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Sunlight and microwave induced preparation of activated carbons and their removal of lead(II) and cadmium(II) from industrial effluent

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ABSTRACT

This study briefs about the conditions for preparation of activated carbons from pectin, citrulline, and cellulose rich *Annona squamosa* shell (custard apple shell) using phosphoric acid (H_3PO_4). The influence of time, temperature, and impregnation ratio on the yield were studied on the preparation of activated carbon by conventional i.e. normal stirring method (CAC), microwave assisted (MAC), and sunlight assisted synthesis (SAC). Also, the characteristics of all the three carbons were determined and found to have high surface areas using Brunauer–Emmett–Teller analysis. The prepared activated carbons were optimized for lead (Pb^{2+}) and cadmium (Cd^{2+}) uptake from aqueous solution and further the same was used to treat industrial effluent. The Langmuir isotherm was used to correlate equilibrium data of the adsorption of Pb^{2+} and Cd^{2+} by the prepared activated carbons.

Keywords: Sunlight; Microwave; Adsorption; Desorption; Effluent

1. Introduction

Activated carbons are non-hazardous carbonaceous products having porous structure and high surface area [1]. These materials can adsorb a wide variety of undesirable species from either gaseous or liquid phase in order to carry out purification of the desired material. Commercially available activated carbons are still considered as expensive materials due to the use of non-renewable and relatively expensive raw materials such as wood and coal [2–4]. Therefore, in recent years, this has prompted a higher research interest in the production of activated carbons from renewable and cheaper precursors which are mainly industrial, agricultural, or fruit wastes. This could be economically recycled and reused [5–8]. Hence, this study has been taken up to explore the possibility of using fruit waste containing pectin, citrulline, and cellulose. The fruit waste custard apple shell (CAS) which is found in many coastal areas of India, was used in this study, is a non-edible waste from which activated carbon was prepared for the removal of Pb^{2+} and Cd^{2+} from aqueous solution. The main objective of the study is the use of different pre-activation steps that were employed in the preparation of the activated carbon using a new adsorbent the CAS. Mainly the use of sunlight, a low cost method which involves in natural drying, microwave which needs power to generate the microwave energy but very time effective, and conventionally assisted preparation of activated carbon which is common stirring method which is adding the precursor and the adsorbent and allowing

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it for stirring and then drying it in oven. After involving these three pre-activation steps, the prepared activated carbons were optimized for the removal of Pb^{2+} and Cd^{2+} from aqueous solution and the same for industrial effluent through adsorption.

2. Materials and methods

In this study, activated carbon from CAS has been prepared through different pre-activation steps. The pre-activation methods used involve use of sunlight, a low cost method which involves in natural drying, microwave which needs power to generate the microwave energy but very less time consuming and conventionally preparation of activated carbon which is common stirring method.

After preparing the activated carbon through these three pre-activation steps, the prepared activated carbons were used for the removal of Pb^{2+} and Cd^{2+} from aqueous solution under optimized conditions and the same was used to remove these metal ions from aqueous industrial effluent. Results of adsorption of these two metal ions by the activated carbons prepared using sunlight (SAC), microwave (MAC), and mechano-chemical mixing (CAC) were compared and reported. Apart from few disadvantages like no selectivity and no controllability of the heating process, the main advantage of sunlight heating is, it is a natural source of heating with no direct contact between the heating source and materials and practically no cost is involved [9]. In the case of microwave, it has interior heating, high heating rates, selective and controllability of the heating process, no direct contact between the heating source and materials, and reduced equipment size [10,11]. To the best of our knowledge, no study has been reported on the preparation of activated carbon from CAS via sunlight, microwave-induced, and conventional activation as shown in Fig. 1.

2.1 Preparation of synthetic stock solutions

All chemicals and reagents used are of analytical grade reagents procured from Sigma-Aldrich and other standard chemical suppliers. One thousand mg/L stock solutions of Pb^{2+} and Cd^{2+} were prepared by dissolving appropriate amount of nitrate salts in Milli-Q water. Phosphoric acid (H_3PO_4) was used as the activating agent. Adjustments of pH were carried out using 0.1 M HCl and 0.1 M NaOH solutions.

2.2. Preparation of activated carbon

CAS was obtained from local fruit market. Prior to drying the shells were washed several times under tap water followed by washing with double distilled water. The shells were dried in hot air oven at 110˚C for 5 h. The dried shells were powdered and sieved through 100 mm standard mesh. For the preparation of activated carbon, pre-activation step was carried out by three different methods. For conventional process, the CAS was added to phosphoric acid at 1:1 weight ratio and stirred well for 4 h to obtain a homogenous mixture (CAC). Similarly for microwave activation, the precursor was added to phosphoric acid at 1:1 ratio and heated in microwave oven at 400 W power for 10 min (MAC) and the final product obtained was dried in oven at 110˚C for 3 h. For sunlight assisted (SAC), the precursor was added to phosphoric acid at 1:1 ratio and was dried in sunlight for 3 d (8 h/d) with constant stirring at regular time intervals (SAC). The carbonization step for all the methods was carried out in a furnace by optimizing the parameters such as effect of activation time (30–180 min), impregnation ratio (1: 0.5–2.5), and activation temperature (500–900˚C) in presence of nitrogen atmosphere. The obtained samples were washed several times with hot and then cold distilled water to bring them to a pH of 6–7 and dried in an oven at 50˚C overnight. The obtained samples were crushed and sieved in a 100 mm mesh size and stored in desiccators.

