is considered as unwanted waste material that actually poses a disposal issue for mill owners [24–26]. It contains proteins, cellulose, hemicellulose, and lignin, possessing hydroxyl, and carboxyl functional groups present to connect with cations [27,28]. Rice husk could be utilized as an excellent adsorbent for the discharge of cobalt ions from aqueous solutions at room temperature because of these properties. Our previous work reported the use of RH as an adsorbent for the removal of lanthanum, cerium, and nickel [24–26]. Moreover, the discharge of dye from aqueous solution was also studied by utilizing anion exchange membranes and leave powder of different plants [29–38]. To extend our research, we shall use RH as an adsorbent for the discharge of cobalt ions from aqueous solutions. Moreover, the adsorption of cobalt ion onto RH has not been studied by any author to the best of our knowledge.

In this research, batch adsorptive removal of cobalt ions by utilizing RH was revealed at room temperature. The effect of operational factors on the percentage of discharge of cobalt ions was explored. Nonlinear kinetic models were applied to experimental data. Moreover, the obtained experimental data were also subjected to nonlinear isotherms. Thermodynamics for adsorption of cobalt ions onto RH was revealed. Moreover, the recovery of cobalt ions and regeneration of RH were also evaluated.

2. Experimental

2.1. Materials

Cobalt oxide (CoO_2), hydrochloric acid (HCl), potassium chloride (KCl), sodium acetate (CH_3COONa), acetic acid (CH_3COOH), boric acid (H_3BO_3), ammonium chloride (NH_4Cl), ammonium hydroxide (NH_4OH), sodium hydroxide (NaOH), sodium phosphate (Na_2HPO_4), and Nitric acid (HNO_3), was provided by Sinopharm Chemical Reagent Co., Ltd., (China). Deionized water was used throughout this research.

2.2. Adsorbent

Rice mill in the Punjab Province of Pakistan provided husk of basmati rice. The required samples were thoroughly washed with water to withdraw dust particles and were oven-dried at 80°C till constant weight was attained. The dried husk was stored in a pre-cleaned airtight container and was utilized without any physical or chemical pre-treatment. The chemical analysis of husk samples was carried out by using neutron activation analysis (NAA) and atomic sorption spectrometry (AAS) methods for their trace metal contents and attained results have been reported elsewhere [24,39]. These results exhibited that the number of metals such as Na, K, Pb, and Fe was present in μg/g of sample. Silica contents were found to be 18.27 (0.62%) of RH. The trace amount of elements present in RH was analyzed by adopting standard methods.

2.3. Adsorption procedure

A known quantity of RH was taken into a 25 cm^3 secured cap culture tube along with 4 cm^3 of the standard acid solution and a fixed quantity of stock radiotracer with a known quantity of cobalt ions concentration solution was added. Consecutively, the contents were equilibrated on a wrist-action mechanical shaker (Vibromatic, USA) at a rate of 500 rpm for specific intervals of time. Then, it was centrifuged at 5,000 rpm for phase separation and the supernatant solution was withdrawn for activity measurement. The radioactivity of solutions before (A_i) and after (A_f) equilibrium was recorded with a NaI well-type scintillation counter (Canberra Inc., United States) coupled with a counter-scaler (Nuclear Chicago). A volume of 1.0 cm^3 was usually utilized to determine the activity. All experiments were performed at room temperature. The percentage adsorption of cobalt ions from aqueous solution was determined using the below relationship:

$$\% \text{ Adsorption} = \frac{A_i - A_f}{A_i} \times 100 \tag{1}$$

where A_i and A_f denote initial and final adsorption of metal ions (counts/min) into an aqueous solution, respectively.

Batch desorption of cobalt ions was done by soaking a specific amount of cobalt ions loaded RH into an aqueous solution of HNO_3 (0.1 mol/L) as a desorbing media for 5 min.

2.4. Characterization

2.4.1. Instrumentation

Fourier transform infrared (FTIR) spectra was recorded by employing attenuated total reflectance with FTIR spectrometer (Vector 22, Bruker) having a resolution of 2 cm^{-1} and total spectral range of 4,000–400 cm^{-1}. Structural features of RH before and after adsorption of cobalt ion were investigated by field emission scanning electron microscopy (FE-SEM, Sirion200, FEI Company, USA). Energy dispersive X-ray (EDX) analysis was utilized to prove the adsorption of cobalt ions onto RH.

3. Results and discussion

3.1. FTIR analysis

FTIR analysis was employed to confirm the adsorption of cobalt ions onto RH. Fig. 1a shows FTIR spectrum of virgin RH. The characteristic absorption band at 3,400-3,200 cm^{-1} is assigned for surface O-H stretching whereas aliphatic C-H stretching had a broadband at 2,921–2,851 cm^{-1}. The peaks at 1,217.0; 1,365.4; 1,737.8; and 1,027.4 cm^{-1} are attributed to carboxyl group on RH in range of reported peaks at 1,208–1,230; 1,367-1,371; 1,740; and 1,029 cm^{-1} for carboxyl group [40,41]. The peaks at 1,737.8; 1,435.6; and 1,365.4 cm^{-1} are attributed with C=O stretching, OH bending of adsorbed H_2O and aliphatic C-H bending, respectively [42]. Moreover, the peak at 1,074.0 cm^{-1} correlated to the anti-symmetric stretching vibration of Si-O, whereas at 476.2 cm^{-1} represents the bending vibration of Si-O-Si bond [40,43,44].

After adsorption of Co(II) onto RH, the variations in the frequencies were crucial to study into the functional groups which are responsible for adsorption of cobalt ions onto RH. FTIR spectrum of cobalt ions loaded RH is represented in Fig. 1b. After adsorption of cobalt ions onto RH, the shifting of peaks to 2,926.0; 1,741.9; and 1,018.4 cm^{-1}, the decline in the intensities of 1,366.0 and 1,217.1 cm^{-1}. A shift of ~12 and 11 cm^{-1} was seen in 1,217.0 and 1,029 cm^{-1} peak. It showed the collaboration of these functional groups for adsorption of cobalt ions.

