

# The Effect of Particle Sizes of Clearing Nut Seed Powder and Rice Husk Powder for Removal Efficiency of Cd<sup>2+</sup> from Synthetic Wastewater

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## Abstract

Biomaterials are considered efficient removers of heavy metals from wastewater through biosorption. This study aimed at investigating the effect of the particle size of clearing nut (*Strychnos potatorum*) seed (CN) powder and rice (*Oryza sativa*) husk (RH) powder for the removal of Cd<sup>2+</sup> in synthetic wastewater. Rice husks and CN were thermally treated at 200 °C for 3 hours and dried at 30 °C for 7 days and powdered (0.5 - 1.0 mm, 150 - 500 μm, < 63 μm). Batch experiments were conducted to study the effect of particle sizes of RH, CN and a mixture of 1:1 RH and CN (RHCN) with contact time of 2, 4, 6 and 8 hours in the removal of Cd<sup>2+</sup>. The characterization of the biomaterials before and after Cd<sup>2+</sup> treatment was analyzed using SEM, FT-IR, XRD and XRF. The Cd<sup>2+</sup> removal percentage increased with the decrement of the particle sizes. The highest significant (P < 0.05) Cd<sup>2+</sup> removal percentage was observed from the particle size of < 63 μm followed by 150 - 500 μm and 0.5 - 1.0 mm. The RHCN mixture had the highest significant (P < 0.05) Cd<sup>2+</sup> removal percentage of all the adsorbent types. The FT-IR and SEM data revealed the chemical interaction between Cd<sup>2+</sup> and biomaterials. Thus, it can be concluded that the reduction of the particle size of RH and CN is effective in the removal of Cd<sup>2+</sup>.

Keywords: Rice husk, Clearing nut, Particle size, Cadmium, Removal efficiency

## 1. Introduction

Heavy metal pollution in the environment is a severe concern due to its gradual accumulation in the food chain and long-term persistence in the ecosystem [24]. Cadmium is a hazardous heavy metal that, unlike other heavy metals, is easily absorbed by plants and enters the food chain [13]. The WHO standards are substantially more rigorous in this scenario, with the maximum permissible limits of Cd<sup>2+</sup> in drinking water fixed at 0.005 mg L<sup>-1</sup>. Chronic exposure to an elevated level of cadmium is known to cause serious health issues i.e; renal dysfunction (Fanconi syndrome), bone degradation (itai-itai syndrome), cancer, hypertension, liver damage, and blood damage [12]. The development of knowledge for their removal from metal-bearing effluents before their release into water bodies and natural streams is consequently receiving more focus. Different methods like Chemical precipitation, chemical oxidation or reduction, filtration, electrochemical treatment, limestone precipitation, ion exchange, adsorption on activated carbon, and membrane processing technologies have historically been used to remove heavy metals such as Cd<sup>2+</sup> from industrial effluent. However, most of these methods are often ineffective and/or expensive, particularly for the removal of heavy metal ions at low concentrations [9]. Thus, the development of effective and environmentally friendly technologies is required to reduce the heavy metal content of

wastewater at discharge to a tolerable level at affordable costs.

In recent years, natural or pre-treated biomaterials have been used as a cost-effective and efficient alternative material in biosorption for the removal of heavy metals from heavy metal-bearing wastewater [5]. Biomaterials are simple, less expensive, non-toxic, and efficient substances with biological origins that may be used to remove contaminants from water [22]. Biomaterials used for wastewater treatment include natural and pre-treated cellulose-based agricultural products, activated charcoal, and modified animal by-products [18]. It was found that certain plant seeds, including those of drumstick, papaya, tamarind, neem, and clearing nut [9] and agricultural wastes such as sawdust, maize cob, coconut shell, banana peel, wood apple shell, crab shell, husks and bran of cereals used to remove heavy metals from industrial wastewater [18]. A clearing nut tree (*Strychnos potatorum* L.) is a deciduous plant belonging to the family Loganiaceae. It was reported that the seeds of clearing nuts have been used as a natural coagulant to remove the turbidity of muddy water for many centuries in rural communities [3]. The presence of natural proteins and lipids containing functional groups such as -COOH, -OH is responsible for the coagulant property of the seeds in turbidity removal [8]. Researchers have reported that the CN was used to remove Cr<sup>6+</sup> [8], Cd<sup>2+</sup> [3], Cu<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> from polluted water [25]. Further, rice husk is one of the abundant lignocellulosic

organic wastes in the rice industry. Rice husk is rich in cellulose, lignin and silica. Recently, some researchers have reported that the rice husk is an efficient remover of dyes, phenols, pesticides, inorganic anions, and heavy metal ions such as  $\text{Cd}^{2+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  from wastewater [8].

Although pre-treated biomaterials are being used in metal removal from wastewater, the biosorbent treatment/chemical modifications have been causing other environmental problems, i.e., the release of excessive quantities of colored organic compounds and toxic chemicals with an unpleasant smell. Hence, attempts were made in this investigation to develop a low-cost, renewable bio adsorbent for the removal of  $\text{Cd}^{2+}$  from aqueous solutions using powders of RH, CN and a combined mixture of RH and CN by simple thermal treatments and changing the particle sizes. Therefore, the influences of various operating parameters such as particle size, contact time and biosorbent type, on the  $\text{Cd}^{2+}$  biosorption were investigated.

## 2. Material and Methods

### 2.1 Preparation of biomaterials

Rice husks (RH) and clearing nut seeds (CN) were collected from Badulla, Sri Lanka and washed with clean water. RH was thermally treated at 200 °C for 3 hours and CN was dried at room temperature for 7 days. The dried biomaterials were pulverized separately using a high-speed universal disintegrator (Model-HSD-80) and Planetary Ball Mill (Model-Alpha) working at 800 rpm for 10 hours and sieved to the working sizes of (1.0 - 0.5) mm, (500 - 150)  $\mu\text{m}$  and < 63  $\mu\text{m}$  using auto sieve shaker (Model-XQM-0.4A). All the biomaterials were stored in airtight containers. Powder morphology, functional groups, phase nature and mineral content were analyzed using Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectrophotometer (FT-IR), X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) respectively. A combination of biomaterial mixture was prepared by combining RH and CN in a 1:1 ratio (RHCN).