2.3. Batch mode adsorption studies

Sorption experiments for CAC, MAC, and SAC were individually conducted at room temperature (30˚C) using temperature controlled orbital shaker. Different Parameters like adsorbent dosage, contact time, pH, and initial metal concentration were studied. Effect of pH on adsorption was evaluated by varying pH from 2–8 using 0.1 M HCl and 0.1 M NaOH for adjustments. The adsorbent dose was varied from 0.5 to $5\,g\,L^{-1}$ for all the three selected materials. The contact time was varied between 5 to 120 min to study the effect of time on sorption. In each one of the experiment conducted, the residual metal ion concentration present in the supernatant was determined using AAS. The experiments were replicated thrice and average values are reported. The relative standard deviations of the values were found to be less than 4%. The amount of metal adsorbed to CAC, MAC, and SAC was determined from Eq. (1) and percent removal was evaluated by Eq. (2).

$$q_e = (C_0 - C_1)\frac{V}{M} \tag{1}$$

$$\%\ \text{Removal} = (C_0 - C_1)/C_0 \times 100 \tag{2}$$

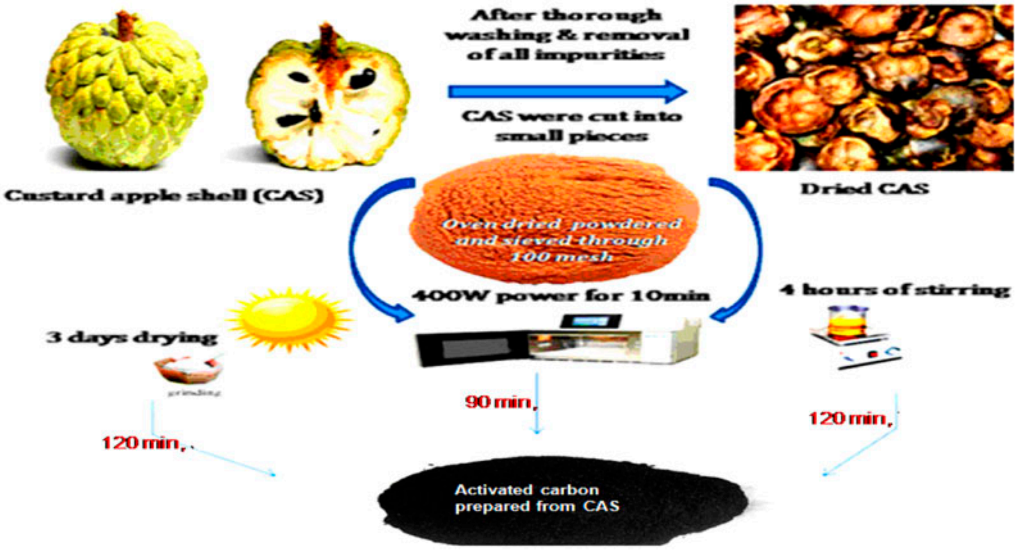

Fig. 1. Schematic representation of the synthesis of activated carbon derived from CAS.

where q_e is the metal uptake (mg/g) by adsorbents, C_0 and C_1 are initial and final metal concentrations (mg/L), V is the Volume (L) of the solution, and M is the mass of the adsorbent (g).

2.4. Instrumentation

SEM (JSM- 6390, Jeol) analysis was performed to study the textural structure of CAS before and after the activation process. Pore structural analysis was carried out by nitrogen adsorption at using a volumetric adsorption analyzer (Micromeritics ASAP 2020). Prior to analysis, the sample was degassed for 120 min under vacuum at 300°C. The sample was then transferred to the analysis system where it was cooled in liquid nitrogen. The specific surface area (SBET) was calculated by the Brunauer–Emmett–Teller (BET) equation; the total pore volume (VT) was evaluated by converting the adsorption volume of nitrogen at relative pressure 0.95 to equivalent liquid volume of the adsorbate, while the micropore volume, micropore surface area, and external surface area were obtained using the *t*-plot method, and surface functional groups of CAC, MAC, and SAC were detected by FTIR spectrometer (FTIR-2000, Perkin-Elmer) from the scanning range of 4,000–400 cm^{-1}.

2.5. Optimization process

The performance of chemical activation process was determined by the product yield, along with its uptake for Pb^{2+} and Cd^{2+} from aqueous solution and industrial effluents. The yield and Pb^{2+} and Cd^{2+}uptakes are determined as follows.

2.5.1. Yield

The yield is defined as the ratio of final weight of the obtained product after washing and drying to the weight of dried precursor initially used. The yield of activated carbon was calculated based on the following equation:

$$\text{Yield}\,\% = \frac{W_f}{W_o} \tag{3}$$

where W_f and W_o are the weight of final activated carbon product (g) and the weight of dried CAS (g), respectively.

2.5.2. Bulk density

Bulk or apparent density was determined as follows, 10 mL cylinder was filled to a specified volume with activated carbon that had been dried in an oven at 80°C for 24 h. The bulk density was then calculated as follows:

$$\text{Bulk density} = \frac{W_C}{V_C} \tag{4}$$

where W_C is the weight of dried activated carbon (g) and V_C is cylinder volume packed with dried activated carbon (mL).