3.2. SEM and EDX studies

SEM was utilized to study structural aspects of RH before and after the adsorption of cobalt ions. Fig. 2a shows

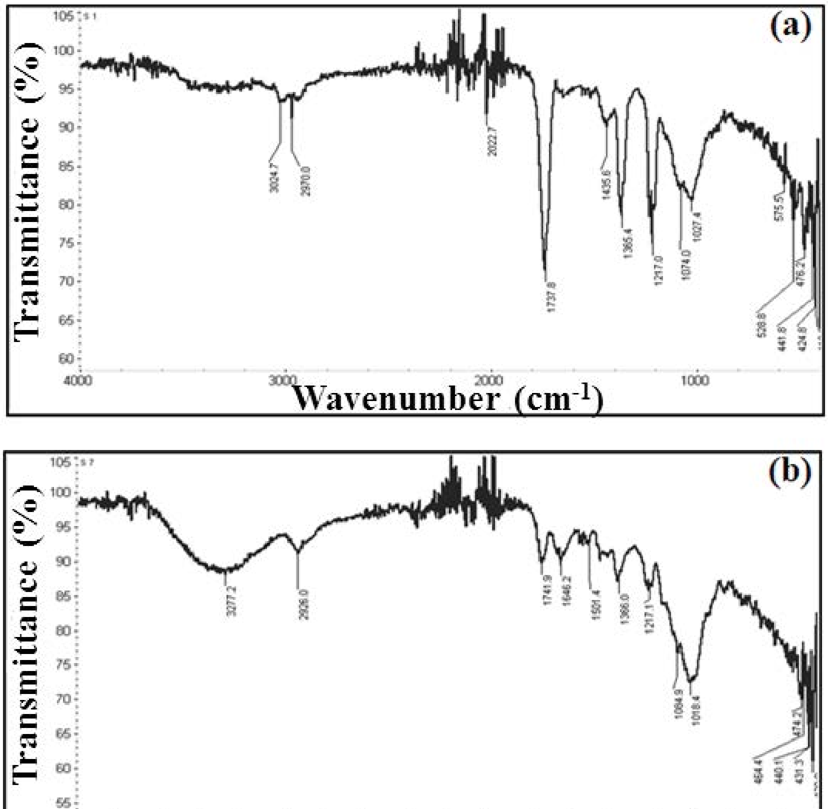

Fig. 1. FTIR spectrum of (a) virgin rice husk and (b) cobalt loaded rice husk.

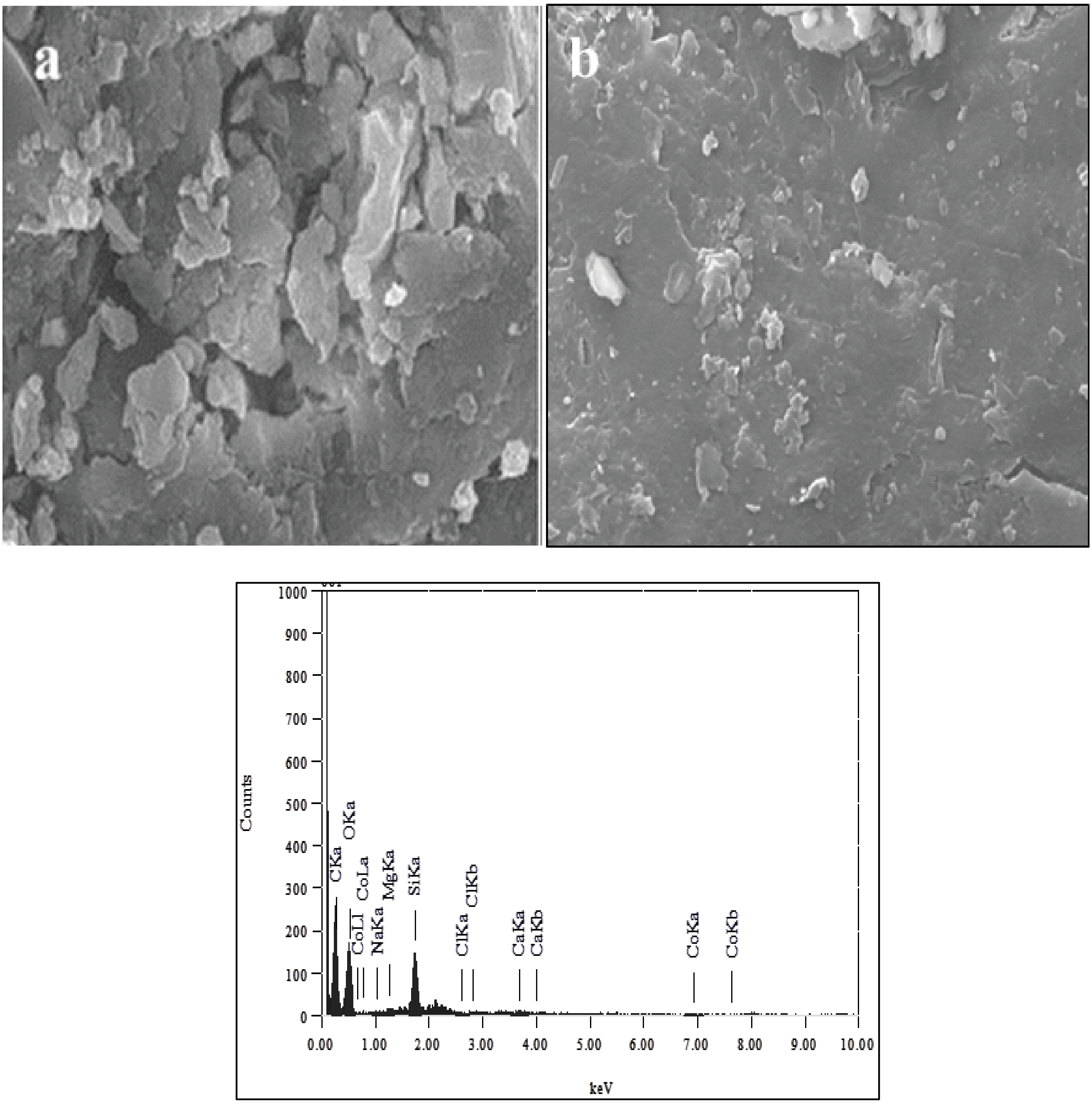

Fig. 2. (a) SEM image of (a) virgin and (b) cobalt ions loaded rice husk. (b) Energy-dispersive X-ray image of cobalt ions loaded rice husk.

SEM micrograph of virgin and cobalt ions loaded RH. It can be seen that surface roughness of RH changed significantly after the adsorption of cobalt ions. The surface of RH became smooth due to the adsorption of cobalt ions onto RH. The pores located on RH were of larger in size than the ionic radius of cobalt (0.088 nm) which promoted the cobalt ions adsorption into the pores of RH.

The presence of cobalt ions onto RH was also confirmed by EDX analysis of cobalt ions loaded RH. Fig. 2b represents the EDX image of cobalt ions loaded RH. The metal ion peaks observed at different energy levels ranging from 0.550 to 7.650 keV proving its successful adsorption onto RH.

3.3. *Effect of operating factors*

The effect of contact time, mass of RH, initial concentration of Co(II) solution, temperature, and pH on the percentage discharge of cobalt ions from aqueous solution was revealed keeping temperature, shaking speed, and other operating parameters constant. The details are given below.

3.3.1. Effect of contact time

Fig. 3 represents the effect of contact time on the percentage removal of cobalt ions from aqueous solution at room temperature. It can be seen that the percentage of discharge of cobalt ions was increased from 29% to 52% with contact time. From Fig. 3, it is clear that adsorption was very rapid in beginning and then there was no significant change in discharge after this equilibrium was attained and no further important enhancement in adsorption occurred with contact time. In the beginning, the fast reaction may be due to the presence of a large number of vacant sites onto RH, and interaction was developed between cobalt ions and adsorption sites. Adsorption slowed down because of the movement of cobalt ions deep into interior pores of RH when all surface sites were occupied. Another reason could be that several empty sites supported rapid adsorption and when these sites were engaged then, there was a competition for lesser remaining sites for the metals ions to be adsorbed which slowed down the rate of adsorption until equilibrium was attained [24].