### 2.2 Physico-chemical characterization of biomaterials

The moisture content of each biomaterial was measured using a digital moisture meter (MB 45 OHAUS) working at 105 °C for 10 minutes. Ash content was measured by introducing 2 g of biomaterials into cleaned and weighed crucibles ( $W_1$ ) and dried at 105 °C for 1 hour in an oven and weighed ( $W_2$ ). The crucibles were ignited in a muffle furnace at 600 °C for 5 hours to a constant weight, cooled and weighed ( $W_3$ ). Ash content and Organic matter content were calculated using the following equations respectively [11].

$$\% \text{ Ash Content (dry basis)} = (W_3 - W_1) / (W_2 - W_1) \times 100 \dots \dots \dots (1)$$

( $W_3 - W_1$ ) - Weight of ash without crucible, ( $W_2 - W_1$ ) - Weight oven dried sample without crucible.

$$\% \text{ Organic matter content} = 100 - (\text{Ash content (\%)} + \text{Moisture content (\%)}), \dots \dots \dots (2)$$

### 2.3 Batch biosorption experiment

A batch biosorption experiment was conducted by adding accurately weighed 1.5 g of each biomaterial with various particle sizes (1.0 - 0.5 mm, 500 - 150  $\mu\text{m}$ , < 63  $\mu\text{m}$ ) into 250 mL conical flasks containing 50 mL of 100 mg/L synthetic  $\text{Cd}^{2+}$  solutions separately in triplicates. The blended mixture (1:1 ratio) was prepared by adding 0.75 g of each biomaterial. The initial pH of the solution was adjusted to 5 and the test solutions were agitated at a constant speed of 150 rpm in a shaker to attain equilibrium at a room temperature of  $25 \pm 2$  °C. The relevant test solutions were taken after 2, 4, 6, and 8 hours of agitation time and transferred into 50 mL centrifuge tubes and centrifuged at 4000 rpm for 20 minutes. Supernatant solutions were analyzed for  $\text{Cd}^{2+}$  availability using Atomic Absorption Spectrophotometer (AAS Model No. GBC 933AA) at 228.8 nm wavelength (standards-  $\text{Cd}(\text{NO}_3)_2$ ). The percentage removal efficiency was calculated using the following equation [11].

$$R (\%) = (C_0 - C_e) / C_0 \times 100 \dots \dots \dots (3)$$

where R is the percentage of  $\text{Cd}^{2+}$  adsorbed by biomass,  $C_0$  is the initial concentration of metal ions in  $\text{mg L}^{-1}$  and  $C_e$  is the concentration of metal ions at time t in  $\text{mg L}^{-1}$

The biomaterial samples, prior and after adsorption were collected and de-moisturized at 40 °C in a humidity control oven for 24 hours. The powder was analyzed by FT-IR (Bruker) by potassium bromide (KBr) pellet method at a wavenumber range of 400.00 – 4000.00  $\text{cm}^{-1}$ . Scanning electron microscope analysis was performed by coating the powder with an ultra-thin film of gold by an ion sputter (JFC-1100), exposed under SEM (JEOL, JX-8100) with voltage ranging from 10 to 25 kV. The X-ray diffraction of the biomass was analyzed (XRD-6000 Shimadzu) and recorded as a function of 2 $\theta$  at a scan speed of 1.2°  $\text{min}^{-1}$  and XRD patterns were recorded from 10° to 70°.

## 3. Results and Discussion

### 3.1 Physicochemical characterization of biomaterials

Rice husk [16] and clearing nut seeds [21] are chemically stable, have high mechanical strength, and are insoluble in water which makes suitability the best adsorbents for heavy metal removal [19]. Heavy metals can be treated using either modified or unmodified biomaterials. Pre-treating biomaterials boosted the adsorption capacity of heavy metals by lowering cellulose crystallinity, increasing surface area or porosity, and removing lignin and hemicelluloses [7]. Therefore, in this study, thermally treated RH and CN were used to evaluate the  $\text{Cd}^{2+}$  removal efficiency. The physicochemical properties of RH and CN on a dry basis are shown in table 1. Percentage moisture, ash & organic matter

contents of adsorbents are reported in the form of mean  $\pm$  standard deviation. The results revealed that the particle size had no significant effect on the physicochemical properties of biomaterials. Mean ash content was significantly higher ( $P < 0.05$ ) in RH for all particle sizes over CN. However, a significant difference was not observed between RH and CN in mean moisture content and organic matter content for all particle sizes.

**Table 1**  
Physico-chemical characterization of RH & CN

Sample Code	Particle Size	%MMC $\pm$ SD	%MAC $\pm$ SD	%MOMC $\pm$ SD
RH	(0.5-1.0) mm	6.37 $\pm$ 0.06 <sup>a</sup>	21.35 $\pm$ 0.59 <sup>a</sup>	72.27 $\pm$ 0.60 <sup>a</sup>
	(150-500) $\mu$ m	5.25 $\pm$ 0.03 <sup>a</sup>	19.02 $\pm$ 0.58 <sup>a</sup>	75.74 $\pm$ 0.60 <sup>a</sup>
	<63 $\mu$ m	4.95 $\pm$ 0.01 <sup>a</sup>	18.12 $\pm$ 1.17 <sup>a</sup>	76.92 $\pm$ 1.16 <sup>a</sup>
CN	(0.5-1.0) mm	9.04 $\pm$ 0.03 <sup>a</sup>	2.56 $\pm$ 0.83 <sup>b</sup>	88.40 $\pm$ 0.80 <sup>a</sup>
	(150-500) $\mu$ m	8.79 $\pm$ 0.17 <sup>a</sup>	2.20 $\pm$ 0.54 <sup>b</sup>	89.01 $\pm$ 0.72 <sup>a</sup>
	<63 $\mu$ m	8.45 $\pm$ 0.08 <sup>a</sup>	1.82 $\pm$ 0.31 <sup>b</sup>	89.73 $\pm$ 0.37 <sup>a</sup>

Mean Moisture Content (MMC), Mean Ash Content Mean Organic Matter Content. Content All values are means of triplicate determination  $\pm$  SD. Different letters in the same column showed statistical differences according to Tukey's test at  $P < 0.05$

### 3.2 XRF analysis

The mineral content RH and CN are given in table 2. Both biomaterials showed high SiO<sub>2</sub> contents over the other minerals. However, RH had very high SiO<sub>2</sub> content over CN whereas CN showed high MgO content over the RH.