2.5.3. Ash content

The ash content was determined by standard methods [12]. An amount of 0.5 g of activated carbon was dried at 80˚C for 24 h and placed into weighed ceramic crucibles. The samples were heated in an electrical furnace at 650˚C for 3 h. Then the crucibles were cooled to ambient temperature and weighed. The percent of ash was calculated as follows:

$$\text{Ash}\,\% = \frac{W_{S3} - W_{S2}}{W_{S1}} \tag{5}$$

where W_{S3} is the weight of crucible containing ash (g), W_{S2} is the weight of crucible (g), and W_{S1} is the weight of original activated carbon used (g).

2.5.4. Moisture content

The moisture content of prepared carbon was determined using oven drying method (Tan *et al.*, 2008). An amount of 0.5 g of activated carbon was placed into weighed ceramic crucible. The samples were dried at 110˚C to constant weight. Then the samples were cooled to ambient temperature and weighed. The moisture content was calculated by the following equation:

$$\text{Moisture}\,\% = \frac{W_{m3} - W_{m2}}{W_{m1}} \tag{6}$$

where W_{m3} is the weight of crucible containing original sample (g), W_{m2} is the weight of crucible containing dried sample (g), and W_{m1} is the weight of original sample used (g).

2.6. Desorption studies

To examine the potential of repeated use of the adsorbent, desorption and regeneration experiments were conducted for CAC, MAC, and SAC. Metal loaded CAC, MAC, and SAC sorbent (0.1 g) was shaken with 20 mL of 0.1 M HCl as the desorbing agent in 50 mL Torson tubes at 50 rpm for 30 min at room temperature. The centrifuged supernatant solutions were analyzed for metal ion detection and metal desorbed CAC, MAC, and SAC were used as a regenerated sorbents. The adsorption–desorption was repeated for five cycles to determine the reusability potential of CAC, MAC, and SAC.

3. Results and discussion

The use of sunlight, microwave, and conventional stirring were studied for production of activated carbon with desirable characteristics, such as relatively high yield, BET surface, and pore volume. The optimum impregnation ratio is reported in literature to range from 0.5 to 2.5 depending on the precursor [13–15]. It was noticed that the yield of activated carbon decreases progressively with increase in activated temperature from 500 to 800˚C, which could be attributed to the higher reaction rate of carbon and carbon dioxide to release more volatiles at a higher pyrolysis temperature and the decrease in yield at higher temperature, is associated with improvement in the textural characteristics. Higher temperature provides a better condition for making carbon with higher adsorption properties. This is more or less certainly due to the simultaneous physical activation effect of carbon dioxide and development of new micropores by the intercalation of H_3PO_4 in the carbon structure at higher temperature. These results for H_3PO_4 activation are in agreement with literature [16]. CAC, MAC, and SAC were prepared to assess the effect of activation and the changes in the physical characteristics of the activated carbon. As seen, the yield of activated carbon decreases in CAC compared to MAC and SAC. This could be due to the carbon burn-off, which well agrees with the existing state of knowledge [17]. However, the adsorption capacity of the SAC has shown great deal of improvement when compared to MAC or CAC.

3.1. Effect of activation time

The effect of activation time on yield of prepared activated carbon is shown in Fig. 2(a). This shows that the yield of CAC, MAC, and SAC decreases with increasing activation time after 90–120 min.

An increase in time from 120 to 180 min at 750˚C and one impregnation ratio leads to a decrease in yield of SAC from 51.3 to 49.15%, while for CAC the decrease in yield was from 48.54 to 44.54% and MAC it was 31.56 to 29.56. A decrease in yield was observed after 120 min for production of activated carbon from CAS using H_3PO_4 which is due to rapid evolution of volatile materials to form stable compounds [18].

3.2. Effect of activation temperature

The effect of activation temperature for 120 min on yield of prepared activated carbon is shown in Fig. 2(b). It can be seen from Fig.2(b) that, as the activation temperature increases from 500 to 900˚C, the yield decreases from 51.13 to 42.13%, 48.54 to