3.3.2. Effect of the mass of RH

Fig. 4 depicts the influence of the mass of RH on the percentage discharge of cobalt ions at ambient temperature. From Fig. 4, it can bee seen that the percentage discharge of cobalt ions from aqueous solution was increased with increasing mass of RH. The increase in percentage adsorption was from 35.35% to 66.45% with 10 cm^3 of 1.70 × 10^{-4} mol/L of cobalt in 1.0 × 10^{-4} mol/L of HNO_3 within 10 min. The optimized amount of RH was 0.2 g because after this the variation in the percentage adsorption was very small. Hence, this optimized amount of RH was utilized in further experiments.

3.3.3. Effect of the initial concentration of cobalt ion

Adsorption of metal ions is dependent on the initial concentration of metal ion solution. Fig. 5 represents the influence of the initial concentration of metal ions on the percentage discharge of cobalt ions from aqueous solution at room temperature. The percentage discharge of Co(II) was decreased with increasing initial concentration of metal ions in solution. Some of the metal ions were left unabsorbed at a higher initial concentration of cobalt ions because of the saturation of adsorption sites. At a low concentration of metal ions, more binding sites were present. With enhancing concentration on metal ions, the number of ions competing for present binding sites onto RH was enhanced. Similar results were reported in our previous work [24–26].

3.3.4. Effect of temperature

Temperature has a crucial influence on the percentage of discharge of cobalt ions from aqueous solutions. The influence of temperature on the percentage discharge of cobalt was revealed and attained results are shown in Fig. 6. Results showed that the percentage discharge of cobalt ion from aqueous solution was enhanced from 42% to 60% with a rise in temperature. With a rise in temperature from 280 to 333 K, the enhancement in adsorption of cobalt ions may be either because of acceleration of some initially slow adsorption stages or to the establishment of some new active sites on the surface of the adsorbent (RH) [24].

3.3.5. Effect of pH

The pH of the adsorption medium is a crucial endowment which controls metal ions adsorption onto different

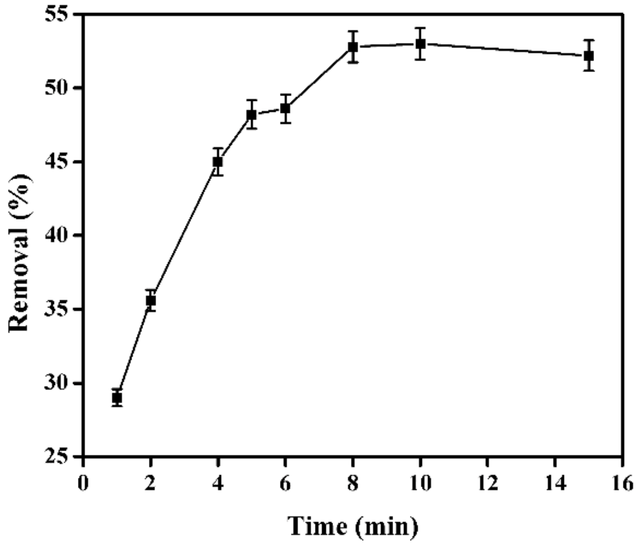

Fig. 3. Effect of contact time on adsorption of cobalt ions onto RH.

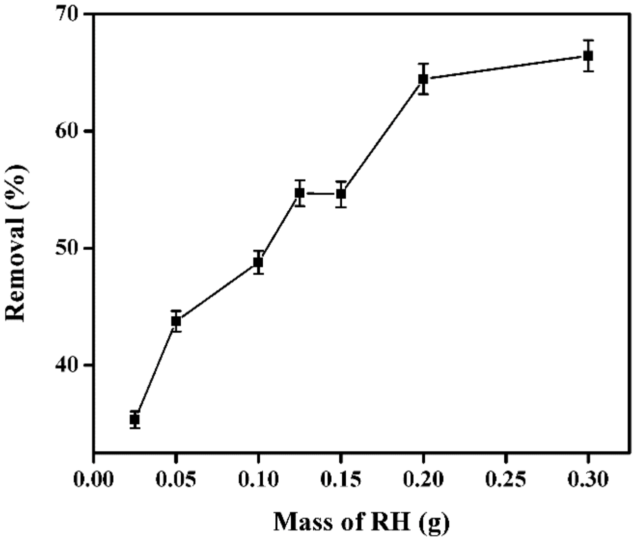

Fig. 4. Effect of the mass of RH on adsorption of cobalt ions onto RH.

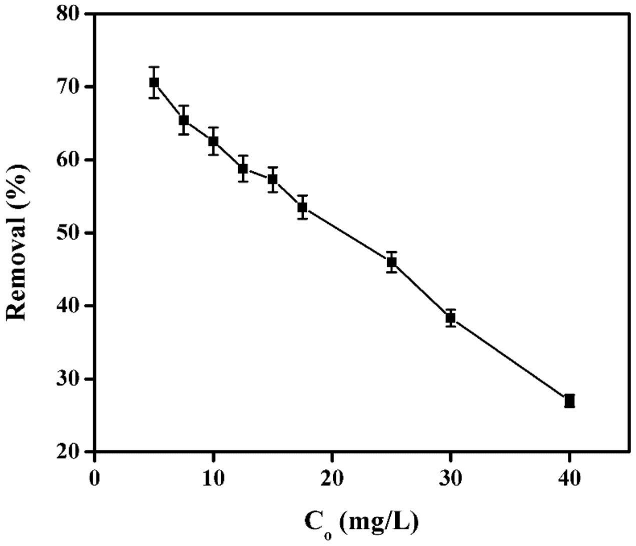

Fig. 5. Effect of initial concentration on adsorption of cobalt ions onto RH.

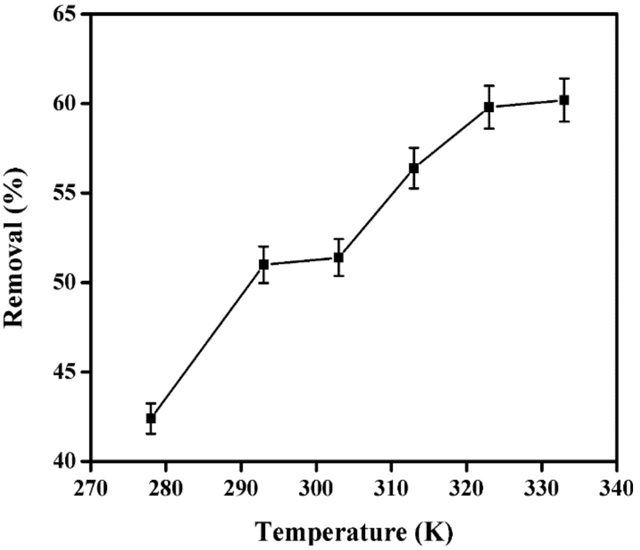

Fig. 6. Effect of temperature on adsorption of cobalt ions onto RH.

adsorbents. The influence of pH on adsorption of heavy metals from aqueous media had been reported by several researchers [45–48]. The metal ions solubility, chemical speciation, and counter ions concentration on the functional groups of the adsorbents were also influenced by pH of adsorbing solution. The adsorption of cobalt ions was revealed from the aqueous media of different pH in the range of 1.0–8.24 employing a fixed quantity of RH and metal ions concentration. Fig. 7 shows result for the influence of pH on adsorption of cobalt ions. It has been observed that the percentage discharge of cobalt ions from aqueous solution by using RH was enhanced with an increase in pH of the solution. The maximum adsorption of cobalt ions onto RH occurred at pH 8.24. Adsorption of cobalt ions in the basic medium may have occurred on the cellulose part of the RH. It could also be because of the surface complex formation phenomenon with several organic components of the RH [49–52].