**Table 2:** XRF analysis for the mineral contents of RH and CN

Component	Mineral Content (%)	
	RH	CN
SiO <sub>2</sub>	85.2 $\pm$ 2.17	53.4 $\pm$ 1.23
MgO	5.71 $\pm$ 0.32	26.3 $\pm$ 0.89
K <sub>2</sub> O	2.26 $\pm$ 0.43	8.84 $\pm$ 0.55
CaO	2.04 $\pm$ 0.12	6.07 $\pm$ 0.23
Al <sub>2</sub> O <sub>3</sub>	1.71 $\pm$ 0.08	1.67 $\pm$ 0.11
Fe <sub>2</sub> O <sub>3</sub>	1.41 $\pm$ 0.07	1.56 $\pm$ 0.17

### 3.3 Batch Biosorption studies

The analyzed results for the effect of particle size (0.5 - 1.0 mm, 150 - 500  $\mu$ m, < 63  $\mu$ m) and contact time in Cd<sup>2+</sup> removal conducted using thermally treated RH, CN and RHCN at varying contact time (2, 4, 6, 8 hours), pH (5), initial metal ion concentration (100 ppm), agitation speed (150 rpm), adsorbent dosage (1.5 g) and room temperature (25  $\pm$  2 °C) are given as a graphical view in Figure 1a-i respectively. The metal removal percentage increased with the decrement of the particle sizes for all the adsorbent types (Fig. 1a-c). All the adsorbent types showed variable metal removal percentages with time. The smaller particle size, in particular, provides a sufficient surface area for metal ion binding adsorption on biomass surfaces. It can be seen that

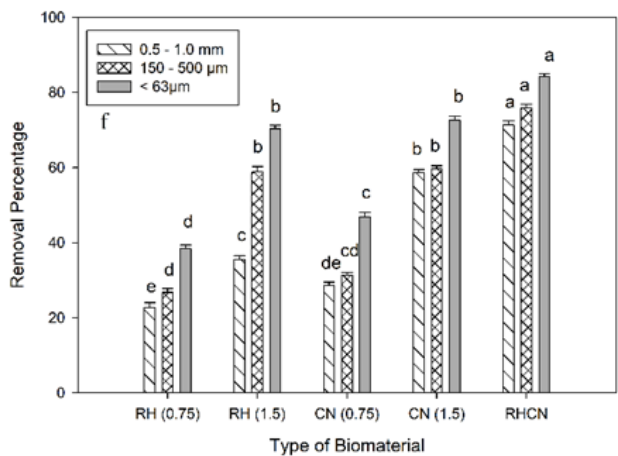
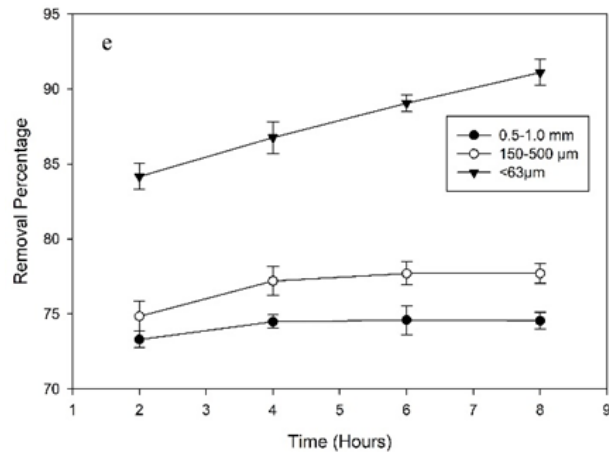
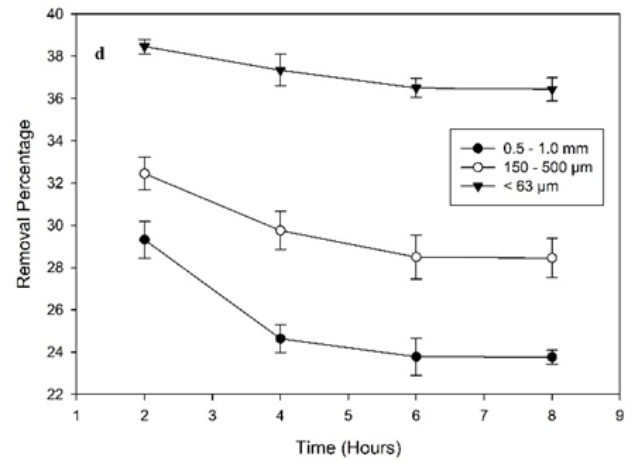
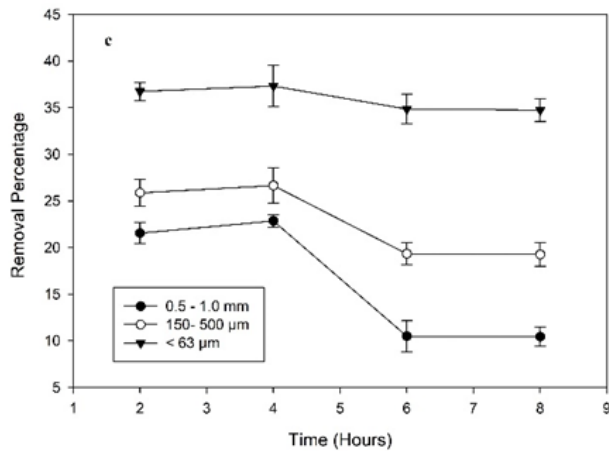
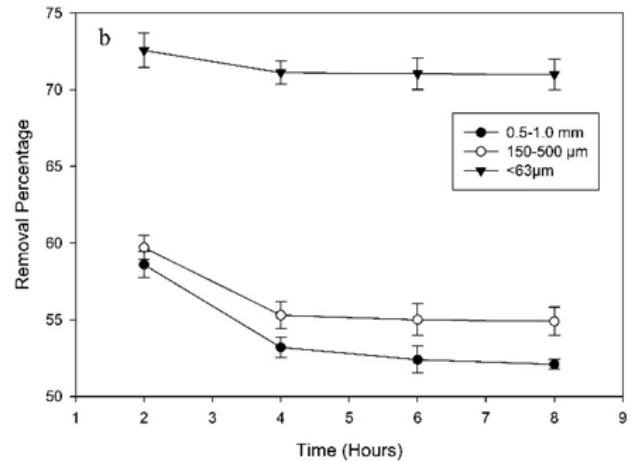
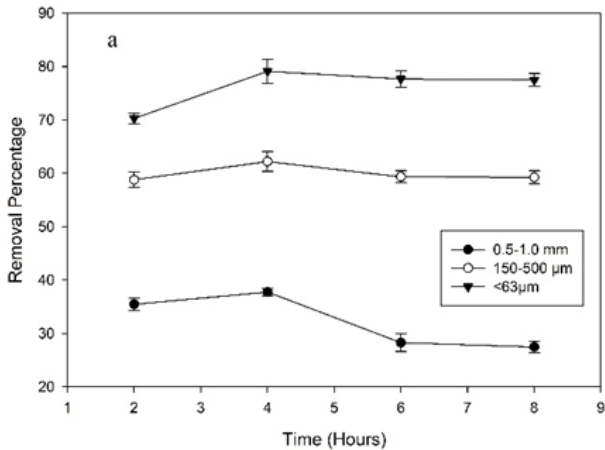
the surface area per volume is higher for small particles. As a result, the surface area increases the number of binding sites and contact surfaces, resulting in more mass transfer and faster sorption than when larger particles are used [10]. Ion-exchange capacities are heavily influenced by surface activity, specifically by the specific surface area available for solute-surface interaction that is accessible to the solute. As a result, the ion-exchange capacity of the adsorbent is projected to rise with increasing surface area [4]. The rate of exchange is typically governed by the rate of ion diffusion within the particle, which is proportional to particle size [15].

