

Cadmium Removal from Wastewater using Carbonaceous Adsorbents Prepared from Sunflower Waste

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ABSTRACT: This study reports the removal of cadmium from wastewater in batch mode, using two carbonaceous adsorbents viz. Sunflower Head Carbon (SHC) and Sunflower Stem Carbon (SSC) prepared from waste biomass of sunflower. The adsorbents were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDX). The results of batch experiment showed that the cadmium removal was dependent on pH, Cd(II) ion concentration, adsorbent dose, contact time and temperature. The highest cadmium adsorption was found at pH = 6.0, initial Cd(II) concentration = 100 mg/L, adsorbent dose = 20 g/L, contact time = 120 min at temperature = 25±1 °C and at 180 rpm. Langmuir and Freundlich isotherm models were applied and Freundlich model was found to fit the data well. The Freundlich adsorption capacity was 1.22 and 1.48 mg/g by SHC and SSC. The kinetic data was well described by pseudo-second-order model with coefficient of correlation 0.9978 for SHC and 0.9981 for SSC. The adsorption process was found to be endothermic in nature. The adsorbents were desorbed using different strengths of HCl ranging from 12.5 mM to 200 mM. The highest desorption efficiency i.e. 55.6 and 52.6% from SHC and SSC was found at 125 mM.

Key words: Cadmium, Adsorption, Chemical activation, Agricultural waste, Sulphuric acid

INTRODUCTION

Heavy metals are the center of attraction for scientific community due to their toxicity (Volesky, 1994). Among them, cadmium is a major threat to public health and environment due to its solubility over a wide range of pH and presence in various industrial wastewaters. The Department of Environment, UK has included cadmium in the red list of priority pollutants (UK red list substances, 1991) and the black list of EEC Dangerous Substances Directive (EEC black list substances, 1976). Cadmium has been categorized as group B1 carcinogen by USEPA (USEPA, 1999). Adsorption process is considered as an effective and sustainable technology for the removal of heavy metals and dyes from industrial effluents over the last few decades and activated carbon has been commercialized

as an ideal adsorbent for this process. However, due to its high cost, it is not conventionally accepted in developing countries. Therefore, emphasis has been laid on searching low cost biomaterials which are locally available and easy to be used as precursors for making biosorbents. In this regard, agricultural biomass has been found to be economically viable, highly competent, easy to handle and environment friendly raw material (Saeed *et al.*, 2009; Evans *et al.*, 1999).

Several agricultural wastes including peanut hull (Wilson *et al.*, 2006), rice bran (Ranjan & Hasan, 2010), sunflower oil cake (Karagoz *et al.*, 2008), sugarcane bagasse pith (Krishnan & Anirudhan, 2003), neem oil cake (Hema & Srinivasan, 2010), jack fruit peel (Inbaraj & Sulochana, 2004), *Cieba pentandra* hull (Rao *et al.*, 2008), coconut shell carbon (Amuda *et al.*, 2007),

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tamarind wood (Singh *et al.*, 2008), orange peel (Lasheen *et al.*, 2012), *Strychnos potatorum* (Saif *et al.*, 2012), citrus peels (Njikam and Schiewer, 2012), rice straw (Ding *et al.*, 2012), *Tectona grandis* (Rao *et al.*, 2010) etc. have been converted into activated carbon (AC) using sulphuric acid treatment and used for heavy metals removal from wastewater. The results of these studies have shown that activated carbons produced by this method have more adsorption capacity than unmodified adsorbents. Keeping this in view, sunflower stems and their deseeded heads were used to prepare the adsorbents as they have neither commercial value nor used as fodder for livestock. In this study, two adsorbents namely, Sunflower Head Carbon (SHC) and Sunflower Stem Carbon (SSC) were prepared, characterized and tested for their cadmium adsorption efficiency from aqueous medium.

MATERIALS & METHODS

The adsorbents were prepared as reported by Jain *et al.* (2010). The deseeded flower heads and stems of sunflower (*Helianthus annuus*) were collected directly from the agricultural fields. The heads and stems were milled separately into fine powder and were mixed with concentrated H_2SO_4 in the ratio of 2:1 (H_2SO_4 : sunflower, v/w) and carbonized at 150 °C in hot air oven for 24h. The charred material was repeatedly washed with deionized water until excess acid was removed and finally soaked in 2% Na_2HCO_3 (w/v) overnight to remove any residual acid from the material. The adsorbent was washed with deionized water several times and dried in hot air oven at 105°C for 8h. The adsorbent obtained was sieved from standard sieve (ASTM No. 50, I.S.S. No. 30) to get the particle

size of d”300 micrometers. The prepared adsorbents were stored in air tight plastic containers for further use. The adsorbents prepared from Sunflower Head and Sunflower Stem were designated as SHC and SSC respectively.

