The sorption of cadmium(II) ions on mercerized rice husk and activated carbon

Mas Rosemal Hakim MAS HARIS[1,*], **Nor Aimi ABDUL WAHAB**[2], **Chong Wan RENG**[1,3],
Baharin AZAHARI[3], **Kathiresan SATHASIVAM**[4]

[1]*School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang-MALAYSIA*
e-mail: mas1@usm.my
[2]*Department of Applied Sciences, Universiti Teknologi Mara, Penang Campus,*
Penang-MALAYSIA
[3]*School of Industrial Technology, Universiti Sains Malaysia,*
11800 Penang-MALAYSIA
[4]*Department of Material Sciences, Faculty of Applied Sciences, AIMST University,*
08000 Sungai Petani, Kedah-MALAYSIA

This work describes the removal of Cd(II) ions in aqueous solution by unmodified and base-modified rice husk (RH) as compared to that by activated carbon (AC). Mercerization of RH was carried out by using dilute solutions (0.013 M) of NaOH, KOH, and Ca(OH)$_2$. The experiments were conducted in duplicate under 1-batch and 2-batch treatments. In the 1-batch treatment, a fresh 200 mg of each adsorbent was used to study the sorption of the Cd(II) ions from 100-mL solutions at an initial concentration of 5 mg L^{-1}. The adsorption percentage increased in the order of unmodified RH (80.13 ± 0.46%) < Ca(OH)$_2$-modified RH (90.74 ± 0.18%) < NaOH-modified RH (93.36 ± 0.23%) ≤ KOH-modified RH (93.78 ± 0.27%) < AC (98.4 ± 0.18%). In the 2-batch treatment, a fresh 100 mg of each adsorbent was placed in 100-mL solutions at an initial concentration of 5 mg L^{-1} of Cd(II) ions for 30 min, and the resulting solutions were filtered. The filtrates were subjected to another fresh 100 mg of each adsorbent for an additional 30 min. The percentage removal of the metal ion using the 2-batch treatment for unmodified RH, base-modified RH, and AC was 97.71%, 98.00 ± 1.00%, and nearly 100%, respectively.

Key Words: Cd(II), sorption, mercerization, base-modified, rice husk, activated carbon

*Corresponding author

Introduction

Industrialization has increased the degradation of our environment through the discharge of wastewaters. This has resulted in significant amounts of heavy metals being deposited into our ecosystems.[1] These metals are not biodegradable and are known to cause severe dysfunctions of the kidneys, reproductive system, liver, brain, and central nervous system.[2]

Cadmium is one of the most readily absorbed and accumulated elements in plants grown on contaminated soil, and it is highly toxic. Cadmium has been used as an intermediate in batteries, as a catalyst in electroplating, as a pigment in paint, and as a plastic stabilizer.[3,4] Cadmium is highly toxic and has an extremely long biological half-life.[5] Cadmium mainly accumulates in the liver and kidneys, which will cause renal dysfunction, hypertension, and anaemia.[4] Due to the dangerous effects of heavy metal ions on the environment and human life, it is necessary to remove Cd(II) ions from wastewater before discharging it into natural water sources or land so that it does not exceed the maximum permissible limit, which is 0.01 mg L^{-1} as stated in the Malaysian Environmental Quality Act of 1974 on environmental quality sewage and industrial effluents.

Various techniques have been applied for the removal of heavy metal ions in wastewater. This includes chemical precipitation, coagulation, ion exchange, oxidation, electrodialysis, membrane separations, reverse osmosis, solvent extraction, and adsorption.[6] Adsorption techniques are regarded as having high potential for future use in industrial wastewater treatment because of their proven efficiency in the removal of organic and inorganic pollutants in aqueous media, and for economic considerations.[7] The different types of adsorbents used for heavy metal ion adsorption are activated carbon (AC), synthetic metal oxides (iron oxides/hydroxides, aluminum oxides/hydroxides, mixed Fe-Al oxides, and doped oxides), microorganisms, and agricultural-based sorbents.[8] AC has proven to be a good adsorbent for the removal of heavy metal ions in the adsorption process due to its microporous structure, large surface area, high adsorption capacity, and high degree of surface reactivity.[9] Nevertheless, the application of AC for wastewater treatment is not feasible due to its high price and the cost associated with regeneration as a result of a high degree of losses in the real process.[10]

Raw agriculture is one of the most promising alternative adsorbents for heavy metal ion removal as it is an inexpensive and unused resource, widely available, and environmentally friendly.[11] Many agricultural wastes, such as cork and yohimbe bark,[12] spent grain,[13] peanut hull pellets,[14] rice milling by-products,[15] grape stalk waste,[16] pectin-rich fruit wastes,[17] and biowaste from the fruit juice industry,[18] have been reported as capable of adsorbing and removing large amounts of metal ions from aqueous solutions.