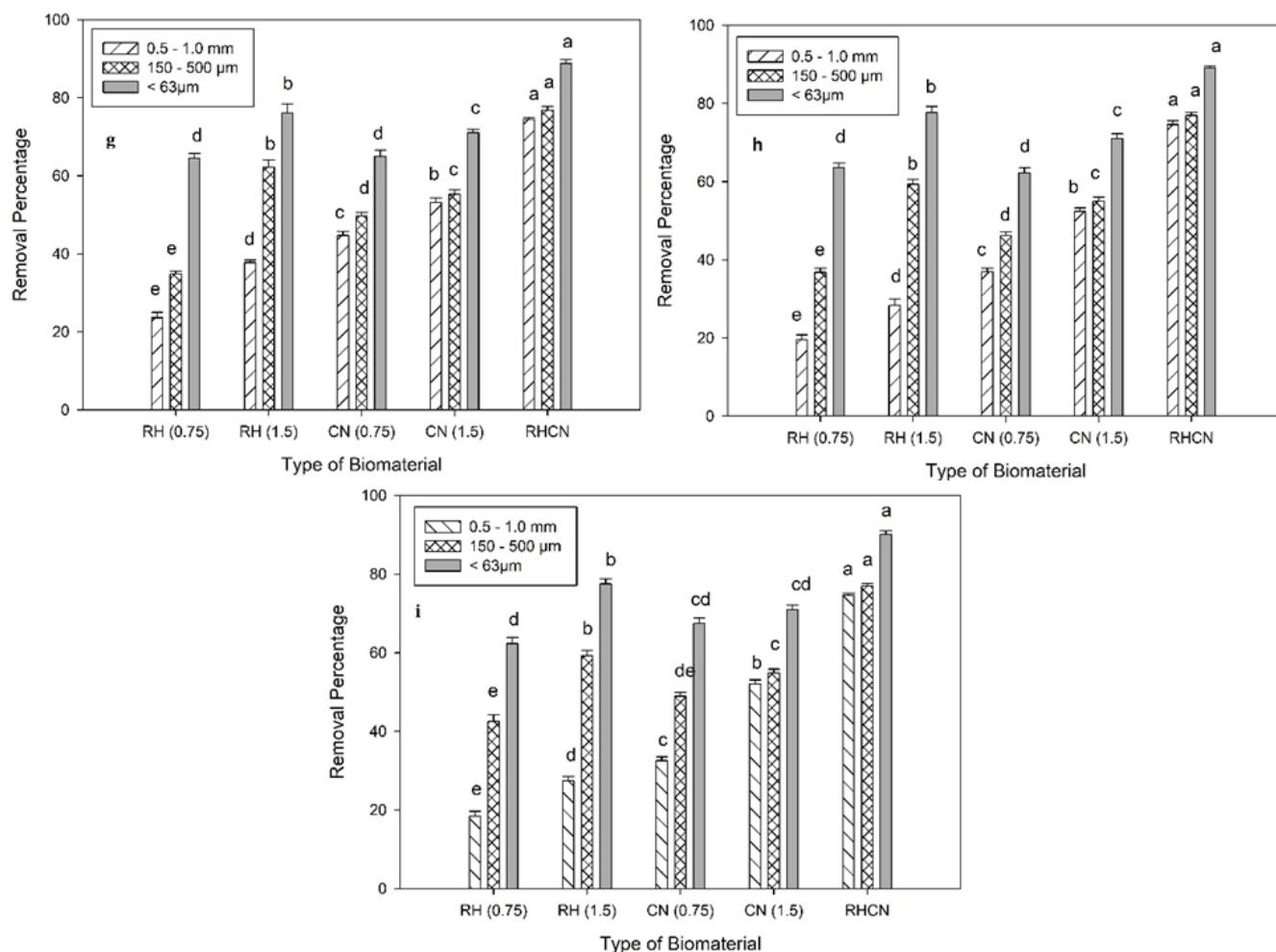
In the current study, the Cd<sup>2+</sup> uptake by all the particle sizes of RH and the combination type RHCN except for the particle size of < 63  $\mu$ m was faster at the initial stages (from 2 to 4 hours) of contact and showed a maximum at 4 hours. Subsequently, it slowed down and became constant after 6 hours as the reaction approached equilibrium (Fig. 1a, c and e). From 2 to 4 hours of contact time, a sharp increase of 12.6 % was observed in the particle size of < 63  $\mu$ m of RH with the incorporation of 1.5 g particles and recorded a maximum removal percentage of 22.23 % at 4 hours contact time. Similar pattern was observed in RH with the incorporation of 0.75 g particles showing a maximum removal percentage of 18.8 % at 4 hours contact time. However, all the particle sizes of CN behaved differently from RH in the removal of Cd<sup>2+</sup> ions (Fig. 1b and d). Irrespective of the particle sizes, CN showed a very high Cd<sup>2+</sup> uptake percentage at the initial (2 hours) contact time over RH. Subsequently, a sharp decrement was observed in metal uptake percentage by CN and after 4 hours of contact time it gradually declined and became constant (Fig. 1b). This pattern was observed in the CN with the incorporation of 0.75 g particles (Fig. 1. d). However, the metal removal percentages showed significant increment ( $P < 0.05$ ) with the increment of the initial number of particles at all time intervals in all particle sizes of RH and CN (Fig 1 a-d). A significant number of vacant sites are available in the early phases of contact; therefore, uptake is faster. The later stages' slowing and constant metal adsorption might be attributed to the difficulty in occupying the remaining vacant sites and being saturated with the available metal ions. [4]. The slowing of metal adsorption at equilibrium may also be due to repulsive interactions between the solute molecules on the adsorbent and in the aqueous solution (bulk phase) [2]. This may be the reason for showing a decrement in Cd<sup>2+</sup> uptake after a certain period by all the biomaterials. Generally, metal biosorption involves complex mechanisms of ion exchange, chelation, adsorption by physical forces, and ion entrapment in inter- and intra-fibrillar capillaries and spaces of the cell structural network of biosorbents [27].