3.4. Adsorption kinetics

Nonlinear kinetic models such as pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich were applied on the time-dependent adsorption data of Co(II) onto RH. IGOR Pro 6.1.2, Wave Metrices software was utilized for the determination of kinetic parameters while using nonlinear equations.

The Lagergren's pseudo-first-order kinetic equation may be represented as [53]:

$$\frac{dQ_t}{dt} = k_1\left(Q_e - Q_t\right) \tag{2}$$

The pseudo-second-order kinetic rate equation can be expressed as [54,55]:

$$\frac{dQ_t}{dt} = k_2\left(Q_e - Q_t\right)^2 \tag{3}$$

Where Q_t is the quantity of Co(II) adsorbed at the time "t" (mg/g), Q_e is the amount of Co(II) adsorbed at equilibrium (mg/g), t is time (min), k_1 is the rate constant of pseudo-first-order model (1/min), k_2 is the rate constant of pseudo-second-order model (g/mg min).

Nonlinear pseudo-first-order:

$$Q_t = Q_e\left(1 - e^{-kt}\right) \tag{4}$$

Nonlinear pseudo-second-order:

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \tag{5}$$

Fig. 8 depicts nonlinear plots of pseudo-first-order and pseudo-second-order kinetic models for the adsorption of Co(II) onto RH. The values of constants and theoretically calculated Q_e are given in Table 1.

To compare the applications of different models, Chi-square test "χ^2" was utilized as a determining tool for the best-fit of kinetic equations which may be measured by the following relationship:

$$\chi^2 = \sum \frac{\left(Q_E - Q_{e,m}\right)^2}{Q_{e,m}} \tag{6}$$

where Q_e is equilibrium capacity attained from experimental data (mg/g), and $Q_{e,m}$ is equilibrium capacity obtained from model (mg/g). The computed values of "χ^2" are given in Table 1. The similarity of data attained from models is generally confirmed by comparison with the experimental data, "χ^2" would be a small number and vice versa. The computed lower values of nonlinear "χ^2" test analysis of Co(II) for pseudo-second-order showed that pseudo-second-order model looks to be more credible for the determination of kinetic constants for the adsorption of Co(II) onto RH.

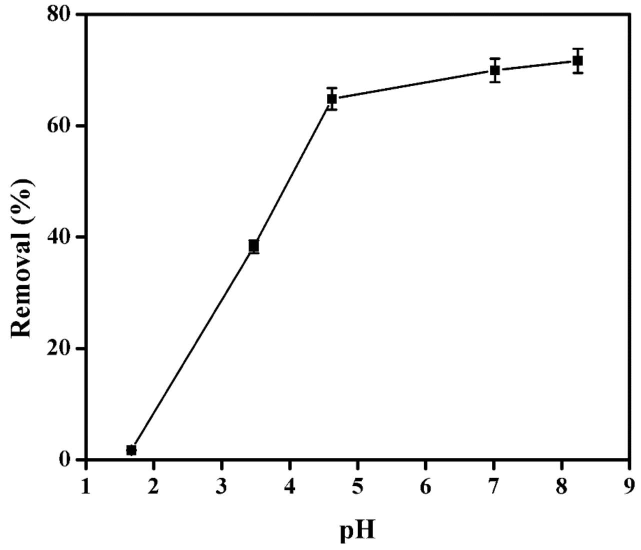

Fig. 7. Effect of pH on adsorption of cobalt ions onto RH.

Table 1
Determined parameters for nonlinear models for the adsorption of cobalt ions onto rice husk (q_e (mg/g), k_1 (1/min), k_2 (g/mg min), k_{ipd} (mg/g min$^{0.5}$), α (mg/g min), β (g/mg), Q_t (mg/g))

Kinetics models	Determined parameters	
Pseudo-first-order	q_e	0.636
	k_1	0.679
	% Error	4.036
	χ^2	0.0060
Pseudo-second-order	q_e	0.737
	k_2	1.166
	% Error	–11.307
	χ^2	0.0014
Elovich	α	8.330
	β	5.416
	χ^2	0.132
Intra-particle diffusion model	k_{ipd}	0.287
	χ^2	0.3716
Experimental q_e	0.663	

For the investigation of rate-controlling step, the intraparticle diffusion model developed by W. Weber and J. Morris was applied to the kinetic data of metal ions adsorption on rice husk. Intraparticle diffusion model can be mathematically shown as follows:

$$Q_t = k_{\text{ipd}} t^{0.5} \tag{7}$$

where k_{ipd} (mg/g min$^{0.5}$) is the rate constant of the intraparticle diffusion equation. The intraparticle model plot for adsorption of Co(II) on RH is presented in Fig. 8. If the line of plot passes through the origin, it shows that the intraparticle diffusion mechanism was only operative during the adsorption process and it is the rate-determining step.

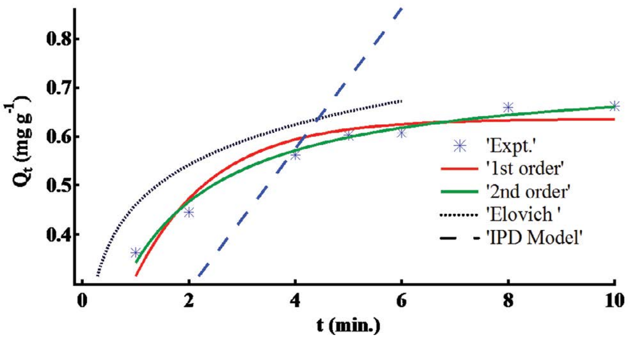

Fig. 8. Nonlinear plots of pseudo-first-order and pseudo-second-order, Elovich, and intraparticle diffusion kinetics models for adsorption of Co(II) onto RH.

It was found that the plot did not pass through the origin, indicating that the intraparticle model was not only governing the adsorption process. Moreover, the Chi-square for the intraparticle diffusion model was found to be high suggesting that this model alone was not sufficient to explain the adsorption mechanism.