The aim of this work was to evaluate the efficiency of Cd(II) ion removal using rice husk (RH). RH is an agricultural waste produced as a by-product of the rice milling industry. The use of RH as an adsorbent will solve both the disposal problem and provide access to cheaper materials. In Malaysia, large quantities of RH are generated as agricultural waste, and disposal of this material has become an issue. Research on heavy metal ion removal using RH has been reported by many researchers.[19−22] In this study, RH was modified with low concentrations of NaOH, KOH, and Ca(OH)$_2$ in order to investigate whether small changes in the structure of fibers increased the capacity of Cd(II) ion removal. The results were then compared to those for AC as the reference.

Experimental

Materials

RH fibers were collected from a rice mill in Seberang Perai, Penang, Malaysia. The main components of RH are carbon and silica (15%-22% SiO_2 in hydrated amorphous forms like silica gel), which gives it the potential to be used as an adsorbent.[23] The chemical composition of RH is 32.40% cellulose, 21.34% hemicellulose, 21.44% lignin, and 15.05% mineral ash. The chemicals used in this study were activated carbon (AJAX Chemicals), sodium hydroxide (Merck), potassium hydroxide (R & M Chemicals), calcium hydroxide (APS Ajak Finechem), and 1000 mg L^{-1} of $Cd(NO_3)_2.4H_2O$ stock solution.

Preparation of adsorbents

RH was washed with running water to remove dirt, dust, and impurities. The fibers were boiled with distilled water for 1 h to remove the soluble sugars and to prevent bacterial growth. The fibers were then washed again with deionized water and the fibers obtained were dried at 110 °C in an oven for 24 h. Later, the dried RH was ground and sieved into a size smaller than 63 μm. The surface area of the RH was characterized according to the method described by Horsfall and Spiff[16] and was found to be 88.75 ± 1.57 m^2 g^{-1}. The AC used in this research was sieved and prepared in sizes smaller than 63 μm to standardize it with the size of the RH.

Chemical treatments on adsorbents

Approximately 2.0 g of $Ca(OH)_2$ was placed in 1 L of distilled water and stirred for 24 h before filtering off the undissolved $Ca(OH)_2$. The clear solution was then analyzed using atomic absorption spectroscopy (AAS; AAnalyst 700, PerkinElmer, Waltham, MA, USA) to determine the amount of Ca^{2+} present in the solution. An alkaline solution of NaOH and KOH was prepared using a similar concentration of $Ca(OH)_2$. In 500-mL conical flasks, 7.50 ± 0.1 g of RH was immersed in 250 mL of 0.013 M NaOH, KOH, and $Ca(OH)_2$ solutions, respectively, followed by agitatation at 200 rpm on a shaker machine for 4 h. After 4 h, the alkaline solution was filtered off using a Buchner funnel under vacuum conditions. The fibers were then washed several times with distilled water until a pH of 7 was achieved. The base-modified fibers were then dried in an oven at 45 °C until a constant weight was obtained.

Aqueous solution preparation

A stock solution of Cd(II) ions (100 mg L^{-1}) was prepared by diluting a standard Cd(II) ion solution of 1000 mg L^{-1} with deionized water. The stock solution of 100 mg L^{-1} was then diluted with deionized water to obtained the desired Cd(II) ion concentration (5 mg L^{-1}). The pH of the solution was adjusted accordingly by using 0.1 M NaOH and 0.1 M HCl.

Equilibrium studies

The overall experiments were divided into 1-batch and 2-batch studies. The 1-batch treatment was carried out by agitating 200 mg of RH at 200 rpm with an orbital shaker in 100 mL of aqueous solution of Cd(II)

ions at different pH levels (pH 3-9), different contact times (10-120 min), and different initial concentrations (5-15 mg L^{-1}). The mixture was then filtered using a Buchner funnel under vacuum, and the Cd(II) ion concentration in the sample was analyzed with AAS. The 2-batch treatment was carried out in order to increase the removal efficiency of Cd(II) ions by RH. The amount of adsorbent was reduced to half of the amount of adsorbent used in the 1-batch treatment, and 100 mg of adsorbent was added to 100 mL of Cd (II) solution of concentrations of 5-15 mg L^{-1}. The mixture was agitated at 200 rpm with an orbital shaker for 30 min at room temperature. After 30 min, the mixture was filtered and the solution was collected. A small portion of solution was taken out and analyzed with AAS, and then 100 mg of fresh adsorbent was added to the solution again to replace the previous adsorbent that had been filtered out. The mixture was then agitated again at 200 rpm for another 30 min. The mixture was again filtered and the supernatant liquid was analyzed using AAS. When equilibrium was established, the supernatant was carefully filtered through Whatman filter paper (No. 1) that was presaturated with distilled water. No adsorption of the metal occurred on the filter paper; a comparative study was done by measuring the concentration of the metal solution before and after filtering, and the results showed an insignificant variation of the concentration of the metal solution meaning that the amount of the metals adsorbed on the filter paper, if any, was negligible. It was then computed to a metal concentration using a standard calibration curve. The amount of Cd(II) ion adsorption onto RH can be calculated by using Eq. (1).