At all periods, the combination type RHCN showed a high metal removal percentage and behaved differently from the other individual adsorbent types (Fig. 1e). Metal removal increased till 4 hours and then became constant for particle sizes of 150- 500  $\mu$ m and 0.5 - 1.0 mm. It's interesting to note that the metal removal percentage by RHCN with a

particle size of < 63 μm increased gradually over 8 hours (Fig. 1e). Further, the results revealed that the combined adsorbent type (0.75 g: 0.75 g combination of RH and CN) showed the highest significant metal removal percentage even over individual adsorbent types initially incorporated with 1.5 g of particles (Fig 1 a-b and e). The highest significant (P < 0.05) metal removal percentage was observed from the particle size of < 63 μm followed by the particle sizes of 150- 500 μm and 0.5 - 1.0 mm for all the adsorbent types (Fig. 1f-i). Furthermore, regardless of particle size and the amount of initial particles, the adsorbent type RHCN (1:1 ratio of RH and CN) had the most

significant (P < 0.05) metal removal percentage of all the adsorbent types at all time intervals. For RH (1.5 g), CN (1.5 g), and RHCN, the removal efficiency of Cd<sup>2+</sup> was enhanced by 98.27 %, 23.8 %, and 18 %, respectively, with the particle size being reduced from (0.5 - 1.0) mm to < 63 μm after two hours of agitation (Fig. 1.f). Similarly, after 8 hours of agitation, the removal efficiency of Cd<sup>2+</sup> was increased by 182.3 % for RH (1.5 g), 36.2 % for CN (1.5 g), and 15.5 % for RHCN by lowering particle size from (0.5 - 1.0) mm to < 63 μm (Fig. 1.i).





**Fig. 1** (a-e)-The metal removal percentages of adsorbent types with variable particle sizes at different contact periods a) Cd<sup>2+</sup> removal by RH with 1.5 g of particle amount with time, b) Cd<sup>2+</sup> removal by CN with 1.5 g of particle amount with time, c) Cd<sup>2+</sup> removal by RH with 0.75 g of particle amount with time, d) Cd<sup>2+</sup> removal by CN with 0.75 g of particle amount with time. Removal of Cd<sup>2+</sup> by adsorbent types at d) 2 hours, e) 4 hours f) 6 hours, g) 8 hours.

A similar metal removal efficiency pattern was observed from the other agitation time intervals (Fig. 1 g-h) and with variable amounts of particles. This confirms that the metal removal efficiency difference between the particle size of 0.5 - 1.0 mm and < 63 μm was low in RHCN over their biomaterials at all time intervals. Adsorption occurs mostly on the pore walls or at particular sites within the particle. The molecule becomes stronger on the surface of other materials due to differences in shape, molecular weight, or polarity, which facilitates separation. The total adsorption rate is determined by the solute diffusion rate in the capillary pores of the adsorbent [16]. This may be the reason for having different biosorption rates shown by different biomaterial combinations.