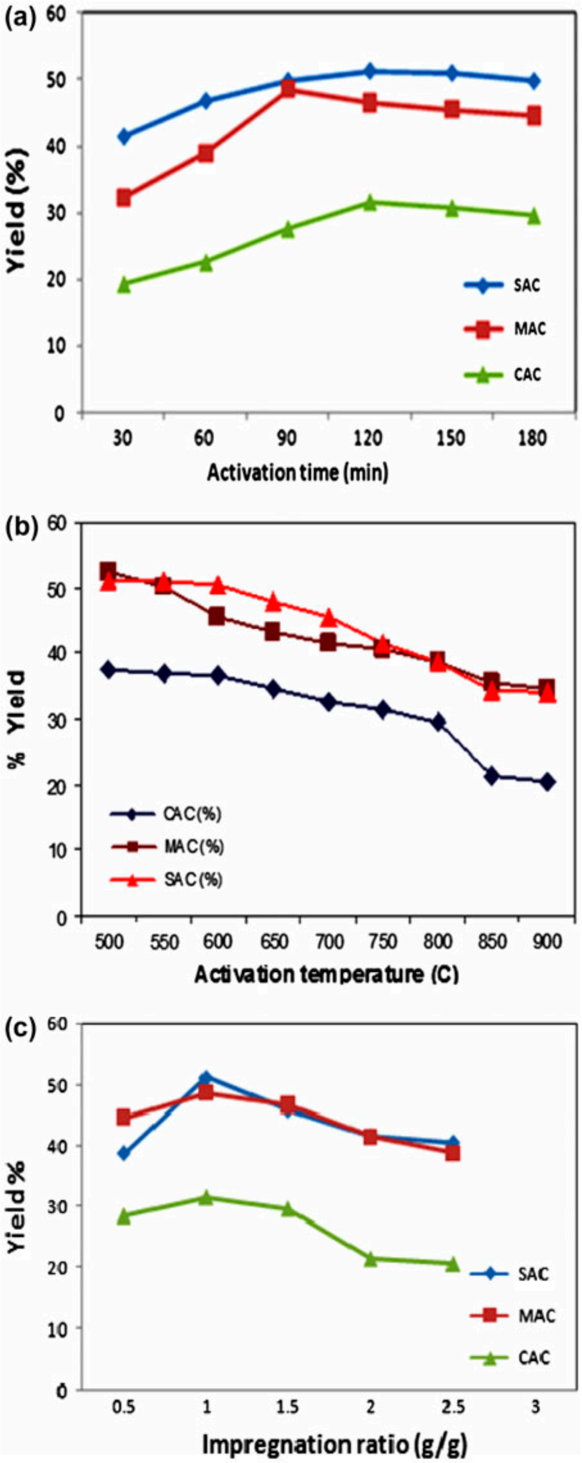

Fig. 2. (a) Effect of activation time on yield, (b) Effect of activation temperature on yiel, and (c) Effect of impregnation ratio on yield.

33.52%, and 31.56 to 25.67% for SAC, MAC, and CAC, respectively. This is due to the loss of volatile materials at higher temperatures [19]. Beyond 550℃ and up to 750℃, yield decrease was noticed since a stable structure of activated carbon is formed. Substantial decrease in yield of the activated carbon was noticed on increase in temperature beyond 750℃. The decrease in yield at high temperature might be due to the sintering effect at high temperature, followed by shrinkage of the char and realignment of the carbon structure which resulted in reduced pore areas as well as volume. Therefore, the temperatures of 750℃ were chosen as optimum activation temperatures for CAC, MAC, and SAC, respectively.

3.3. Effect of Impregnation Ratio

Fig. 2(c) shows the effects of impregnation ratio, activator to precursor weight ratio, on yield of prepared activated carbon. It was noticed that as the impregnation ratio increases from 1 to 2.5, the yield I observed to decrease. An increase in impregnation ratio from 0.5 to 2.5 leads to a decrease in yield for CAC, MAC, and SAC, respectively. This decrease is due to the continuous removal of tar material from the pores [20–22]. More increase in the concentration of H_3PO_4 activator perhaps leads to the excessive dehydration and destruction of mesopores and turning them to larger pores which reduces the adsorption efficiency [23]. Therefore, the ratio of 1:1 was chosen as optimum impregnation ratio for CAC, MAC, and SAC respectively.

4. Characterization of the activated carbon

4.1. FT-IR analysis

The FT-IR spectra of prepared activated carbons are given in Table 1. When comparing the spectra, it can be observed that the disappearance of few adsorption bands in the carbon spectrum indicates the carbonization and activation process. This suggests the decomposition of these groups and subsequent release of their byproducts as volatile matter by chemical activation at high temperatures. The spectrum of activated carbon prepared by CAC, MAC, and SAC shows significant adsorption bands. These bands are quite similar to those reported for different biomass-based activated carbons [24]. The broad intensive band located at around 3,400 cm^{-1} is typically attributed to the O–H stretching vibration in hydroxyl groups, the intensity marginally decreases when these bands are compared between the starting material and CAC, MAC, and SAC. The bands at the range of 1,600 cm^{-1} also suggested changes in the amino groups present in the starting material. A decrease in intensity of the band corresponding to C=O groups in the range of

Table 1
FTIR data for prepared activated carbon

Wave number (cm^{-1})			CAS before activation	Functional group
CAC	MAC	SAC		
3,417	3,471	3,417	3,415	O–H stretching of the hydroxyl group
2,924	2,900	2,924	2,924	C=C–H stretching
1,732	1,737	1,732	1,710	C=C stretching
1,432	1,433	1,432	1,433	C=O stretching of the –COOH group
1,176	1,166	1,161	1,176	C=O stretching of the carbonyl group

1,700 cm^{-1} to 1,740 cm^{-1} suggests that the activated carbon contains less C=O groups than the raw material in all the three forms of activation. The band around 1,645 cm^{-1} range formed in CAC, MAC, and SAC is ascribed to the aromatic ring or C=C stretching vibration which indicates the aromatization of the precursor.

The peak appearing at 1,125 and 1,100 cm^{-1} are characteristics of C–O stretching in lactonic, alcoholic groups, and carboxylate moieties as shown in Fig. 3. The pH_{pzc} was determined to be about 5.6, 5.7, and 5.6 for SAC, MAC, and CAC, respectively. Thus, it could be inferred that the prepared activated carbon is less acidic in nature.