$$q_e = (C_o - C_e) \frac{V}{W} \tag{1}$$

Here q_e is the Cd(II) ions adsorbed onto the RH (mg g^{-1}) at equilibrium, C_o is the initial Cd(II) ion concentration (mg L^{-1}), C_e is the final Cd(II) ion concentration in the solution (mg L^{-1}) V is the volume (L) of the solution and W is the amount of RH adsorbent (g) used.

FTIR analysis

Fourier transform infrared (FTIR) spectroscopy was used to examine any changes in the structure of the fibers that arose after chemical treatment. A PerkinElmer System 2000 FTIR spectrometer was used to obtain the spectrum for each sample. Samples were ground and mixed with KBr (sample-to-KBr ratio of 1:100). They were then pressed into transparent thin pellets. The FTIR spectrum of each sample was obtained in the range of 4000400 cm^{-1}. Spectral outputs were recorded in the transmittance mode as a function of wave number.

Results

Characterization of the adsorbents

The infrared spectra for unmodified, Ca(OH)$_2$-modified, NaOH-modified, and KOH-modified RH are presented in Figure 1. As expected, all peaks assigned for unmodified and base-modified RH were quite similar, because only low concentrations of each of the base solutions were used for modification. The broad band at around 3300 cm^{-1} is attributed to the various hydroxyl groups' presence on all of the fibers. The band at around 1730 cm^{-1} belonging to the C=O stretching of methyl ester and carboxylic acid in hemicelluloses was observed at 1739, 1737, and 1734 cm^{-1} for unmodified, KOH-modified, and NaOH-modified RH, respectively. Interestingly, the disappearance of the band at around 1730 cm^{-1} for Ca(OH)$_2$-modified RH suggests complete dissolution

(removal) of hemicelluloses. $Ca(OH)_2$ is able to remove hemicelluloses because it possesses 2 hydroxyl groups and, as such, is a stronger base compared to KOH or NaOH at suitably low (i.e. soluble) concentrations. The peak attributed to the C=C stretching of lignin was observed at 1639, 1647, 1639, and 1650 cm^{-1} for unmodified, $Ca(OH)_2$-modified, NaOH-modified, and KOH-modified RH, respectively. The band within 1034 and 1061 cm^{-1} in the unmodified/base-modified RH is attributed to the OCH_3 group in lignin, indicating the base modification; particularly, $Ca(OH)_2$-modified RH is unable to remove lignin as compared to its ability to totally remove hemicelluloses.
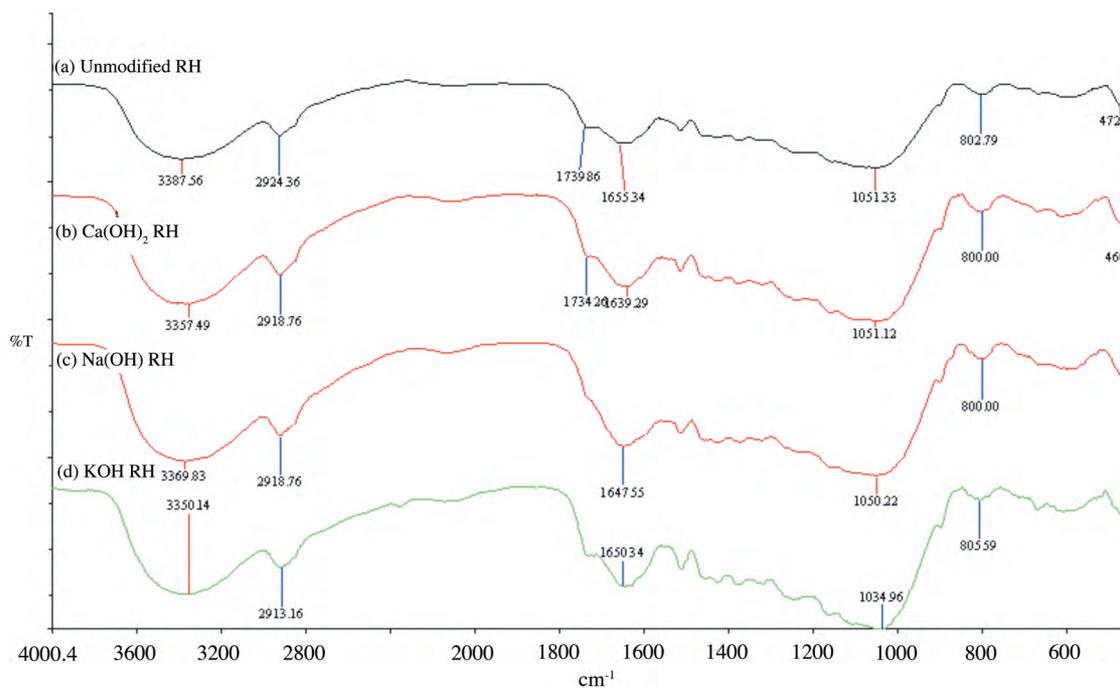
Figure 1. FTIR spectra for (a) unmodified RH, (b) $Ca(OH)_2$-modified RH, (c) NaOH-modified RH, and (d) KOH-modified RH.