Elovich kinetic model is associated with adsorption capacity and was established in 1934 by Zeldovich based on the kinetic law of chemisorption. Elovich kinetic model can be used to explain the adsorption process and written as follows [56]:

$$\frac{dQ_t}{d_t} = \alpha \exp\left(-\beta Q_t\right) \tag{8}$$

where α is initial adsorption rate (mg/g min), β is desorption constant (g/mg), dQ_t/dt is change in metal ions concentration with time, and Q_t is metal ions concentration adsorbed at equilibrium (mg/g). Elovich equation was used to describe adsorption rate of Co(II) onto RH. A nonlinear plot for adsorption of Co(II) onto RH is given in Fig. 8. The value of χ^2 for adsorption of Co(II) along with Elovich constants is given in Table 1. Although no mechanistic evidence of the adsorption process was provided by the Elovich equation, it has proved suitable for highly heterogeneous adsorption systems [57].

3.5. Adsorption isotherms

Proper quantification of the adsorption method is needed for the application of the adsorption process on the commercial level. Adsorption equilibrium is essential for the analysis and design of the adsorption process. It gives fundamental data of physicochemical procedure for studying the applicability of process as a unit operation. The experimental data was evaluated employing nonlinear Langmuir, Freundlich, and Dubinin–Radushkevich adsorption isotherms for this purpose.

3.5.1. Nonlinear Langmuir isotherm

Langmuir model presumed homogeneity of adsorbing surface and no interactions between adsorbed species possessing uniform energies of adsorption onto the surface and no trans-migration of adsorbate species in the plane of the surface. The difference in adsorption capacities of two adsorbents for the same adsorbate is considered to be high because of the physicochemical properties of them or the chemistry of solution possessing adsorbing species.

Nonlinear Langmuir adsorption isotherm is expressed as:

$$C_{\text{ads}} = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{9}$$

where C_e is the metal ions concentration of solution (mol/L) at equilibrium. The constant Q_m is monolayer adsorption capacity (mol/g) and K_L (L/mol) is related to energy of adsorption. In general, Q_m and K_L are functions of pH, ionic media, and ionic strength. The value of Q_m for adsorption of Co(II) onto RH was measured by nonlinear Langmuir isotherm. Herein, Wavemetrices IGOR Pro 6.1.2 software was utilized for determination of isotherm endowments while using nonlinear equations. Nonlinear Langmuir isotherm model are shown in Fig. 9 and the values of constants are given in Table 2.

A significant endowment of Langmuir isotherm can be shown in terms of a dimensionless constant "separation factor" parameter, "R_L" that is utilized to determine if an adsorption system is "favorable" or "unfavorable" and can be shown as follows:

$$R_L = \frac{1}{\left(1 + K_L C_0\right)} \tag{10}$$

where C_0 is the initial concentration of metal ions (mol/L) and K_L is the Langmuir adsorption equilibrium constant (L/mol). The value of R_L shows the adsorption process to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The values of R_L for adsorption of Co(II) onto RH were measured from Langmuir constant K_L and initial concentrations of metal ion and results are given in Table 2 which established that adsorption of Co(II) onto RH was favorable. It was showed by fractional values of R_L between 1 and 0.

3.5.2. Nonlinear Freundlich isotherm

Nonlinear Freundlich isotherm is expressed as:

$$C_{\text{ads}} = K_F C_e^{1/n} \tag{11}$$

where "K_F" and "n" are Freundlich constants indicating adsorption capacity and adsorption intensity respectively. C_e is the concentration of adsorbate at equilibrium in aqueous solution (mol/L). The good fit of adsorption data to Freundlich isotherm shows that there is almost no limit to the quantity adsorbed and multilayer adsorption will take place. Nonlinear Freundlich isotherm was applied to experimental data. The nonlinear plot of Freundlich isotherm is represented in Fig. 9 and the values of K_F and n are given in Table 2. The heterogeneous surface of the RH was signified by the value of n. The values of "n" ranges from 2–10 representing good adsorption, 1–2 moderate adsorption, and less than one shows poor sorption [58].

3.5.3. Nonlinear Dubinin–Radushkevich isotherm

The nonlinear D–R equation can be expressed as:

$$C_{\text{ads}} = C_m \exp\left(-\beta\varepsilon^2\right) \tag{12}$$

where C_{ads} is the quantity of Co(II) adsorbed onto RH, C_m (mol/g) is the maximum quantity of metal ions that can be adsorbed onto RH under the optimized experimental conditions, β is a constant related to adsorption energy, and ε (Polyanyi potential) = $RT\ln\left(1+\frac{1}{C_e}\right)$ where R is the universal gas constant (kJ/mol K), T is absolute temperature (K), and C_e is the equilibrium concentration of metal ions in solution (mol/g).

From b value, the mean adsorption energy (E) can be calculated as [59]:

Table 2
Langmuir, Freundlich, and Dubinin–Radushkevivh (D–R) isotherms parameters by nonlinear method (Q_m (mol/g), K_L (L/mol), K_F ((mg/g) (L/mg)$^{1/n}$), C_m (mol/g), β (mol²/J²), E (kJ/mol))

Adsorption isotherms	Isotherm parameters	
Langmuir isotherm	Q_m	1.59×10^{-5}
	K_L	7,528
	R_L	0.164–0.610
	χ^2	8.24×10^{-14}
Freundlich isotherm	K_F	$2.50 \times 10^{-4} \pm 9.44 \times 10^{-9}$
	n	2.20 ± 0.007
	χ^2	5.06×10^{-12}
Dubinin–Radushkevich isotherm	C_m	$7.41 \pm 0.577) \times 10^{-5}$
	β	$(4.68 \pm 0.162) \times 10^{-5}$
	E	10.34 ± 0.357
	χ^2	3.4×10^{-12}

$$E = \frac{1}{\sqrt{2\beta}} \tag{13}$$

which is the mean free energy for transfer of one mole of solute from infinity to surface of adsorbent.

The D–R constants for nonlinear form were calculated from the plot of C_{ads} vs. C_e by utilizing a computer program Wavemetrices Igor Pro 6.2.1.2 and are given in Table 2 along with their respective (χ^2) values which can be utilized as a best fitting tool in the nonlinear method. The values of "C_m" and "β" along with measured adsorption free energy are also given in Table 2. The nonlinear plot for adsorption of Co(II) onto RH are given in Fig. 9. Low numerical values of "χ^2" for nonlinear represents that experimental data fitted well to D–R isotherm.

The β value of $(4.68 \pm 0.162) \times 10^{-5}$ was utilized for the determination of adsorption free energy (E) and measured E values was 10.34 ± 0.357 kJ/mol. It showed that adsorption of Co(II) onto RH was chemical adsorption. Moreover, the higher value of E is for a stronger bond between metal ions and adsorption sites onto RH.