4.2. SEM analysis of prepared activated carbons

The SEM micrographs of raw CAS, CAC, MAC, and SAC are shown in Fig. 4(a). A porous spongy texture in the case of SAC and MAC can be seen in Fig. 4(b) and (c). The micrographs in Fig. 4(d) show the morphological changes due to conventional stirring, the surface texture shows more spongy structure. It is suggested that the formation of textural spongy structures were due to well-dispersed activated carbon in the microwave assisted synthesis, where as only rough surfaces could be observed for raw CAS as shown in Fig. 4(a). Interestingly, some platy crystals were observed for CAC possibly due to the conventional stirring and due to the basic character of the carbon surface resulted from the Π electrons of graphene layers [25].

4.3 Surface area of prepared activated carbons using BET

The characteristics of CAC, MAC and SAC prepared at optimum conditions are summarized in Table 2. These results show that the surface areas of CAC, MAC and SAC are 1181.3, 1151.3, and 1021.5 m^2/g, respectively.

These values are higher than those reported results in literature [26]. The other important characteristic is maximum Pb^{2+} and Cd^{2+} uptake. Although the surface area of SAC is lower than that of MAC and CAC, its maximum Pb^{2+} and Cd^{2+} uptake is higher

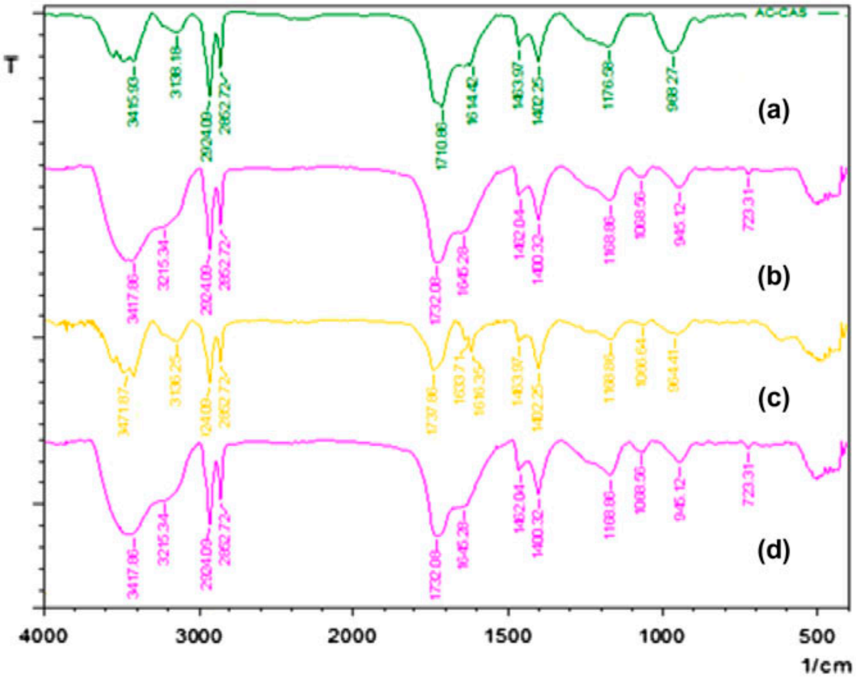

Fig. 3. FTIR spectra of raw CAS (a), CAC (b), MAC (c), and SAC (d).