The adsorbents were characterized for various physico-chemical properties, viz., bulk density, water soluble content, acid soluble content, moisture content, ash content, conductivity, decolorizing power according to standard methods. C, H, N, S and O were determined using Thermo CHNSO Elemental Analyzer System (Flash, EA, 1112 series, Italy). The surface area of the adsorbents was measured using BET nitrogen adsorption – desorption method (Micromeritics, model ASAP-2010, Japan). The pH_{zpc} was determined as reported by Nomanbhay & Palanisamy (2005). The physico-chemical characteristics of the adsorbents are given in Table 1.

The surface characterization of the adsorbents was done using Fourier Transform Infrared Spectroscopy (FTIR) (model Perkin Elmer, Spectrum BX), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). The functional groups on the surface of adsorbents were determined in the range of 4000-400/cm of used and unused adsorbents. The surface morphology and texture of the adsorbents was determined using SEM technique at 1500x magnification along with EDS (model Quanta 200 EFG, FEI, Netherlands). In each adsorption experiment, a known quantity of the adsorbent @ 4.0 – 24.0 g/L was added to 50 mL of Cd(II) aqueous solution of predetermined concentration (5-500 mg/L) and pH (2.0 - 7.0) at 25 ± 1 °C and was shaken at 180 rpm in a thermostatic orbital shaker for 180 min. After that, the adsorbents were

Table 1. Physico-chemical characteristics of Sunflower Head Carbon (SHC) and Sunflower Stem Carbon (SSC)

Parameters	SHC	SSC
pH	3.7	4.1
pH_{zpc}	3.8	4.2
Electrical conductivity ($\mu S/cm$)	434.8	363.4
Moisture content (%)	2.5	2.8
Ash (%)	4.2	3.8
Bulk density (g/cc)	0.810	0.616
Solubility in water (%)	2.3	1.8
Solubility in acid (%)	10.3	8.3
Decolourizing power (mg/g)	85	90
Particle size (μm)	300	300
BET surface area (m^2/g)	2.5577	2.6622
Cation Exchange Capacity (meq/g)	70.9	98.0
<i>Elemental Analysis (%)</i>		
C	51	44
H	3.1	2.8
N	-	8.5
S	-	-
O	45.9	44.7

separated from the mixture by centrifugation. The residual Cd(II) concentration in the supernatant was determined using Atomic Absorption Spectrophotometer (Shimadzu AA 6300, Japan). All the experiments were conducted in triplicate and the results were averaged. The percent cadmium removal (*R* %) was calculated using equation 1.

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

Where *C_i* and *C_e* were the initial and residual concentration of metal ion in mg/L. The metal uptake capacity *q_e* (mg/g) for each Cd(II) concentration at equilibrium was determined using equation 2.

$$q_e \text{ (mg/g)} = \left[\frac{C_i - C_e}{M} \right] \times V \quad (2)$$

where, *C_i* and *C_e* are same as in equation (1), *V* is the volume of the solution in L and *M* is the mass of the dry adsorbent (g).

RESULTS & DISCUSSION

The physico-chemical characteristics of the adsorbents are given in Table 1. The result of elemental analysis revealed that the adsorbents were mainly composed of carbon, hydrogen and oxygen. The surface area of SHC and SSC was 2.55 and 2.66 m²/g respectively (Table 1).

The FT-IR spectra, the corresponding frequencies and the functional groups of native and cadmium loaded SHC and SSC are given in Table 2. The broad band in the region of 3494.77 - 3240.19/cm may be due to -O×H stretching in hydroxyl, carboxyl, phenolic, alcoholic and -N-H group. The presence of NH₂ was verified by -N-H bending at 1569.95/cm in native SHC and at 1517.87/cm in native SSC. The peaks were shifted to 1512.09/cm in exhausted SHC and to 1510.10/cm in exhausted SSC. The band at 2948.96/cm, 1382.87/cm and 1346.22/cm in native SHC and 1317.29/cm in native

SSC indicated the presence of -C-H vibrations in -CH₂ or -C=C×H group (methyl or methylene group). The peak got shifted to 2930.42 and 1312.18/cm SHC and SSC-Cd loaded. The peak located at 1743.53/cm is characteristic of carbonyl group (-C=O) stretching from aldehydes and ketones. The band at 1122.49/cm indicates the presence of secondary hydroxyl group. The peak at 1008.70 and 1018.34/cm in SHC native and SHC-Cd loaded and 1003.64 and 1020.21/cm in SSC native and SSC-Cd loaded is due to -C-O of ether group. The peaks in the Cd(II) loaded adsorbents got shifted indicating the binding of Cd(II) ions with various functional groups.