3.6. Adsorption thermodynamics study

The feasibility and spontaneity of the adsorption process were revealed by thermodynamic study. The change in Gibb's free energy (Δ*G*°), enthalpy (Δ*H*°), and entropy (Δ*S*°) were calculated from below relationships:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{14}$$

$$K_c = \frac{C_a}{C_e} \tag{15}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{16}$$

where K_c, Δ*G*°, Δ*H*°, and Δ*S*° are equilibrium constant, change in Gibb's free energy (KJ/mol), enthalpy (KJ/mol), and entropy (J/mol K), respectively. The plot of ln K_c vs. 1/*T* for the adsorption of Co(II) onto RH is shown in Fig. 10. The values of adsorption enthalpy (Δ*H*°) and entropy (Δ*S*°) were determined from the slope and intercept of Fig. 10 and are given in Table 3. The positive value of enthalpy (Δ*H*°) shows that adsorption of Co(II) onto RH is an endothermic process. Similarly, the positive value of entropy (Δ*S*°) denotes an increase in randomness at the adsorbent–adsorbate interface during adsorption of Co(II) onto RH. Contrary, the values of Gibb's free energy (Δ*G*°) were also calculated from Eq. (14) and are given in Table 3. The decrease in values of Gibb's free energy with rise in temperature shows a decline in the feasibility of adsorption at elevated temperature. Moreover, its negative value showed that the adsorption process is spontaneous in nature.

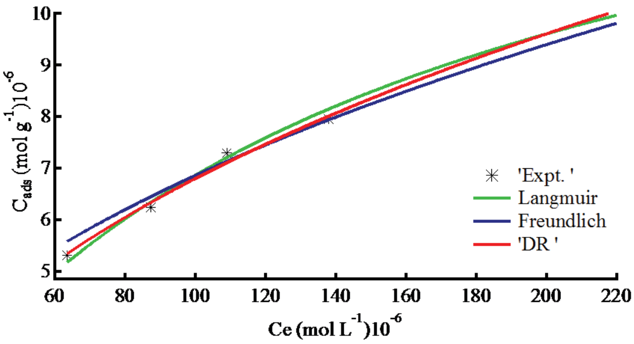

Fig. 9. Nonlinear plots of Langmuir, Freundlich, and D–R isotherms of cobalt ions adsorption onto RH.

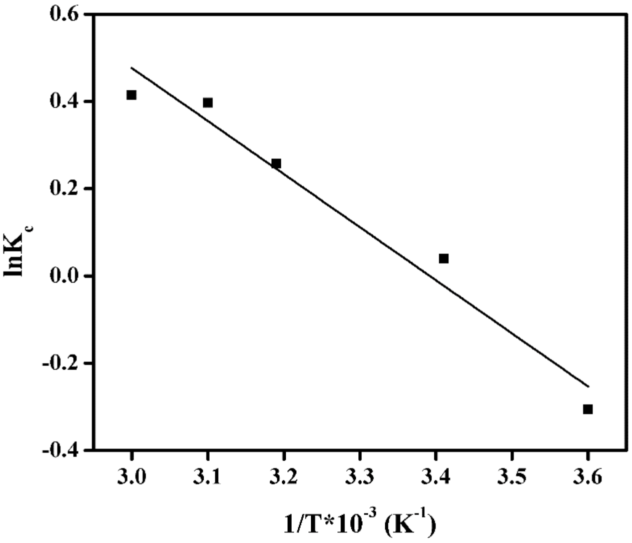

Fig. 10. Plot of 1/*T* vs. lnK_c for adsorption of cobalt ions onto RH.

3.7. Recovery of cobalt ions

The regeneration of adsorbent (RH) and recovery of Co(II) are significant aspects of wastewater treatment. Several efforts were made to recover loaded Co(II) from RH surface by utilizing HNO_3 as desorbing media. HNO_3 solution of different molarities was used by utilizing batch mode. Fixed quantity of metal loaded RH was shaked with HNO_3 for specific intervals of time for regeneration of Co(II). A series of experiments were carried with changing concentrations of HNO_3 solutions for desorption of Co(II) from RH. Maximum recovery of Co(II) (~97%) was attained with 0.1 mol/L HNO_3 solution.

3.8. Applicability of method

The discharge of cobalt was revealed from an ordinary tap water sample employing 0.0001 mol/L of HNO_3 solution, 25 min shaking time, and adsorbent weight of 300 mg in order to verify the applicability of the developed method on real samples. Table 4 represents attained results along with the calculated composition of the tap water sample. It exhibited that the measured concentration of cobalt in the tap water sample was very low. Thus, the discharge efficiency of cobalt was revealed by spiking the sample with 10.0 mg/L of cobalt. Table 4 shows that concentration of cobalt from spiked tap

Table 3
Thermodynamic parameters for adsorption of Co(II) onto RH

		$\Delta G°$ (KJ/mol)					
$\Delta H°$ (KJ/mol)	$\Delta S°$ (J/mol)	278 K	293 K	303 K	313 K	323 K	333 K
10.11	34.29	–9.522	–10.04	–10.38	–10.72	–11.07	–11.41

Table 4
Calculated composition of tap water sample

Cations/anions	Concentration (mg/L)
Ca	31.52
Mg	12.90
Na	15.42
K	2.23
Fe	0.02
Mn	0.01
Zn	0.11
Cu	0.01
Pb	0.01
CO_3^{2-}	7.00
HCO_3^{2-}	140.00
Cl^-	2.80
NO_3^-	2.00
SO_4^{2-}	12.00
Co	10.00[a]
Co	3.22[b]
Co	1.36[c]

[a] Concentration after spiking.
[b] Concentration after decontamination.
[c] Concentration after two consecutive decontamination steps.

water in a single step was decreased by 67.80%, however, by shaking the aliquot with the same weight of fresh RH discharge the cobalt from spiked tap water sample up to 86.40%, representing that RH has high potential to discharge cobalt from such matrix.

4. Conclusions

In summary, the adsorptive discharge of Co(II) from aqueous solution by RH was revealed at room temperature. The percentage discharge of Co(II) from aqueous solution was enhanced with the contact time, the mass of RH, temperature, and pH while declined with an initial concentration of Co(II). Results of adsorption kinetics showed that experimental data obeyed nonlinear pseudo-second-order kinetics. Results of equilibrium isotherm showed that experimental data fitted well to nonlinear Langmuir isotherm model. Adsorption thermodynamic study represents that adsorption of Co(II) onto RH was an endothermic and spontaneous process. Moreover, the recovery of Co(II) was attained maximum for HNO_3 (0.1 mol/L) solution. Therefore, we concluded that RH could be employed as an excellent adsorbent for the discharge of Co(II) from aqueous solution.

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References

[1] H.S. Saeedeh Hashemian, Saeedeh ragabion adsorption of cobalt(II) from aqueous solutions by Fe_3O_4/bentonite nanocomposite, Water Air Soil Pollut., 226 (2015) 2212.

[2] M. Yousefi, M.H. Dehghani, S.M. Nasab, V. Taghavimanesh, S. Nazmara, A.A. Mohammadi, Data on trend changes of drinking groundwater resources quality: a case study in Abhar, Data Brief, 17 (2018) 424–430.

[3] V.K.K. Upadhyayula, S. Deng, M.C. Mitchell, G.B. Smith, Application of carbon nanotube technology for removal of contaminants in drinking water: a review, Sci. Total Environ., 408 (2009) 1–13.