### 3.4 Characterization of Biomaterials

#### 3.4.1 FT-IR Characterization

The FTIR differences of spectra in pure plant biomass adsorbent of RH, CN and RHCN were qualitatively compared to the spectra obtained in Cd<sup>2+</sup> ion-treated biomaterials to determine whether the observed differences are due to the interaction of the metal ions with functional groups in the wave number range of 400- 4000 cm<sup>-1</sup> (Fig. 2a-c). FT-IR spectra of RH, CN and RHCN biomaterials before and after the biosorption indicated significant changes in the observed peaks. The differences in adsorption peaks of untreated biomass and Cd<sup>2+</sup> treated plant biomass explained the functional groups involved in the biosorption process. The intensities of all adsorption peaks showed a clear reduction in all Cd<sup>2+</sup> treated biomaterials over the untreated biomaterials (Fig- 2 a-c). The presence of a range of ionizable functional groups such as carboxyl, hydroxyl, and amine were confirmed by FTIR spectroscopic examination of the biomass, and these groups are implicated in practically all potential binding mechanisms. The FTIR spectra investigation revealed functional groups (carboxyl,

hydroxyl, and amino) that can interact with  $\text{Cd}^{2+}$  ions. Around  $3,600 - 3,100 \text{ cm}^{-1}$ , a broad absorption peak was observed with maximum absorption at  $3,297 \text{ cm}^{-1}$  (Fig 2 a). This peak indicates the presence of  $-\text{OH}$  stretching of cellulose [20,17], and was observed in the other two biomaterials showing the maximum absorption at  $3295 \text{ cm}^{-1}$  for CN and  $3293 \text{ cm}^{-1}$  for RHCN respectively (Fig. 2 a and b). The  $\text{CH}_2$  stretching vibrations showed characteristic absorption peaks at about  $2924.09 \text{ cm}^{-1}$ ,  $2919.40 \text{ cm}^{-1}$  and

$2920.89 \text{ cm}^{-1}$  for RH, CN and RHCN respectively. However, the intensity of the  $\text{CH}_2$  stretching peak was higher in CN in comparison with RH (Fig. 2b). Further, the peak shown in the range of  $2358 \text{ cm}^{-1}$ - $2359 \text{ cm}^{-1}$  indicates the C-O stretching in carbonyls and carboxylic acids in both materials [14].

However, the intensity of this peak was lower in RH in comparison with CN. Moreover, intense peaks indicating Si-O stretching [26] were observed at  $1035 \text{ cm}^{-1}$  for RH (Figure

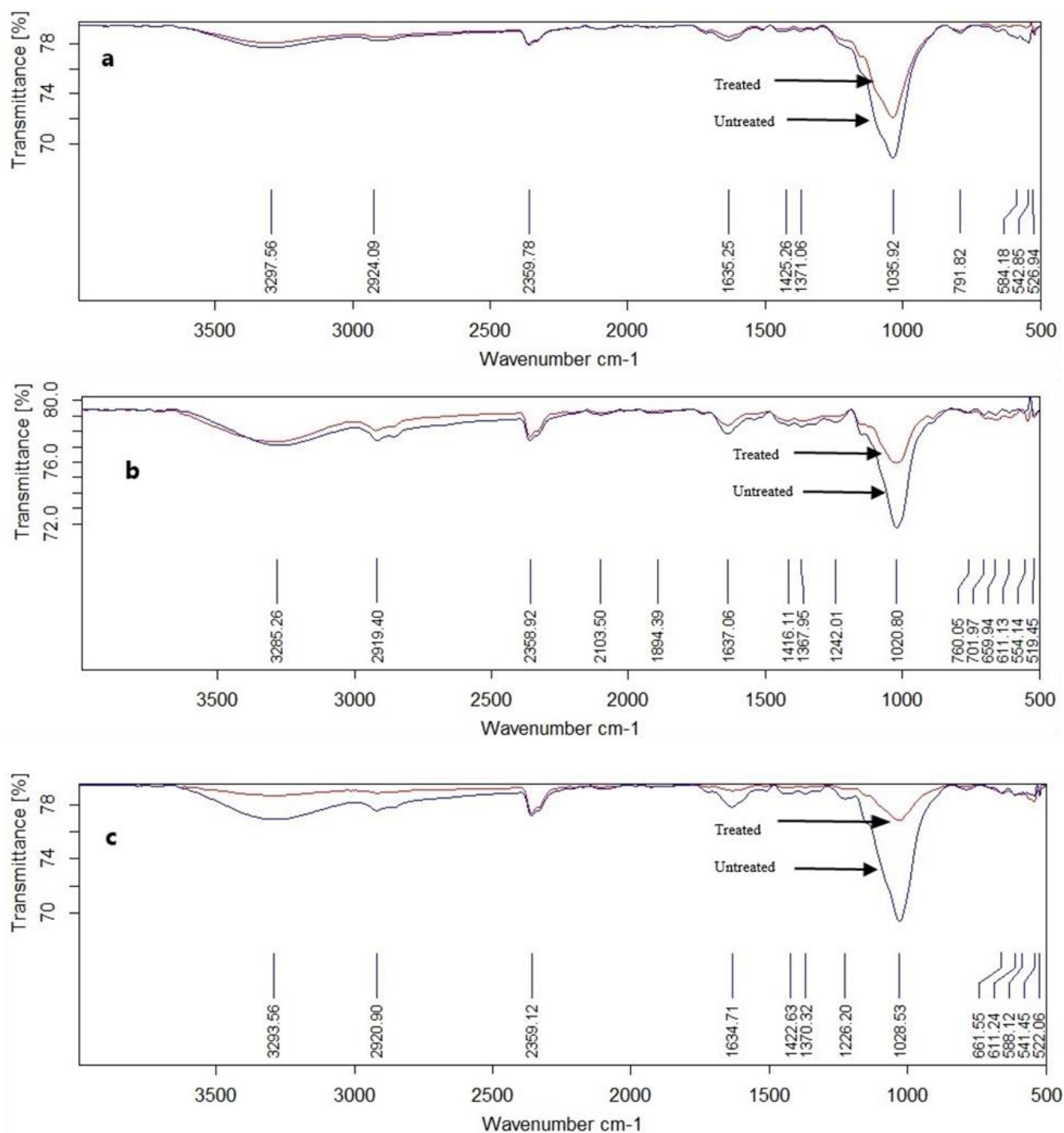


Fig. 2- FT-IR spectrum of  $\text{Cd}^{2+}$  treated and untreated biomaterials (a)  $\text{Cd}^{2+}$  treated and untreated RH, (b)  $\text{Cd}^{2+}$  treated and untreated CN, (c)  $\text{Cd}^{2+}$  treated and untreated RHCN