The surface morphology of SHC and SSC was observed by Scanning Electron Microscopy (SEM). SEM images of the pristine and Cd(II) loaded adsorbents are given in Fig. 1A-D. The images revealed that the surface texture is uneven and irregular. After the adsorption of cadmium, the bright flakes of cadmium are visible on the surface of the adsorbents.

The presence of cadmium was also confirmed by Energy Dispersive X-Ray Analysis (EDX). The EDX images of pristine and Cd(II) loaded activated carbons are shown in Fig. 2A-D.

The effect of pH on Cd(II) adsorption was studied in the pH range of 2.0 - 7.0, keeping initial Cd(II) concentration = 100 mg/L and adsorbent dose = 20.0 g/L at a stirring speed of 180 rpm and temperature of 25±1°C for a contact period of 180 min. The effect of pH onto studied adsorbents for Cd(II) adsorption is depicted in Fig. 3(a). A control was also run for Cd(II) removal without any adsorbent to quantify any adsorption on the container. The results of control experiment (without adsorbent) indicated that there was no removal of Cd(II) up to pH 7.0, but when the pH was >7.0, Cd(II) precipitated as cadmium hydroxide in the solution leading to Cd(II) removal from the solution. Keeping this in view, the adsorption studies were undertaken in the pH range of 2.0 to 7.0.

Table 2. Fundamental FTIR frequencies of Native and Cd(II) loaded Sunflower Head Carbon (SHC) and Sunflower Stem Carbon (SSC)

Adsorbents (Native and Cadmium loaded)	Fundamental frequencies (1/cm)				
	-OH/N-H	-C-H	-C=O	-OCH ₃ /-C-N	Bending vibrations
SHC (Native)	3494.77-3240.19	2948.96	1743.53	1122.49, 1008.70	763.76, 536.17, 491.21
SHC-Cd(II)	3492.26-3238.46	2930.42	1740.67	1120.32, 1003.64	572.82, 480.24, 418.42
SSC (Native)	3429.20-3296.05	2896.88	1677.95	1199.64, 1018.34	472.53, 420.45
SSC- Cd(II)	3425.16-3288.2	2997.29	1764.75	1126.35, 1020.21	667.32, 416.60

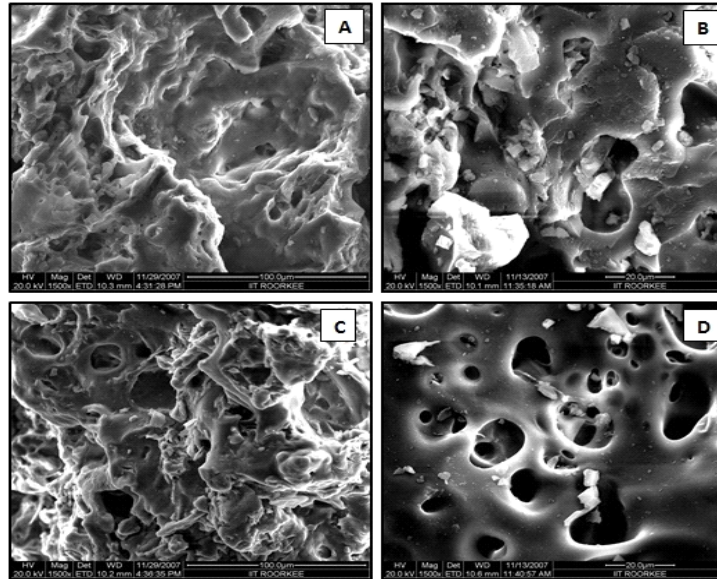


Fig. 1. SEM of (A) Native SHC (B) Cd(II) loaded SHC (C) Native SSC and (D) Cd(II) loaded SSC