Effect of initial pH

The pH of solution has been identified as the most important variable governing metal ion uptake because it influences the ionization of functional groups at the surface of an adsorbent, and the hydrogen ions themselves may compete strongly with the adsorbates.[24,25] Furthermore, pH affects the surface charge of the adsorbent, the degree of ionization, and the speciation of adsorbate. Hence, comparative studies on metal ion uptake must be carried out in solutions of similar pH value, as any variation in the pH can drastically change the adsorption capacity of an adsorbent.[26] With this in mind, the uptake of Cd(II) ions by unmodified, KOH-modified, NaOH-modified, and $Ca(OH)_2$-modified RH was investigated at various pH levels (Figure 2). At the initial pH of 3, it was observed that the adsorption was poor. This was attributed to the active sites being widely protonated, which limits the adsorbing sites for the metal ions.[27] In the pH range of 3-7, a prominent increase in adsorption was observed. The increase in metal removal as the pH increases can be explained on the basis of the decrease

in competition between protons and metal cations for the same binding sites.[28] Furthermore, the decrease in the positive surface charges results in a lower electrostatic repulsion between the surface and metal ions.[29] The further increase in adsorption was insignificant as the optimum biosorption for Cd(II) ions was reached at a pH of about 6.
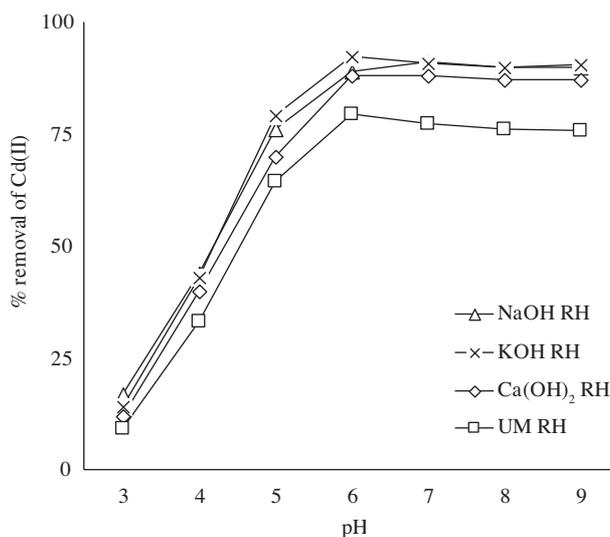
Figure 2. The effect of pH on the percentage removal of 5 mg L^{-1} Cd(II) ions by unmodified and base-modified (NaOH, KOH, and Ca(OH)$_2$) RH.