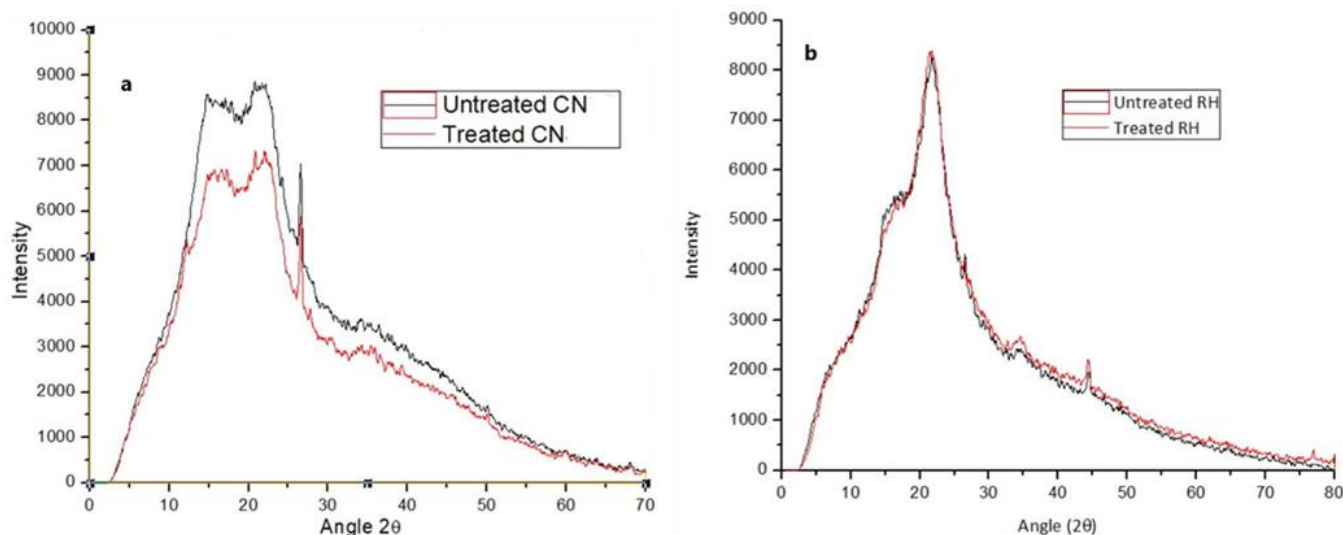


Fig. 3 - XRD analysis of Cd<sup>2+</sup> treated and untreated biomaterials. a) CN, b) RH.

2 a), at 1020 cm<sup>-1</sup> for CN (Figure 2b) and 1028 cm<sup>-1</sup> for RHCN (Figure 2c). In comparison to Cd<sup>2+</sup> untreated biomaterials, the FT-IR spectra of all treated biomaterials revealed a slight shift in the area of 1634– 522 cm<sup>-1</sup>. Qualitative analysis of FTIR peaks confirmed an intensity reduction in the peak obtained for cadmium-treated biomaterials around 1035 cm<sup>-1</sup> – 1020 cm<sup>-1</sup> in comparison with Cd<sup>2+</sup> untreated biomaterials in all spectra. This confirms that there is a reduction in peak intensities after the metal ion binding process (Fig. 1 a-c).

These peak intensity reductions were especially visible around 1010–1060 cm<sup>-1</sup>, 3293-3297 cm<sup>-1</sup> and 1200–1270 cm<sup>-1</sup>. Three characteristic absorption bands at 1200–1270 cm<sup>-1</sup>, 1010–1060 cm<sup>-1</sup> and 900–800 cm<sup>-1</sup>, corresponding to symmetric, asymmetric stretching of S=O and stretching of C-O-S, respectively, can be used to confirm the attachment of sulfonyl groups to polysaccharides [6]. Interestingly, the intensity reduction observed in the peak of 1028 cm<sup>-1</sup> for RHCN after Cd<sup>2+</sup> treatment was significantly higher than that of the other treated individual biomaterials (Fig. 2c). These results indicated the involvement of these functional groups in the biosorption process. The reduction in the above-mentioned peak intensities and shifting of peaks in both biomaterials (Figure 2b and 2d) after the treatment confirms the involvement of hydroxyl, Si-O and C-O in the adsorption of Cd<sup>2+</sup> ions by the adsorbent [23,21]. A series of small peaks were observed in the range of 791 cm<sup>-1</sup> to 519 cm<sup>-1</sup> in all spectra and the intensities of the peaks of that region were reduced in Cd<sup>2+</sup> treated biomass in comparison with metal untreated biomass. Further, absorption peaks observed at 791 cm<sup>-1</sup> for RH and 760 cm<sup>-1</sup> for CN were shifted in combined biomaterial type RHCN with the maximum absorption at 786 cm<sup>-1</sup>. The peak at 659.94 cm<sup>-1</sup> which was only available in CN, was observed in the combined type RHCN (661.55 cm<sup>-1</sup>) with a slight shift. The analysis of the FTIR spectra showed the presence of