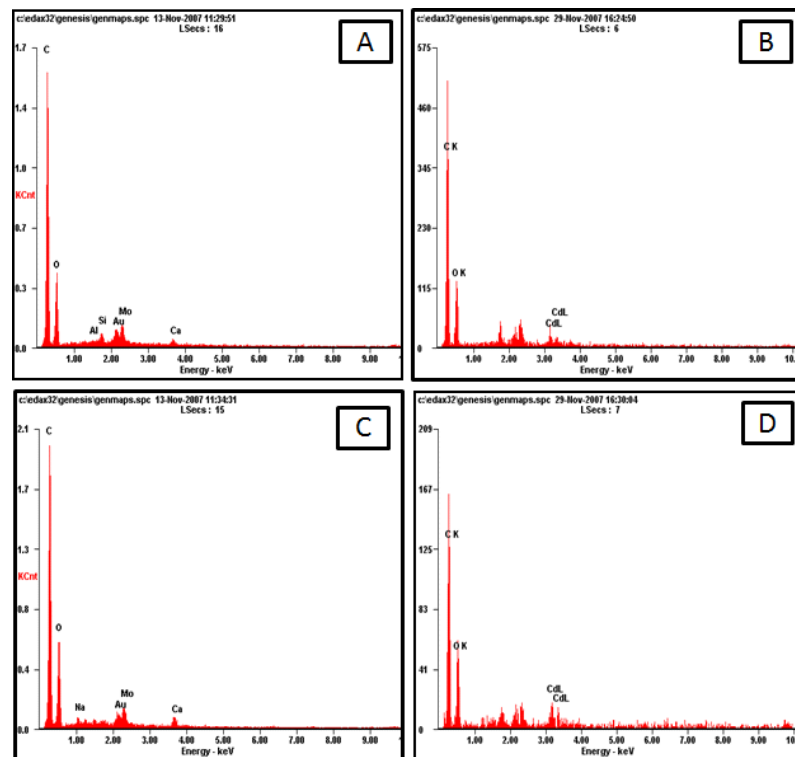


Fig. 2. EDX of (A) Native SHC (B) Cd(II) loaded SHC (C) Native SSC and (D) Cd(II) loaded SSC

The nature of the adsorbent and the speciation of metal ions in the aqueous solution play an important role in the adsorption of metal ions. In deionized water, cadmium exists as Cd^{2+} , $\text{Cd}(\text{OH})^+$, $\text{Cd}(\text{OH})$ and $\text{Cd}(\text{OH})_2(\text{s})$ (Garg *et al.*, 2008). Leyva-Ramos *et al.*, (1997) reported that, if pH of the solution is lesser than

7.0, Cd^{2+} is the predominant ionic species but it is precipitated as $\text{Cd}(\text{OH})_2$ at higher pH. At pH 8.0, 90% cadmium exists as Cd^{2+} and remaining as $\text{Cd}(\text{OH})^+$.

It is evident from Fig. 3(a) that the percent adsorption of cadmium increased with the increase in pH and became maximum at pH 6.0. All the further

Table 3. Adsorption capacity of Sunflower Head Carbon (SHC) and Sunflower Stem Carbon (SSC) at different initial Cd(II) concentration and doses

Initial Cd(II) conc. (mg/L)	Adsorption capacity [q_e (mg/g)]	
	SHC	SSC
5	0.3	0.3
10	0.5	0.5
25	1.2	1.2
50	2.4	2.4
75	3.3	3.4
100	4.3	4.4
200	7.6	3.0
250	8.8	9.6
500	15.8	17.3
Adsorbent dose (g/L)	Adsorption capacity [q_e (mg/g)]	
	SHC	SSC
4.0	16.0	17.0
8.0	8.7	9.1
12.0	6.2	6.6
16.0	5.0	5.1
20.0	4.3	4.4
24.0	3.6	3.7

experiments were carried out at pH 6.0. The percent adsorption of Cd(II) increased from 60.4 - 84.7% and 64.5 - 87.1% respectively onto SHC and SSC as pH was increased from 2.0 - 6.0. This phenomenon can be explained on the basis of pH_{zpc} . The surface of the adsorbent is negative if $pH > pH_{zpc}$, it is positive, if $pH < pH_{zpc}$ and neutral if $pH = pH_{zpc}$ (Leyva-Ramos *et al.*, 2005). So, in the present study, as the pH was greater than pH_{zpc} i.e. pH was 6.0 and pH_{zpc} was 3.8 and 4.2 for SHC and SSC respectively (Table 1), therefore, the surface of the adsorbent was found to be negative thus increasing the percent removal with the increase in pH due to electrostatic attraction between cadmium ions in the solution and the surface of the adsorbent. The adsorption capacity of SHC increased from 3.0 to 4.3 mg/g while that of SSC increased from 3.2 to 4.4 mg/g as pH increased from 2.0 - 6.0. Maximum adsorption capacity for the adsorbents was at pH 6.0.