Effect of contact time and initial metal concentration on metal adsorption

Figure 3 illustrates time-course studies on the adsorption of Cd(II) ions performed by contacting 5 mg L^{-1} of the solutions containing metal ions at pH 6 with 200 mg of AC and the unmodified and base-modified RH in 100 mL of the solutions. The Cd(II) ions showed a fast rate of adsorption during the initial 10 min (first stage), and equilibrium (second stage) was reached after 30 min. Figure 4 depicts the comparison of the percentage removal of Cd(II) ions at equilibrium by unmodified RH (69.15 ± 0.34%), AC (96.76 ± 0.54%), NaOH-modified RH (81.42 ± 0.47%), KOH-modified RH (77.84 ± 0.84%), and Ca(OH)$_2$-modified RH (79.08 ± 0.64%). The metal ions have to encounter the boundary layer effect before diffusing from the boundary layer film onto the adsorbent surface, followed by the diffusion of the metal ions into the porous structure of the adsorbent, which will eventually need a longer contact time. The time profile of the metal ion uptake by the adsorbent is a single, smooth, and continuous curve leading to a saturation point. In addition, the initial metal ion concentration increases the number of collisions between ions and the adsorbent, which enhances the adsorption process. The 2-stage adsorption, the first stage of which is quantitatively predominant and the second slower stage of which is quantitatively insignificant, has been extensively reported in the literature.[30] The rapid stage is attributed to the abundant availability of active sites on the biomass and the gradual occupancy of these sites; the adsorption becomes less efficient in the slower stage.[31] As expected, AC gives a higher removal of Cd(II) ions because of its large surface area and pore volume, which gives it a unique adsorption capacity.[32] The low maximum uptake level of Cd(II) ions on unmodified RH can be explained, similar to the explanation provided by Okieimen et

al.,[33] in terms of the difference in the ionic size of metals, the nature and distribution of active groups on the biosorbent, and the mode of interaction between the metal ions and the biosorbent.
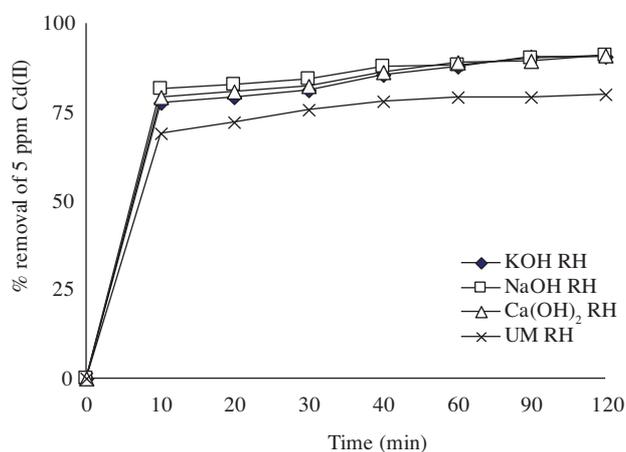
Figure 3. Effect of contact time on the percentage removal of 5 mg L^{-1} Cd(II) ions by unmodified and base-modified (NaOH, KOH, and Ca(OH)$_2$) RH.
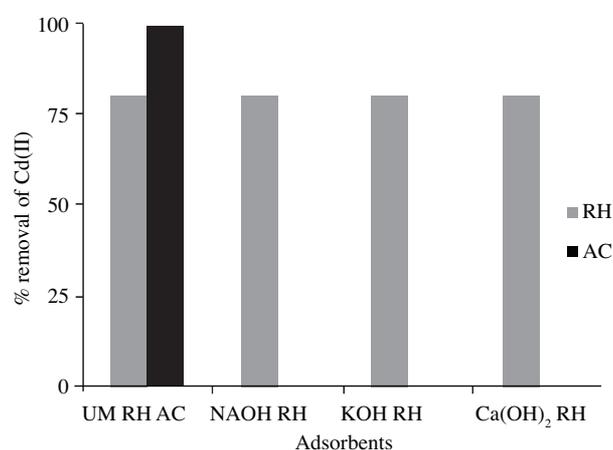
Figure 4. Comparison of the percentage removal of 5 mg L^{-1} Cd(II) ions by unmodified and base-modified (NaOH, KOH, and Ca(OH)$_2$) RH and AC.

Effect of chemical modification

A low concentration of alkaline solution (0.013 M KOH, NaOH, and Ca(OH)$_2$) was used in the chemical modification because the intention was to remove only the hemicelluloses while maintaining the overall surface structure of RH. This is supported by results of the FTIR spectral analysis (Figure 1), which revealed that almost all of the functional groups of RH existed after the chemical modification. The adsorption percentage increased in the order of unmodified RH (80.13 $\pm$ 0.46%) < Ca(OH)$_2$-modified RH (90.74 $\pm$ 0.18%) < NaOH-modified RH (93.36 $\pm$ 0.23%) $\leq$ KOH-modified RH (93.78 $\pm$ 0.27%) < AC (98.4 $\pm$ 0.18%). Treatment of RH with Ca(OH)$_2$ resulted in the fairly complete removal of the hemicelluloses, which seemed to affect the performance of Cd(II) ion removal by Ca(OH)$_2$-modified RH. The lower removal observed suggests that hemicelluloses play a role in the metal-binding process. Furthermore, the interaction site of the fibers with divalent calcium ions is stronger compared to the monovalent sodium and potassium ions, which hinders the adsorption of Cd(II) ions.[34] As expected, AC exhibited the best adsorption capacity. The improvement on the performance of RH after base modification is due to the increased surface area of the RH as the results of the etching process by base solution. This etching process tends to increase the surface roughness of RH and thus increases the surface area. This helped to increase the availability of active binding sites for the adsorption of Cd(II) ions. Furthermore, treatment of RH with alkaline solutions tends to remove the base soluble materials on the surface of the RH, and this increases the adsorption capacity.[35] The removal of this material will increase the adsorption of Cd(II) ions. Therefore, partial chemical treatment on RH is adequate to increase the Cd(II) removal efficiency.