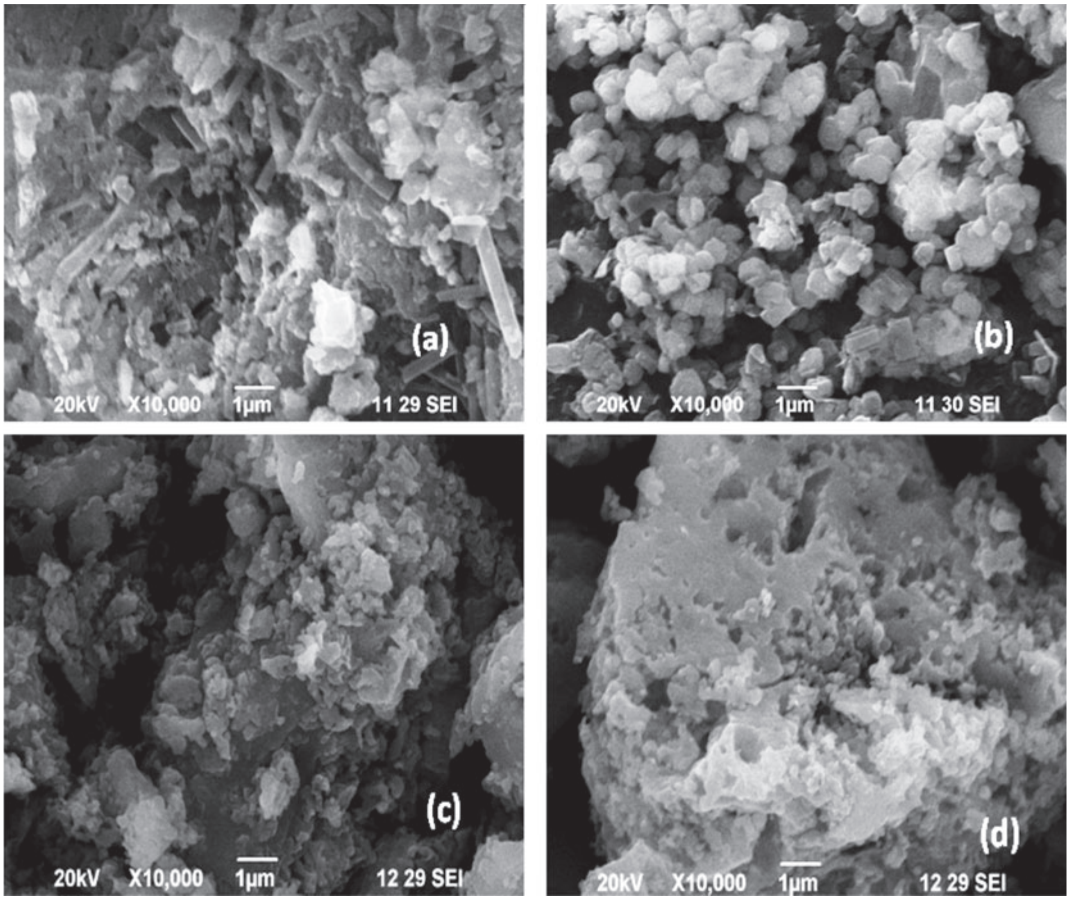

Fig. 4. (a) SEM images for raw custard apple shell (CAS), (b) Sunlight assisted activated carbon (SAC), (c) Microwave assisted activated carbon (MAC), and (d) Conventional assisted activated carbon (CAC).

Table 2
Characteristics of the activated carbons

S.no.	Surface and physical properties	Adsorbents		
		CAC	MAC	SAC
1	Surface area (m^2/g)	1181.3	1151.4	1021.5
2	Average pore radius (A˚)	12.93	12.46	10.54
3	Total pore volume (mg/L)$^*10^{-3}$	693.0	740.7	874.2
4	Mesh size	80–100	80–100	80–100
5	Bulk density (g/mL)	0.257	0.312	0.452
6	Ash content (%)	6.32	5.42	4.23
7	Moisture content (%)	13.56	12.23	11.56
8	Point zero charge (pH_{pzc})	5.5	5.7	5.6

than that of MAC and CAC which may be possibly due to smaller ionic radius formed by SAC compared to MAC and CAC which enables the formation of activated carbon with high portion of micropores. These micropores are preferred for adsorption of Pb^{2+} and Cd^{2+} which have a molecular size of the micropores formed by SAC.

4.4. Characteristics of the prepared activated carbons

The bulk density, ash content, and moisture content were determined for the prepared activated carbons CAC, MAC, and SAC. The bulk density (g/mL) of SAC was determined to be 0.452 which was higher than MAC and CAC. The moisture content (%) of SAC, MAC, and CAC were determined to be 11.56, 12.23, and 13.56%, respectively.

5. Batch mode adsorption studies

5.1. Effect of pH on adsorption

The pH of a solution is an important parameter for batch adsorption process, as it affects the surface charge of the adsorbents and the degree of ionization of adsorbate during adsorption process. It is well known that pH influences metal ion sorption due to

Table 3
Effect of pH on adsorption (Dose 1.5 g L^{-1}, Initial concentration 50 mg L^{-1}, temperature 303 K and time 30 min)

		CAC % Removal		MAC % Removal		SAC % Removal	
S. no.	pH	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
1	2	68.5	61.5	58.3	55.78	71.54	69.34
2	3	72.8	75.43	61.8	64.23	82.80	71.33
3	4	79.78	77.58	68.48	67.68	85.34	71.48
4	5	87.56	5.34	77.13	70.84	98.12	96.24
5	6	96.78	95.65	87.34	85.65	98.7	97.65
6	7	95.34	91.45	82.54	81.21	93.24	90.15

the competition between metal ions and H^+ ions for active sorption sites. The effect of H^+ ion concentration on removal of Pb^{2+} and Cd^{2+} by CAC, MAC, and SAC was studied at different pH ranging from 2 to 8 (Table 3).

It was noticed that Pb^{2+} and Cd^{2+} adsorption is observed to increase with increase in pH from 2 to 6. Beyond pH 6 the removal efficiency was found to decrease for all the three adsorbents. This might be due to the formation of soluble hydroxides. Hence, further sorption experiments were carried out at pH 6 for CAC, MAC, and SAC.

5.2. Kinetics of adsorption

The rate of metal sorption is important parameter for selecting a wastewater treatment system. In order to study the effect of contact time, sorption experiments were conducted at different time intervals (10–120 min) for removal of Pb^{2+} and Cd^{2+} ions onto CAC, MAC, and SAC. The uptake of Pb^{2+} and Cd^{2+} equilibrium was achieved within 40 min. To analyze the mechanism and rate of adsorption of Pb^{2+} and Cd^{2+} ions onto CAC and MAC, experimental data was fitted to pseudo-first-order and pseudo-second-order models.

5.3. Pseudo-first-order kinetic model

The Lagergren's rate equation is one of the most widely used rate equations for study of adsorption of an adsorbate from aqueous solution. The linear form of Lagergren's pseudo-first-order equation is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

where q_e is the amount of metal adsorbed at equilibrium (mg/g), q_t is the amount of metal adsorbed at time t, and k_1 is the first-order reaction rate constant.