The effect of Cd(II) concentration on its removal was studied at pH = 6.0, adsorbent dose = 20.0 g/L, stirring speed = 180 rpm, contact time = 180 min, temperature = 25 ± 1 °C by varying initial Cd(II) concentration from 5.0 - 500 mg/L. The results are given in Fig. 3(b). The data shows that the percent Cd(II) adsorption decreased with the increase in Cd(II) concentration. The percent removal by SHC and SSC decreased from 99.2 - 63.1% and 99.7 - 69.1% respectively when Cd(II) concentration was increased from 5.0 - 500 mg/L. This may be due to the fact that, at low initial concentration, the numbers of adsorption sites are more thus leading to an increased removal of cadmium ions. While at higher concentration, almost all the binding sites are filled and no site is available

for further adsorption of Cd(II) ions thus leading to a decrease in percentage removal (El-Latif *et al.*, 2013). Similar results have been reported by Zheng *et al.*, (2008) who have also reported that the percent Cd(II) adsorption decreases with the increase in Cd(II) ion concentration. The adsorption capacity of the adsorbents increased with the increase in initial Cd(II) concentration (Table 3). Adsorption capacities of SHC and SSC for Cd(II) increased from 0.3 - 15.8 mg/g and 0.3 - 17.3 mg/g respectively. This may be due to the increase in driving force of cadmium ions for mass transfer at higher initial cadmium concentration which leads to increase in number of collisions among metal ions and the surface of adsorbent thus increasing the adsorption capacity with increase in initial cadmium concentration (Taty-Costodes *et al.*, 2003).

The effect of adsorbent dose on Cd(II) removal was studied at constant temperature (25 ± 1 °C) and stirring speed (180 rpm) by varying the adsorbent dose from 0.2 g/50 mL - 1.2 g/50 mL keeping the volume of solution = 50 mL and initial Cd(II) concentration = 100 mg/L at pH = 6.0. The results so obtained are depicted in Fig. 3(c). The results showed that Cd(II) adsorption increased from 64.3 - 85.5% and 67.8 - 88.8% by SHC and SSC respectively with the increase in adsorbent dose from 0.2 g/50mL to 1.2 g/50mL. The increase in percent removal with increase in adsorbent dose may be due to increase in number of active sites and surface area for adsorption of more and more ions (Oliviera *et al.*, 2008). The adsorption capacity of SHC and SSC decreased with the increase in adsorbent dose from 0.2 g/50 mL to 1.2 g/50 mL

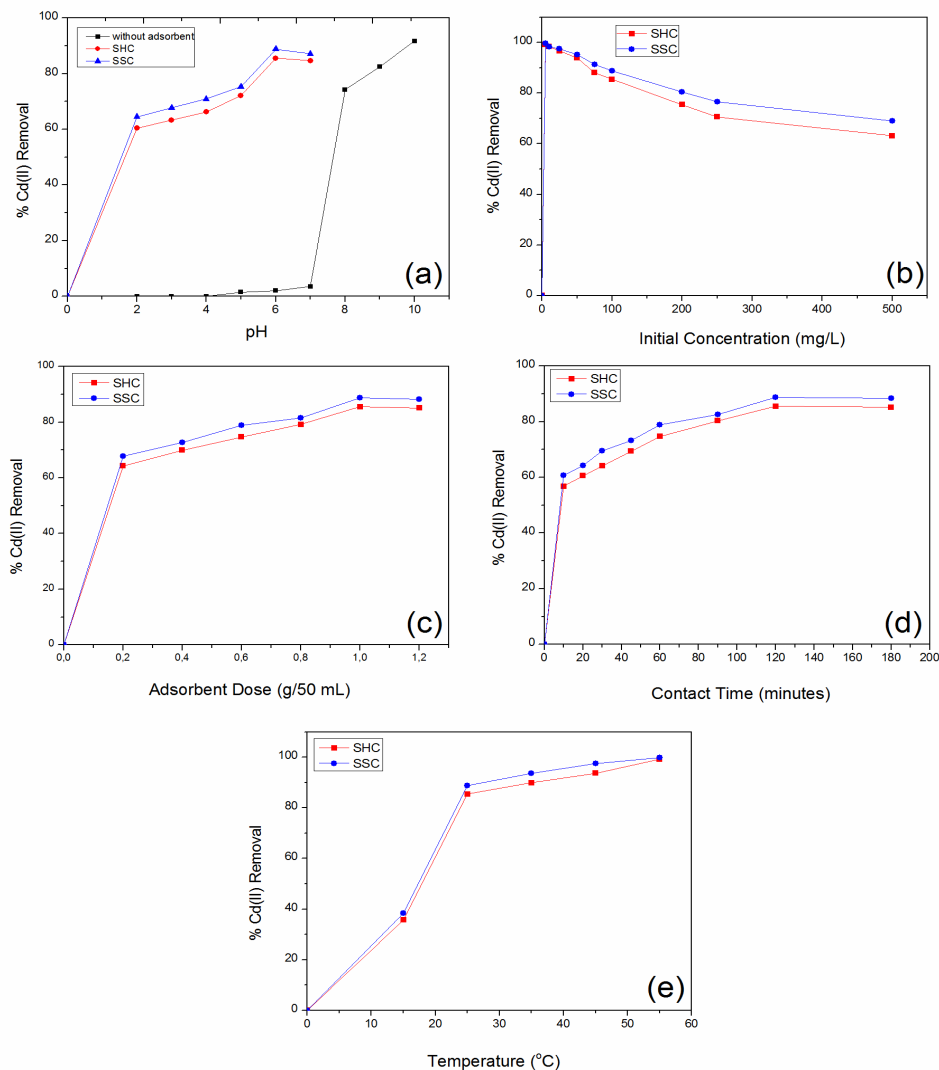


Fig. 3. Cd(II) sorption by SHC and SSC at different process parameters .