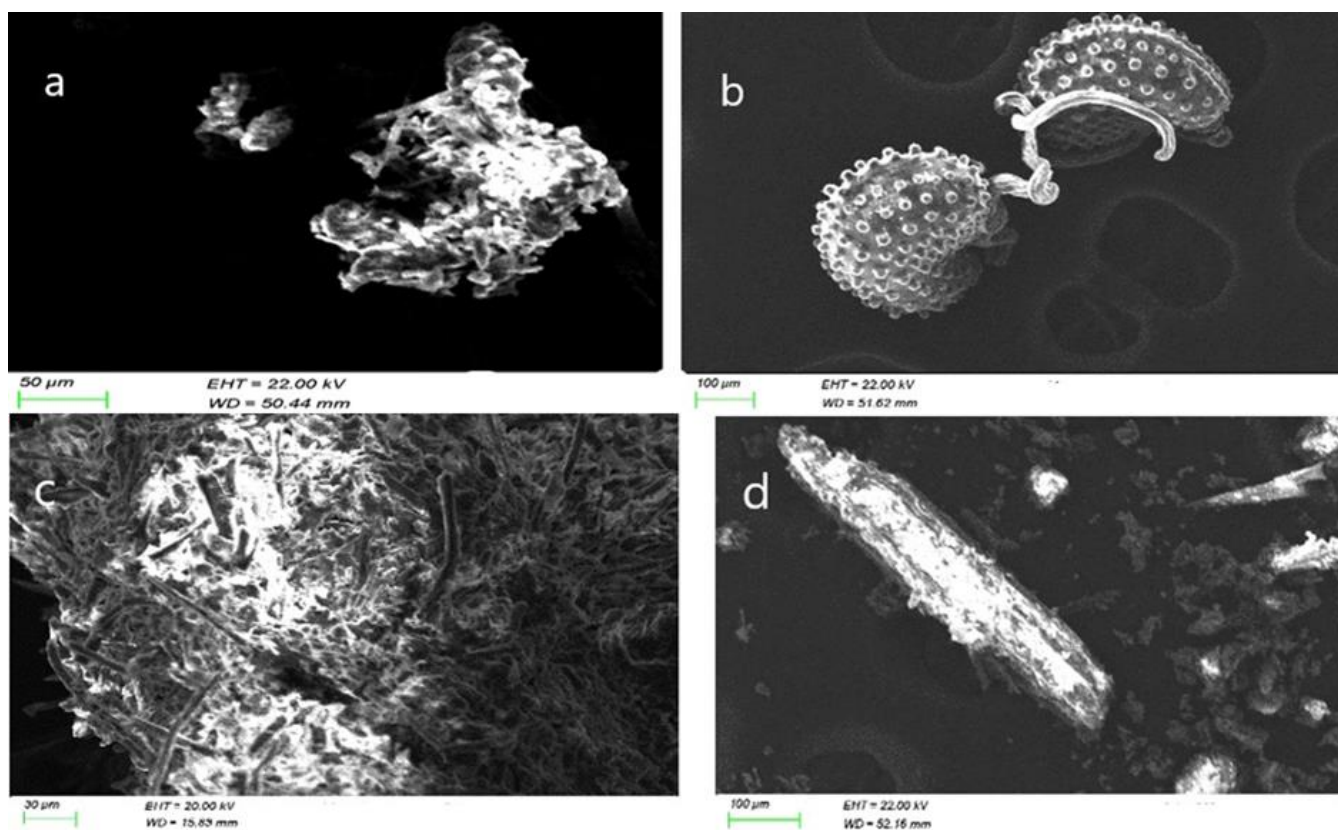
ionizable functional groups (i.e., carboxyl, hydroxyl and amino) that can interact with metal ions Cd<sup>2+</sup>.

### 3.4.2 XRD analysis

The diffracted X-ray intensities were recorded as a function of 2θ using a copper target, at a scan speed of 1.2 min<sup>-1</sup>. XRD patterns recorded from 10° to 70° for CN and RH before and after biosorption are depicted in Fig. 3a and b. The XRD spectra of both biomaterials before and after the biosorption revealed that both biomaterials are in amorphous nature indicating poor crystallinity. Further, the shifts in 2θ values were observed in Cd<sup>2+</sup> -loaded biomass in both biomaterials [1]. Further, the shift was more prominent in CN over RH.

### 3.4.3 SEM characterization

The SEM micrographs of RH and CN plant biomass before and after Cd<sup>2+</sup> biosorption are depicted in Figure 4. It is evident from analysis that the surface areas of plant biomass are uneven, and heterogeneous with pores on the surfaces. SEM images of native biomass (Fig. 4a and c) showed the number of pores with different pore areas. Further, pores facilitate the good possibility for metal ions to be adsorbed. This morphological pattern obtained by SEM reveals that both biomaterials are highly fibrous and contain a large active surface area. The SEM images of both biomaterials before and after the treatment confirm the changes in surface morphology after the treatment. Before the adsorption of Cd<sup>2+</sup>, uneven surface texture along with a lot of irregular surface format was observed. After adsorption, the particles have granular, complex, uneven and porous surface textures that were not found in the native biomass of RH and CN (Fig. 4 b and d).



**Fig. 4** - SEM analysis of Cd<sup>2+</sup> treated and untreated biomaterials. a) untreated RH (Mag = 5.00 K X), b) Cd<sup>2+</sup> treated RH (Mag = 5.00 K X), c) untreated CN (Mag = 1.00 K X), d) Cd<sup>2+</sup> treated CN (Mag = 1.00 K X)

#### 4. Conclusions

The 1:1 mixture of both rice husk powder and clearing nut seed powder is the most efficient agent for the removal of Cd<sup>2+</sup> from wastewater. The adsorption of Cd<sup>2+</sup> is highly influenced by the particle size and the initial amount of biomaterials. Better removal of Cd<sup>2+</sup> was observed for the particle size of < 63 µm for both biomaterials. This study revealed that the decrease in particle size causes an elevation in the removal efficiency of Cd<sup>2+</sup> due to the presence of a large surface area for biosorption. The FTIR analysis indicated the involvement of various functional groups in biomaterial in metal ion removal. The SEM analysis suggested that the adsorbent possesses an irregular surface structure with tiny pores on it, which could be related to the metal uptake by the adsorbent. However, further investigations should be carried out to identify the optimum conditions for the removal of Cd<sup>2+</sup> ions from aqueous solutions using different surface-modified RH and CN as adsorbents.

#### 5. References

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