[4] M. Abbas, S. Kaddour, M. Trari, Kinetic and equilibrium studies of cobalt adsorption on apricot stone activated carbon, J. Ind. Eng. Chem., 20 (2014) 745–751.

[5] F. Fang, L. Kong, J. Huang, S. Wu, K. Zhang, X. Wang, B. Sun, Z. Jin, J. Wang, X.-J. Huang, J. Liu, Removal of cobalt ions from aqueous solution by an amination graphene oxide nanocomposite, J. Hazard. Mater., 270 (2014) 1–10.

[6] X. Yang, F. Jie, B. Wang, Z. Bai, High-efficient synergistic extraction of Co(II) and Mn(II) from wastewater via novel microemulsion and annular centrifugal extractor, Sep. Purif. Technol., 209 (2019) 997–1006.

[7] J. Mizera, G. Mizerová, V. Machovič, L. Borecká, Sorption of cesium, cobalt and europium on low-rank coal and chitosan, Water Res., 41 (2007) 620–626.

[8] V.K. Gupta, C.K. Jain, I. Ali, M. Sharma, V.K. Saini, Removal of cadmium and nickel from wastewater using bagasse fly ash—a sugar industry waste, Water Res., 37 (2003) 4038–4044.

[9] A. Ahmadpour, M. Tahmasbi, T.R. Bastami, J.A. Besharati, Rapid removal of cobalt ion from aqueous solutions by almond green hull, J. Hazard. Mater., 166 (2009) 925–930.

[10] J. Oliva, J. De Pablo, J.-L. Cortina, J. Cama, C. Ayora, Removal of cadmium, copper, nickel, cobalt and mercury from water by Apatite II™: column experiments, J. Hazard. Mater., 194 (2011) 312–323.

[11] I.A. Aguayo-Villarreal, D. Cortes-Arriagada, C.K. Rojas-Mayorga, K. Pineda-Urbina, R. Muñiz-Valencia, J. González, Importance of the interaction adsorbent – adsorbate in the dyes adsorption process and DFT modeling, J. Mol. Struct., 1203 (2020) 127398–127406.

[12] Mandeep, A. Gulati, R. Kakkar, Graphene-based adsorbents for water remediation by removal of organic pollutants: theoretical and experimental insights, Chem. Eng. Res. Design, 153 (2020) 21–36.

[13] Y.A. Patil, B. Sadhu, D.R. Boraste, A.L. Borkar, G.S. Shankarling, Utilization of Cucurbit[6]uril as an effective adsorbent for the remediation of Phthalocyanine and Procion golden yellow dyes, J. Mol. Struct., 1202 (2020) 127278–127286.

[14] R. Kueasook, N. Rattanachueskul, N. Chanlek, D. Dechtrirat, W. Watcharin, P. Amornpitoksuk, L. Chuenchom, Green and facile synthesis of hierarchically porous carbon monoliths via surface self-assembly on sugarcane bagasse scaffold: Influence of mesoporosity on efficiency of dye adsorption, Microporous Mesoporous Mater., 296 (2020) 110005–10014.

[15] A.I. Borhan, D. Gherca, Ş. Cojocaru, N. Lupu, T. Roman, M. Zaharia, M.N. Palamaru, A.R. Iordan, One-pot synthesis of hierarchical magnetic porous γ-Fe_2O_3@$NiFe_2O_4$ composite with solid-phase morphology changes promoted by adsorption of anionic azo-dye, Mater. Res. Bull., 122 (2020) 110664–110675.

[16] B. Fonseca, H. Figueiredo, J. Rodrigues, A. Queiroz, T. Tavares, Mobility of Cr, Pb, Cd, Cu and Zn in a loamy sand soil: a comparative study, Geoderma, 164 (2011) 232–237.

[17] X. Tan, M. Fang, C. Chen, S. Yu, X. Wang, Counterion effects of nickel and sodium dodecylbenzene sulfonate adsorption to multiwalled carbon nanotubes in aqueous solution, Carbon, 46 (2008) 1741–1750.

[18] X. Tan, Q. Fan, X. Wang, B. Grambow, Eu(III) sorption to TiO_2 (Anatase and Rutile): batch, XPS, and EXAFS Studies, Environ. Sci. Technol., 43 (2009) 3115–3121.

[19] V.K. Gupta, S. Agarwal, T.A. Saleh, Chromium removal by combining the magnetic properties of iron oxide with adsorption properties of carbon nanotubes, Water Res., 45 (2011) 2207–2212.

[20] M. Havelcová, J. Mizera, I. Sýkorová, M. Pekař, Sorption of metal ions on lignite and the derived humic substances, J. Hazard. Mater., 161 (2009) 559–564.

[21] X. Wu, X. Tan, S. Yang, T. Wen, H. Guo, X. Wang, A. Xu, Coexistence of adsorption and coagulation processes of both arsenate and NOM from contaminated groundwater by nanocrystallined Mg/Al layered double hydroxides, Water Res., 47 (2013) 4159–4168.

[22] P. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, S. Hu, M.H. Zhao, C. Lai, Z. Wei, C. Huang, G.X. Xie, Z.F. Liu, Use of iron oxide nanomaterials in wastewater treatment: a review, Sci. Total Environ., 424 (2012) 1–10.

[23] G. Zhao, J. Li, X. Ren, C. Chen, X. Wang, Few-layered graphene oxide nanosheets As superior sorbents for heavy metal ion pollution management, Environ. Sci. Technol., 45 (2011) 10454–10462.

[24] S. Zafar, M.I. Khan, M. Khraisheh, S. Shahida, T. Javed, M.L. Mirza, N. Khalid, Use of rice husk as an effective sorbent for the removal of cerium ions from aqueous solution: kinetic, equilibrium and thermodynamic studies, Desal. Water Treat., 150 (2019) 124–135.

[25] S. Zafar, M.I. Khan, M. Khraisheh, S. Shahida, N. Khalid, M.L. Mirza, Effective removal of lanthanum ions from aqueous solution using rice husk: impact of experimental variables, Desal. Water Treat., 132 (2019) 263–273.

[26] S. Zafar, M.I. Khan. M. Khraisheh, M.H. Lashari, S. Shahida, M.F. Azhar, P. Prapamonthon, M.L. Mirza, N. Khalid, Kinetic, equilibrium and thermodynamic studies for adsorption of nickel ions onto husk of *Oryza sativa*, Desal. Water Treat., 167 (2019) 277–290.

[27] A. Demirbas, Heavy metal adsorption onto agro-based waste materials: a review, J. Hazard. Mater., 157 (2008) 220–229.

[28] D.W. O'Connell, C. Birkinshaw, T.F. O'Dwyer, Heavy metal adsorbents prepared from the modification of cellulose: a review, Bioresour. Technol., 99 (2008) 6709–6724.

[29] M.I. Khan, M.H. Lashari, M. Khraisheh, S. Shahida, S. Zafar, P. Prapamonthon, A. Rehman, S. Anjum, N. Akhtar, F. Hanif, Adsorption kinetic, equilibrium and thermodynamic studies of Eosin-B onto anion exchange membrane, Desal. Water Treat., 155 (2019) 84–93.