- a) Effect of pH- Initial Cd(II) concentration = 100 mg/L, dose = 20 g/L, temperature = 25 ± 1 °C, contact time = 180 min and stirring speed = 180 rpm
- (b) Effect of initial Cd(II) concentration - pH = 6.0, adsorbent dose = 20 g/L, temperature = 25 ± 1 °C, contact time = 180 min and stirring speed = 180 rpm
- (c) Effect of adsorbent dose - pH = 6.0, Initial Cd(II) concentration = 100 mg/L, temperature = 25 ± 1 °C, contact time = 180 min and stirring speed = 180 rpm
- (d) Effect of contact time - pH = 6.0, Initial Cd(II) concentration = 100 mg/L, adsorbent dose = 20 g/L, temperature = 25 ± 1 °C, and stirring speed = 180 rpm
- (e) Temperature - pH = 6.0, Initial Cd(II) concentration = 100 mg/L, adsorbent dose = 20 g/L, contact time = 180 min and stirring speed = 180 rpm

(Table 3). Adsorption capacities decreased from 16.1 - 4.3 mg/g and 16.9 - 4.4 mg/g respectively. This may be due to the saturation of adsorption sites of the adsorbents in the early stages (Sari and Tuzen, 2008). A list of adsorption capacities of some of the adsorbents reported by different researchers is given in Table 4 and the results of the present study are comparable with the available literature. The rate of Cd(II) removal was determined by taking 1.0 g of each of the adsorbent in 50 mL of 100 mg/L metal solution for different time intervals from 10 to 180 min at a

constant pH = 6.0, stirring speed = 180 rpm and temperature = 25 ± 1 °C. The results so obtained are depicted in Fig. 3(d). The results showed that the adsorption of Cd(II) increased with the increase in contact time from 10 to 120 min for fixed Cd(II) concentration and sorbent dose in the system. The adsorption equilibrium was achieved within 120 min as maximum Cd(II) removal i.e. 85.5% by SHC was achieved within this contact time after which it became constant and there was no further Cd(II) adsorption. Similarly, the adsorption equilibrium was achieved

Table 4. Adsorption capacity (mg/g) of various adsorbents for Cd(II) adsorption

Adsorbent	Adsorption capacity (mg/g)	Reference
<i>P. hysterophorus</i> weed	35.8	Ajmalet <i>et al.</i> ,2006
Pomelo peel	21.8	Saikaew <i>et al.</i> ,2009
NaOH Treated Rice Husk	20.2	Kumar & Bandyopadhyay, 2006
Waste Chinese herb	17.5	Liu <i>et al.</i> , 2006
<i>Eucalyptus</i> bark	14.5	Ghodbane <i>et al.</i> , 2008
Chemically modified orange peel	13.7	Lasheen <i>et al.</i> , 2012
<i>Mischanthus sacchariflorus</i>	13.24	Kim <i>et al.</i> ,2013
<i>Areca catechu</i> heartwood powder	10.7	Chakravarty <i>et al.</i> ,2010
Rice polish	9.7	Singh <i>et al.</i> ,2005
Sludge of Nishino DWTP	9.2	Siswoyo, <i>et al.</i> , 2014
Olive stone	6.9	Blazquez <i>et al.</i> ,2005
Sugarcane bagasse	6.9	Ibrahim <i>et al.</i> , 2006
Sludge of Miyamchi DWTP	5.3	Siswoyo, <i>et al.</i> , 2014
Coconut copra meal	4.9	Ho & Ofomaja, 2006
SSC	4.4	Present study
SHC	4.3	Present study
Maize com cob	2.5	Garg <i>et al.</i> ,2008
Jatropha Oil Cake	2.5	Garg <i>et al.</i> ,2008
Sugarcane bagasse	2.4	Garg <i>et al.</i> ,2008
<i>Withania frutescens</i> plant	0.002	Chiban <i>et al.</i> , 2012

within 120 min for SSC with a percent removal of 88.8%. The results showed that the adsorption was faster in early stages which may be due to availability of large number of vacant sites for adsorption of Cd(II) ions.