5.4. Pseudo-second-order kinetic model

The kinetic data were also analyzed by pseudo-second-order kinetic model. Based on the sorption equilibrium capacity pseudo-second-order model can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order adsorption. The values and correlation coefficients (R^2) for pseudo-first- and second-order model are represented in Table 4. It was observed that the theoretical q_e values were very close to the obtained experimental values which show appropriateness to the model and further the better fit is supported by the respective correlation coefficients being closer to one. These observations suggest that sorption by CAC, MAC, and SAC follows pseudo-second-order reaction, which suggest that the process controlling the rate may be a chemical sorption involving valence forces through sharing or exchanging of electrons between sorbate and sorbent.

Table 4
Pseudo-first- & second-order kinetic for Pb^{2+} and Cd^{2+} parameters with experimental values obtained at 30°C

		CAC		MAC		SAC	
Model	Constants	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
Experimental	q_e (mg/g)	40.84	27.56	39.48	27.34	65.30	48.56
Pseudo-first order	q_e (mg/g)	5.28	3.45	8.49	6.21	5.288	9.98
	k_1 (min^{-1})	0.086	0.088	0.024	0.056	0.002	0.035
	R^2	0.887	0.927	0.909	0.912	0.970	0.893
Pseudo-second order	q_e (mg/g)	42.25	25.65	32.45	25.23	66.11	40.89
	k_2 (g mg^{-1} min^{-1})	0.016	0.011	0.461	0.023	0.081	0.025
	R^2	0.999	0.998	0.999	0.999	0.998	0.991

5.5. Adsorption isotherms

5.5.1. Langmuir isotherm

The Langmuir isotherm assumes monolayer adsorption process and linear form of Langmuir isotherm after rearrangement is given as

$$\frac{C_e}{q_e} = \frac{1}{bV_m} + \frac{C_e}{V_m} \tag{9}$$

where C_e is the concentration of metal solution at equilibrium (mg^{-1}), q_e is the amount of metal adsorbed per unit mass of adsorbent (mg/g), V_m is the amount of adsorbate at complete monolayer coverage (mg/g), and b is a constant that relates to the heat of adsorption (L/mg).

5.5.2. Maximum Pb^{2+} and Cd^{2+} uptake

The maximum uptake of Pb^{2+} and Cd^{2+} by CAC, MAC, and SAC prepared at optimum conditions have been determined by fitting experimental equilibrium data from the respective equations. The calculated constants of Langmuir isotherm for the three samples along with R^2 values are presented in Table 5. This table shows that the maximum uptake by CAC, MAC, and SAC is 105.67, 110.34, and 120.15 mg/g for Pb^{2+} and 102.56, 103.63, and 110.14 mg/g for Cd^{2+}, respectively. The Pb^{2+} and Cd^{2+} uptake of SAC at a given metal ion concentration is higher than that of MAC and CAC; this may be due to the ability of H_3PO_4 to produce carbon structure with high percentage of micropores by stirring method as compared to that obtained using sunlight and microwave. It can be seen from the results that the prepared activated carbons are effective adsorbents for removal of Pb^{2+} and Cd^{2+} from aqueous solutions.

5.6 Thermodynamics of adsorption

In order to describe the thermodynamic behavior of sorption of Pb and Cd onto SAC, MAC, and CAC, at equilibrium, temperature was varied from 303 K to 323 K by use of an orbital shaker. Thermodynamic parameters including change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were derived. The calculated ΔG° values of Pb and Cd for SAC, MAC, and CAC were found to be negative which indicates the spontaneous process of present system. The negative values of ΔH° and ΔS° indicates the exothermic nature and decrease in the randomness of solid–liquid interface during the sorption.

6. Removal of Pb^{2+} and Cd^{2+} from industrial effluent

The prepared activated carbons were used as adsorbents on industrial effluent containing Pb^{2+} and Cd^{2+} under the optimized conditions established through the experiments conducted above. From the effluent, the insoluble portion was filtered off and the filtrate was taken. The Pb^{2+} and Cd^{2+} concentration in the effluent was measured by AAS to be 29.8 and 18.1 mg/L and the pH of the effluent was 1.5. In order to gain maximum removal of the metal ions from industrial effluents, the pH of the effluents solution was adjusted to optimized pH 6. The results of removal of the two metal ions in question before and after treatment are summarized in Table.6. It can be observed that approximately 93.82 and 84.47% by SAC, 88.25 and 69.61% by MAC, 90.61 and 77.34% by CAC in the order of Pb^{2+} and Cd^{2+}, respectively, could be removed from the effluent using the worked

Table 6
Raw characteristics of industry wastewater before and after treatment

Parameter	Value before adsorption	Value after adsorption		
		SAC	MAC	CAC
pH	1.5	6	5.5	6.1
Pb^{2+} (mg/L)	29.8	1.54	3.5	2.8
Cd^{2+} (mg/L)	18.1	2.81	5.5	4.1

Table 5
Pb^{2+} and Cd^{2+} equilibrium isotherm results

Sample	V_m (mg/g)		b (l/mg)		R^2	
	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
CAC	105.67	102.56	0.154	0.095	0.998	0.999
MAC	110.34	103.63	0.198	0.115	0.999	0.998
SAC	120.15	110.14	0.218	0.119	0.994	0.991