Adsorption isotherms

The Langmuir isotherm model assumes the uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface.[36] The linear form of the Langmuir isotherm equation is given in Eq. (2).

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \tag{2}$$

Here C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mg g^{-1}), and Q_o and b are Langmuir constants respectively related to adsorption capacity and rate of adsorption. When C_e/q_e was plotted against C_e, a straight line with a slope of $1/Q_o$ was obtained. The value of Q_o was determined from the Langmuir plot in the concentration range of 5-15 mg L^{-1} and then the b value was calculated and tabulated (Table 1). The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L, which is given in Eq. (3).

$$R_L = \frac{1}{1 + bC_0} \tag{3}$$

The values of R_L were 0.49, 0.19, 0.18 and 0.31 for unmodified, KOH-modified, NaOH-modified and Ca(OH)$_2$-modified RH, respectively suggesting the isotherm to be favorable at the concentrations studied. The Freundlich isotherm model[37] considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption and can be represented by Eq. (4).

$$\ln q_e = \ln K_f + \frac{1}{n} \left(\ln C_e \right) \tag{4}$$

Here C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mg g^{-1}), and K_f and n are Freundlich constants. The Freundlich constants were derived from the slopes and intercepts of log q_e versus log C_e and are presented in Table 1. K_f can be defined as the adsorption capacity that represents the quantity of metal ions adsorbed onto the fibers for a unit equilibrium concentration and value of $n > 1$ giving an indication of the favorability of the adsorption process. As seen from Table 1, a high regression correlation coefficient, R^2, was shown by the Langmuir model for the metal ions. This indicates that the Langmuir model is very suitable for describing the adsorption equilibrium of the metal ions by the base-modified and unmodified RH. Thus it is reasonable to conclude that the adsorptions of metal ions on fibers consisting of homogeneous adsorption sites are very similar to each other.

Kinetics modeling

Two simplified kinetic models were adopted to examine the mechanism of the adsorption process. First, the kinetics of adsorption was analyzed by the Lagergren pseudo-first-order equation[38] as depicted in Eq. (5).

$$\log \left(q_e - q_t \right) = \log q_e - \frac{k_1 t}{2.303} \tag{5}$$

Here q_e and q_t are the amounts of the metals adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the rate constant for adsorption. Values of k_1 at ambient temperature were calculated from

the plots of log $(q_e - q_t)$ versus t for a concentration of 5 mg L^{-1} for Cd(II) ions. The set of R^2 values obtained were poor and the experimental q_e values did not agree with the calculated values obtained from the linear plots (Table 2). On the other hand, the pseudo-second-order equation based on equilibrium adsorption[39] is expressed by Eq. (6)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (6)$$

Here k_2 (g mg^{-1} min^{-1}) is the rate constant for second-order adsorption. The linear plot of t/q_t versus t at ambient temperature yielded a set of R^2 values greater than 0.998 for Cd(II) ions at 5 mg L^{-1} It also showed good agreement between the experimental and calculated q_e values (Table 2), indicating the applicability of this model to describe the adsorption process of the metals onto the fibers.

Table 1. Langmuir and Freundlich isotherm constants and correlation coefficients for the adsorption of activated carbon (AC), unmodified RH (UM RH), NaOH-modified RH, KOH-modified RH, and Ca(OH)$_2$-modified RH at pH 6 (25 °C).

Isotherm	Type of adsorbent				
Langmuir	AC	UM RH	NaOH RH	KOH RH	Ca(OH)$_2$ RH
Q_o (mg g^{-1})	7.46	10.41	8.50	8.24	10.46
b (mg L^{-1})	21.28	0.21	0.90	0.98	0.47
R^2	0.996	0.965	0.998	0.991	0.995
R_L	.009	0.49	0.19	0.18	0.31
Freundlich					
K_f (mg g^{-1})	9.51	1.89	3.77	3.76	3.20
n	2.37	1.49	1.96	1.96	1.62
R^2	0.994	0.999	0.995	0.997	0.999

Table 2. Comparison of the pseudo-first-order and pseudo-second-order adsorption rate constants and the calculated and experimental q_e values obtained for an initial concentration of 5 mg L^{-1} of metal ions.