[30] M.I. Khan, T.M. Ansari, S. Zafar, A.R. Buzdar, M.A. Khan, F. Mumtaz, P. Prapamonthon, M. Akhtar, Acid green-25 removal from wastewater by anion exchange membrane: adsorption kinetic and thermodynamic studies, Membr. Water Treat., 9 (2018) 79–85.

[31] M.I. Khan, S. Zafar, A.R. Buzdar, M.F. Azhar, W. Hassan, A. Aziz, Use of citrus Sinensis leaves as a bioadsorbent for removal of congo red dye from aqueous solution, Fresenius Environ. Bull., 27 (2018) 4679–4688.

[32] M.I. Khan, S. Zafar, M.A. Khan, S. Zafar, F. Mumtaz, P. Prapamonthon, A.R. Buzdar, *Bougainvillea glabra* leaves for adsorption of congo red from wastewater, Fresenius Environ. Bull., 27 (2018) 1456–1465.

[33] M.I. Khan, M.A. Khan, S. Zafar, M.N. Ashiq, M. Athar, A.M. Qureshi, M. Arshad, Kinetic, equilibrium and thermodynamic studies for the adsorption of methyl orange using new anion exchange membrane (BII), Desal. Water Treat., 58 (2017) 285–297.

[34] M.I. Khan, S. Zafar, M.A. Khan, A.R. Buzdar, P. Prapamonthon, Adsorption kinetic, equilibrium and thermodynamic study for the removal of Congo Red from aqueous solution, Desal. Water Treat., 98 (2017) 294–305.

[35] M.I. Khan, S. Akhtar, S. Zafar, A. Shaheen, M.A. Khan, R. Luque, A. Rehman, Removal of Congo red from aqueous solution by anion exchange membrane (EBTAC): adsorption kinetics and themodynamics, Materials, 8 (2015) 4147–4161.

[36] M.I. Khan, S. Zafar, H.B. Ahmad, M. Hussain, Z. Shafiq, Use of morus albal leaves as bioadsorbent for the removal of congo red dye, Fresenius Environ. Bull., 24 (2015) 2251–2258.

[37] M.A. Khan, M.I. Khan, S. Zafar, Removal of different anionic dyes from aqueous solution by anion exchange membrane, Membr. Water Treat., 8(2017) 259–277.

[38] M.I. Khan, L. Wu, A.N. Mondal, Z. Yao, L. Ge, T. Xu, Adsorption of methyl orange from aqueous solution on anion exchange membranes: adsorption kinetics and equilibrium, Membr. Water Treat., 7 (2016) 23–38.

[39] S. Zafar, N. Khalid, M.L. Mirza, Potential of rice husk for the decontamination of silver ions from aqueous media, Sep. Sci. Technol., 47 (2012) 1793–1801.

[40] V.C. Srivastaa, I.D. Mall, I.M. Mishra, Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA, J. Hazard. Mater., 134 (2006) 257–267.

[41] S.K. Kazy, P. Sar, S.P. Singh, A.K. Sen, S.F. D'Souza, Extracellular polysaccha-rides of a copper sensitive and a copper resistant *Pseudomonas aeruginosa* stain: synthesis, chemical nature and copper binding, World J. Microbiol. Biotechnol., 18 (2002) 583–588.

[42] S.K. Kazy, S. D'Souza, P. Sar, Uranium and thorium sequestration by a *Pseudomonas* sp.: mechanism and chemical characterization, J. Hazard. Mater., 163 (2009) 65–72.

[43] X. Ying-Mei, Q. Ji, H. De-Min, W. Dong-Mei, C. Hui-Ying, G. Jun, Z. Qiu-Min, Preparation of amorphous silica from oil shale residue and surface modification by silane coupling agent, Oil Shale, 27 (2010) 37–46.

[44] L. Ludueña, D. Fasce, V.A. Alvarez, P.M. Stefani, Nanocellulose from rice husk following alkaline treatment to remove silica, BioResources, 6 (2011) 1440–1453.

[45] M.B. Ibrahim, W.L. Jimoh, Bioremediation of Ni(II) and Cd(II) from aqueous solution, Indian J. Sci. Technol., 4 (2011) 487–491.

[46] H. Omar, S. Abu-Kharda, L. Abd El-Baset, R. Abu-Shohba, Efficiency of Dry (*Psidium guava*) leaves for the removal of cesium-137 from aqueous solutions, Arabian J. Nucl. Sci. Appl., 45 (2012) 505–515.

[47] J.T. Nwabanne, P.K. Igbokwe, Copper(II) uptake by adsorption using palmyra palm nut, Adv. Appl. Sci. Res., 2 (2011) 166–175.

[48] M. Torab-Mostaedi, Biosorption of lanthanum and cerium from aqueous solutions using tangerine (*Citrus reticulata*) peel: equilibrium, kinetic, and thermodynamic studies, Chem. Ind. Chem. Eng., 19 (2013) 79–88.

[49] S. Larous, A.-H. Meniai, M.B. Lehocine, Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust, Desalination, 185 (2005) 483–490.

[50] A. Özer, D. Özer, A. Özer, The adsorption of copper(II) ions on to dehydrated wheat bran (DWB): determination of the equilibrium and thermodynamic parameters, Process Biochem., 39 (2004) 2183–2191.

[51] J. Egila, B. Dauda, T. Jimoh, Biosorptive removal of cobalt(II) ions from aqueous solution by *Amaranthus hydridus* L. stalk wastes, Afr. J. Biotechnol., 9 (2010) 8192–8198.

[52] M. Malakootian, A. Almasi, H. Hossaini, Pb and Co removal from paint industries effluent using wood ash, Int. J. Environ. Sci. Technol., 5 (2008) 217–222.

[53] S. Largergren, Zur theorie der sogenannten adsorption geloster stoffe, Kungl. Svens. Vetenskapsakad., Handl., 24 (1898) 1–39.

[54] Y.-S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem., 34 (1999) 451–465.
[55] Y.-S. Ho, Effect of pH on lead removal from water using tree fern as the sorbent, Bioresour. Technol., 96 (2005) 1292–1296.
[56] E. Demirbas, M. Kobya, E. Senturk, T. Ozkan, Adsorption kinetics for the removal of chromium(VI) from aqueous solutions on the activated carbons prepared from agricultural wastes, Water SA, 30 (2004) 533–539.
[57] Y.S. Ho, G. McKay, Application of kinetic models to the sorption of copper(II) on to peat, Adsorpt. Sci. Technol., 20 (2002) 797–815.
[58] B. Subramanyam, A. Das, Linearized and non-linearized isotherm models comparative study on adsorption of aqueous phenol solution in soil, Int. J. Environ. Sci. Technol., 6 (2009) 633–640.
[59] A. Itodo, H. Itodo, Sorption energies estimation using Dubinin–Radushkevich and Temkin adsorption isotherms, Life Sci. J., 7 (2010) 31–39.