Table 7
Effect of other bivalent metals on removal of Pb^{2+} by SAC

S.no.	Sorption system	q_e (mg/g) SAC	% Decrease in q_e SAC
1	Pb^{2+}	134.23	–
2	Pb^{2+}–Cd^{2+}	121.54	9.45
3	Pb^{2+}–Cu^{2+}	131.25	2.22
4	Pb^{2+}–Co^{2+}	133.78	0.33
5	Pb^{2+}–Zn^{2+}	134.15	0.15
6	Pb^{2+}–Cd^{2+}–Cu^{2+}–Co^{2+}–Zn^{2+}	115.45	8.99

Table 8
Effect of other bivalent metals on removal of Cd^{2+} by SAC

S.no.	Sorption system	q_e (mg/g) SAC	% Decrease in q_e SAC
1	Cd^{2+}	109.8	–
2	Cd^{2+}–Pb^{2+}	88.54	19.36
3	Cd^{2+}–Cu^{2+}	101.65	7.42
4	Cd^{2+}–Co^{2+}	95.7	12.8
5	Cd^{2+}–Zn^{2+}	99.45	9.42
6	Cd^{2+}–Pb^{2+}–Cu^{2+}–Co^{2+}–Zn^{2+}	78.89	28.15

out optimized conditions. Since the activated carbons are biodegradable, they can be easily disposed off after recovering Pb^{2+} and Cd^{2+} from the biosorbent by desorption.

7. Removal of Pb^{2+} and Cd^{2+} in presence of other bivalent metal ion

The effect of other bivalent metals in the removal of Pb^{2+} using SAC was studied and the data is represented in Table 7. As the data represent, it was observed that there was no significant decrease in the removal percentage of Pb^{2+}in presence of Cu^{2+}, Zn^{2+}, and Co^{2+}. Where as in presence of Cd^{2+}, the decrease noticed was 9.45% and in the multiple metal system 8.99% was noticed. This proves that the sorbent had preferential adsorption of Pb^{2+} and no significant decrease in the sorption with the interferences of other metals.

Table 9
Data on desorption of prepared activated carbons

Cycle no.	CAC Pb^{2+}	CAC Cd^{2+}	MAC Pb^{2+}	MAC Cd^{2+}	SAC Pb^{2+}	SAC Cd^{2+}
1	95.5	96.53	90.15	92.40	88.50	89.50
2	89.4	90.40	86.45	89.34	85.34	85.34
3	65.34	78.14	71.34	75.34	65.34	69.23
4	54.56	56.20	52.13	50.23	50.12	52.16
5	32.34	34.10	29.34	32.12	39.12	35.12

The other bivalent metals role in the removal of Cd^{2+} was studied and the data are reported in Table 8. As observed from the data, there was a decrease of 19.36% in the sorption of Cd^{2+} in presence of Pb^{2+} and 7–13% in presence of Cu^{2+}, Zn^{2+}, and Co^{2+}. In presence of multiple-metal system, 18.3% decrease was noticed.

8. Desorption studies

Desorption and revival of the biosorbent is of vital significance in assessing its possible potential for commercial applications. In order to make the sorption process most economical, desorption and regeneration potential of prepared activated carbons were studied using 0.1 M HCl as desorbing agent. An amount of 0.1 g of Pb^{2+} and Cd^{2+} loaded CAC, MAC, and SAC were kept in contact with 20 mL of 0.1 M HCl for 30 min and desorbed acidic solution was analyzed by AAS to determine the metal ion concentration. The data on desorption of Pb^{2+} and Cd^{2+} from the metal loaded activated carbons are presented in Table 9. It can be seen that the adsorbents can be effectively recycled for two cycles without affecting the efficiency. The adsorption efficiency is observed to reduce in the subsequent cycles as shown in the table.

9. Conclusions

Activated carbons were successfully prepared from raw CAS employing three different pre-activation steps. For CAC 56% yield; 98.61 mg/g Pb^{2+}; 86.56 mg/g Cd^{2+}; while for MAC 48.54% yield; 102.34 mg/g Pb^{2+}; 95.45 mg/g Cd^{2+}; and for SAC 51.13% yield; 103.95 mg/g Pb^{2+}; 98.45 mg/g Cd^{2+} uptake was achieved at optimum conditions of 120 min activation time, 750°C activation temperatures for SAC; 90 min and 750°C for MAC; 120 min, 750°C for CAC with a impregnation ratio of one for all the three prepared activated carbons. The Langmuir isotherm was used to correlate the equilibrium data of adsorption, showing maximum Pb^{2+} and Cd^{2+} uptake of 120.15, 110.14 for SAC; 110.34, 103.63 for MAC and 105.67, 102.56 mg/g for CAC, respectively. As a significant application, the prepared activated carbons were tried out as adsorbent for removal of Pb^{2+} and Cd^{2+} from the industrial effluent using the optimized conditions, which was found to be successful. The adsorption preference of the activated carbon was studied in binary and multiple systems and was observed that there was a preferential adsorption of

Pb^{2+} and Cd^{2+} in presence of other bivalent metals. Desorption of Pb^{2+} and Cd^{2+} from the metal loaded activated carbons resulted approximately 90% of Pb^{2+} and Cd^{2+} getting desorbed from the activated carbons during the first cycle while the efficiency remained almost unchanged during two repeated cycles thus confirming that the adsorbent can be effectively recycled for two cycles without losing efficiency.

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