Adsorbent	Initial concentration (mg L^{-1})	q_e (Exp)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
			k_1	q_e (Cal)	R^2	k_2	q_e (Cal)	R^2
UM RH	5	1.91	0.161	0.567	0.962	0.239	1.96	0.999
KOH RH	5	2.23	0.137	0.644	0.864	0.200	2.27	0.998
NaOH RH	5	2.23	0.138	0.400	0.7456	0.417	2.25	0.999
Ca(OH)$_2$ RH	5	2.15	0.094	0.416	0.865	0.317	2.03	0.998

Comparison between 1-batch and 2-batch treatments

The 1-batch and 2-batch treatments were applied for the removal of 5 mg L^{-1} Cd(II) ions by unmodified RH, base-modified RH, and AC (Figure 5). For unmodified RH, the overall removal of the metal ion increased from 79.13% for the 1-batch treatment to 97.71% for the 2-batch treatment. For NaOH-modified RH, the removal

increased from 92.44% to 98.25%. The percentage removal of the metal ion by KOH-modified RH (98.0 $\pm$ 1.00%) and Ca(OH)$_2$-modified RH (98.0 $\pm$ 1.00%) were quite similar (statistically no difference) to that of NaOH-modified RH and, as such, are not shown in Figure 5. When AC was used as the adsorbent, nearly 100% removal of the metal ion was accomplished. This can be attributed to the likely very large surface area of AC as compared to that of the unmodified and base-modified RH.
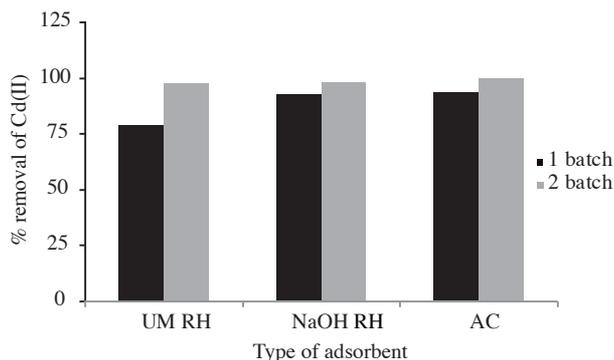
Figure 5. Comparison of the percentage removal of 5 mg L^{-1} Cd(II) ions by 1-batch and 2-batch treatments using unmodified RH, NaOH-modified RH, and AC.

Conclusions

The present work establishes that mercerization of RH using only dilute (0.013 M) solutions of NaOH, KOH, and Ca(OH)$_2$ results in the increase of the removal of Cd(II) ions in aqueous solutions as compared to that by unmodified RH. The adsorption percentage increased in the order of unmodified RH (80.13 $\pm$ 0.46%) < Ca(OH)$_2$-modified RH (90.74 $\pm$ 0.18%) < NaOH-modified RH (93.36 $\pm$ 0.23%) $\leq$ KOH-modified RH (93.78 $\pm$ 0.27%) < AC (98.4 $\pm$ 0.18%). Furthermore, greater and faster uptake of Cd(II) ions by the adsorbents, reaching close to 98.00% within 60 min, can be accomplished using the 2-batch treatment. Thus, this study reveals that with mercerization using dilute alkaline solution or by using the 2-batch treatment approach, RH can be utilized as an efficient, low-cost biosorbent for the removal of Cd(II) ions from aqueous solutions.

Acknowledgements

References

1. Sanyahumbi, D.; Duncan, J. R.; Zhao, M. R.; Hille, R. *Biotechnol. Lett.* **1998**, *20*, 745-747.

2. Manahan, S. E. *Environmental Chemistry*, CRC Press, Boca Raton, FL, 2004.

3. Pino, G. H.; de Mesquita, L. M. S.; Torem, M. L., Pinto, G. A. S. *Miner. Eng.* **2006**, *19*, 380-387.

4. Perez-Marin, A. B.; Meseguer Zapata, V.; Ortuno, J. F.; Aguilar, M.; Saez J.; Llorens, M. *J. Hazard. Mater.* **2007**, *B139*, 122-131.