The effect of temperature on Cd(II) adsorption by SHC and SSC is given in Fig. 3(e). The adsorption of Cd(II) by SHC and SSC increased from 35.7 - 99.2% and 38.3 - 99.9% respectively with the increase in temperature from 15 °C to 55 °C. The adsorption capacity also increased with increase in temperature from 15 °C to 55 °C. It increased from 1.8 to 4.9 mg/g for SHC and 1.9 to 4.9 mg/g for SSC. It can be inferred from the results that the Cd(II) adsorption by SHC and SSC was endothermic in nature. The increase in percent removal with the increase in temperature may be due to the increase in number of active sites due to bond rupture at higher temperature (Fan *et al.*, 2008). Since, the adsorption is endothermic in nature, the amount of Cd(II) adsorbed at equilibrium increased with the increasing temperature.

The adsorption data were analyzed using Langmuir and Freundlich isotherm models given in equation 3 and 4 respectively:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (3)$$

$$\log_{10} q_e = \log_{10} (K_f) + \left(\frac{1}{n}\right) \log_{10} (C_e) \quad (4)$$

Where C_e and q_e have already been explained in section 2.3. Q_0 (mg/g) is the maximum Langmuir

adsorption capacity and b (L/mg) is the Langmuir constant related to free energy. The Langmuir constants Q_0 and b were calculated from the slope and intercept of the Langmuir plot of C_e versus C_e/q_e (Table 5). The maximum adsorption capacity (Q_0) was found to be higher for SSC i.e. 17.6 mg/g, while it was 15.95 mg/g for SHC. The coefficient of correlation, R^2 , for Langmuir isotherm was 0.8798 and 0.8821 for SHC and SSC respectively (Table 5). The Langmuir separation factor (R_L) which is a dimensionless constant indicates whether the adsorption process is favorable or not. R_L was calculated for the studied adsorbents using equation 5:

$$R_L = \frac{1}{1 + bC_i} \quad (5)$$

where, b and C_i (mg/L) have already been mentioned. The criterion for favorable adsorption was chosen on the basis of R_L values. If R_L values are greater than 1.0, adsorption is unfavorable, if R_L values are equal to 1.0, adsorption is linear, if R_L values are between 0 and 1, adsorption is favorable and if R_L values are equal to 0, adsorption is irreversible. For the present system, the R_L values were between 0 and 1 (0.04 - 0.834) for both the adsorbents indicating the favorable adsorption of Cd(II) onto the studied adsorbents.

According to Freundlich model, K_f (mg/g) is the Freundlich adsorption capacity related to binding energy of the adsorbent whereas n is the Freundlich constant called function of strength of the adsorption process. The Freundlich constants K_f and n were

Table 5. Langmuir and Freundlich isotherm constants and R^2 for adsorption of Cd(II) onto Sunflower Head Carbon (SHC) and Sunflower Stem Carbon (SSC)

Adsorbent	Langmuir Parameters			Freundlich Parameters		
	Q_o (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n (L/mg)	R^2
SHC	15.95	0.04	0.88	1.22	2.09	0.9973
SSC	17.61	0.05	0.88	1.48	2.14	0.9919

Q_o : Langmuir adsorption capacity, K_f : Freundlich adsorption capacity, b : Langmuir constant, n : Freundlich constant, R^2 : Coefficient of Correlation

Table 6. Kinetic model parameters for Cd(II) adsorption onto Sunflower Head Carbon (SHC) and Sunflower Stem Carbon (SSC)

Adsorbent	q_e (exp) (mg/g)	q_e (cal) (mg/g)	K_1 (1/min)	R^2	q_e (exp) (mg/g)	q_e (cal) (mg/g)	K_2 (g/mg/min)	R^2
SHC	4.28	2.25	0.0221	0.7131	4.28	4.51	0.02142	0.9978
SSC	4.44	2.03	0.0203	0.7042	4.44	4.65	0.0234	0.9981

q_e (exp): experimental adsorption capacity, q_e (cal): calculated adsorption capacity, K_1 : equilibrium rate constant of pseudo-first order equation, K_2 : equilibrium rate constant of pseudo-second order equation, R^2 : Coefficient of Correlation

calculated from the slope and intercept of the plot of C_e versus q_e . The coefficient of correlation R^2 , for Freundlich isotherm was found to be 0.9973 and 0.9919 for SHC and SSC respectively (Table 5). The relative adsorption capacity [K_f (mg/g)] was found to be 1.218 and 1.478 mg/g for SHC and SSC respectively (Table 5). The adsorption intensity of the adsorbents (n) calculated from the Freundlich model (Table 5) was greater than 1.0 indicating that the adsorption of Cd(II) onto the studied adsorbents was a favourable chemical process (chemisorption). The isotherms with n values greater than unity are classified as L-type isotherms which show that there is high affinity between adsorbate and adsorbent surface (Boparai *et al.* 2011). The value of the correlation coefficient, R^2 for Freundlich isotherm is greater than 0.99 and also greater than the R^2 values of Langmuir model indicating the applicability of the Freundlich model for Cd(II) adsorption. The applicability of Freundlich model suggests that the adsorption of Cd(II) ions onto adsorbents was multilayer.