5. Liu, C.; Li, F.; Luo, C.; Liu, X.; Wang, S.; Liu, T.; Li, X. *J. Hazard. Mater.* **2009**, *161*, 1466-1472.

6. Feng, D.; Aldrich, C. *Hydrometallurgy* **2004**, *73*, 1-10.

7. Garg, V. K.; Amita, M.; Kumar, R.; Gupta, R. *Dye Pigments* **2004**, 63, 243-250.

8. Rao, K. S.; Mohapatra, M.; Anand, S.; Venkateswarlu, P. *Int. J. Eng. Sci. Tech.* **2010**, *2*, 81-103.

9. Hameed, B. H.; Mahmoud, D. K.; Ahmad, A. L. *J. Hazard. Mater.* **2008**, *158*, 499-506.

10. Park, D.; Yun, Y.; Jo, J. H.; Park, J. M. *Ind. Eng. Chem. Res.* **2006**, *45*, 5059-5065.

11. Sapuan, S. M.; Leenie, A.; Harimi, M.; Beng, Y. K. *Mater. Design* **2006**, *27*, 689-693.

12. Villaescusa, I.; Martinez, N.; Miralles, N. *J. Chem. Technol. Biotechnol.* **2000**, *75*, 812-816.

13. Low, K. S.; Lee, C. K.; Liew, S. C. *Process Biochem.* **2000**, *36*, 59-64.

14. Johnson, P. D.; Watson, M. A.; Brown, J. I.; Jefcoat, A. *Waste Manage.* **2002**, *22*, 471-480.

15. Tarley, C. R. T.; Arruda, M. A. Z. *Chemosphere* **2004**, *54*, 987-995.

16. Martinez, M.; Miralles, N.; Hidalgo, S.; Fiol, N. *J. Hazard. Mater.* **2006**, *B133*, 203-211.

17. Schiewer, S.; Patil, S. B. *Bioresour. Technol.* **2008**, *99*, 1896-1903.

18. Senthilkumaar, S.; Bharathi, S.; Nithyanandhi, D.; Subburam, V. *Bioresour. Technol.* **2000**, *75*, 163-165.

19. Ajmal, M.; Khan, H. A.; Ahmad S.; Ahmad A *Water Res* **1998**, *32*, 3085-3091.

20. Wong, K. K.; Lee, C. K.; Low, K. S.; Haron, M. J. *Chemosphere* **2003**, *50*, 23-28.

21. Ghani, N. T.; Hefny, M.; El-Chaghaby, G. A. F. *Int. J. Environ. Sci. Tech.* **2007**, *4*, 67-73.

22. Naiya, T. K.; Bhattacharya, A. K.; Mandal, S.; Das, S. K. *J. Hazard. Mater.* **2009**, *163*, 1254-1264.

23. Khalid, N.; Ahmad, S.; Toheed, A.; Ahmad, J. *Appl. Radiat. Isotopes* **2000**, *52*, 30-38.

24. Pagnanelli, F.; Esposito, A.; Toro, L.; Veglio, F. *Water Res.* **2003**, *37*, 627-633.

25. Pehlivan, E.; Yanik, B. H.; Ahmetli, G.; Pehlivan, M. *Bioresour Technol.* **2008** *99*, 35203527.

26. Schiewer, S.; Volesky, B. In *Environmental Microbe-Metal Interactions*; Lovely, D. R., Ed.; ASM Press, Washington, DC, 2000.

27. Tobin, J. M.; Cooper, D. G.; Neufeld, R. J. *App. Environ. Microbiol.* **1984**, *47*, 821-824.

28. Schiewer, S.; Volesky, B. *Environ. Sci. Technol.* **1995**, *29*, 3049-3058.

29. Reddad, Z.; Gerente, C.; Andres, Y.; LeCloirec, P. *Environ. Sci. Technol.* **2002**, *36*, 2067-2073.

30. Sağ, Y.; Kutsal, T. *Process Biochem.* **1996**, *31*, 561-572.

31. da Costa, A. C. A.; Leite, S. G. F. *Biotechnol. Lett.* **1991**, *13*, 559-562.

32. Ajay, K. M.; Mishra, G. K.; Rai, P. K.; Rajagopal, C.; Nagar, P. N. *J. Hazard. Mater.* **2005**, *B122*, 161-170.

33. Okieimen, F. E.; Ogbeifeur, D. E.; Nwala, G. N.; Kumsah, C. A. *Bull. Environ. Contam. Toxicol.* **1985**, *34*, 866-870.

34. Chubar, N.; Calvalho, J. R.; Correia, M. J. N. *Colloids Surf.* **2004**, *238*, 51-58.

35. Kumar, U.; Bandyopadhay, M. *Bioresour. Technol.* **2006**, *97*, 104-109.

36. Langmuir, I. *J. Am. Chem. Soc.* **1918**, *40*, 1361-1403.

37. Freundlich, H. M. F. *J. Phy. Chem.* **1906**, *57*, 385-470.

38. Ho, Y. S. *Scientometrics* **2004**, *59*, 171-177.

39. Ho, Y. S.; McKay, G. *Resour. Conserv. Recycl.* **1999**, *25*, 171-193.