The rate of metal adsorption is an important criterion for determining the process optimization and reactor designing for successful application (Iqbal *et al.*, 2009). So, the kinetic data obtained from batch experiments was tested by applying pseudo-first order and pseudo-second order models to explore the sorption rate law. The linear plots of $\log_{10}(q_e - q_t)$ versus time for first order model and t/q_t versus time for second-order model were plotted for the studied adsorbents using following equations 6, 7.

$$\log_{10}(q_e - q_t) = \log_{10} q_e - \frac{k_1}{2.303} t \quad (6)$$

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

The results of kinetic model parameters for Cd(II) calculated from the linear plots of pseudo-first order and pseudo-second order kinetic models are presented in Table 6. The low correlation coefficient values obtained from the pseudo-first order model (0.7131 for SHC and 0.7042 for SSC) indicated that the sorption of metal ions did not follow pseudo-first order model. The calculated q_e values (2.25 and 2.03 mg/g for SHC and SSC) from the pseudo-first order equation for the sorption of Cd(II) were significantly different from that of experimental q_e values (4.2 and 4.4 mg/g or SHC and SSC respectively).

Based on the correlation coefficient values, which were close to unity (0.9978 for SHC and 0.9981 for SSC), the adsorption of Cd(II) onto the studied adsorbents was best explained by pseudo-second order kinetics. Moreover, the calculated and experimental q_e values for Cd(II) were very close to each other (4.28 and 4.51 mg/g for SHC and 4.44 and 4.65 mg/g by SSC) which further confirmed that data followed the pseudo-second order kinetics.

For desorption studies, the adsorbents were gently washed with distilled water to remove any un-adsorbed metal ion and then treated with hydrochloric acid of varying strengths ranging from 0.0125 to 0.200 M (12.5 mM to 200 mM) for a contact period of 60 min at 25 °C having 50 mL of HCl at above said strengths at a shaking speed of 180 rpm. The desorbed metal ions in the solution were separated by centrifugation and analyzed. The desorption efficiency was calculated using equation 8 as reported by Kannan & Thambidurai, (2008):

$$\text{Desorption ratio (\%)} = \frac{\text{Amount of metal ion desorbed}}{\text{Amount of metal ion sorbed}} \times 100 \quad (8)$$

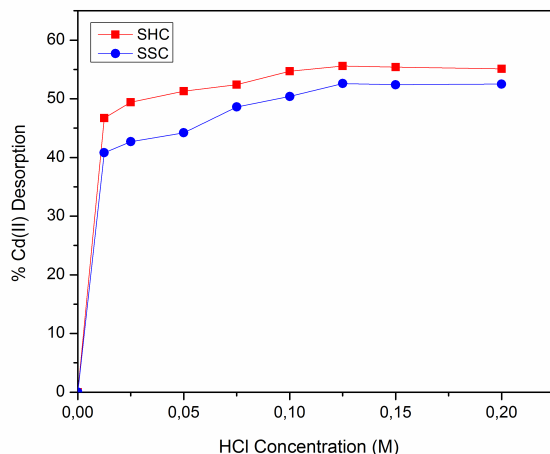


Fig. 4. Desorption of Cd(II) from SHC and SSC by HCl (at different HCl conc.) at desorbing agent volume = 50 mL, contact time = 60 min, temperature = 25±1°C, stirring speed =180 rpm

The results showed that, at higher concentration of HCl, desorption was more, however, when HCl of more than 0.125M (125 mM) concentration was used, there was no further increase in desorption (Fig. 4). Desorption efficiency was found to be 55.6 and 52.6% respectively from SHC and SSC (Fig. 4). This can be explained due to the fact that the protons (H^+) released from the HCl compete with Cd(II) ions and displace them from the surface of the adsorbent (Levy-Ramos *et al.*, 2005).

CONCLUSIONS

The results of this study revealed that the adsorption efficiency of adsorbents was 4.3 and 4.4 mg/g. The data fitted well to Freundlich model with correlation coefficient to be unity thus showing multilayer adsorption. Kinetic data fitted well to pseudo – second order model with coefficient of correlation to be 0.9978 and 0.9981 for SHC and SSC respectively. Desorption was 55.6% from SHC and 52.6% from SSC. It can be concluded from the present study that, SHC and SSC can be used as low cost adsorbents in batch mode reactors for the removal of Cd(II).

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