



Performance evaluation of low cost adsorbents in reduction of COD in sugar industrial effluent

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ARTICLE INFO

Article history:

Received 25 April 2008

Received in revised form

12 November 2008

Accepted 17 February 2009

Available online 25 February 2009

Keywords:

COD

Dates nut carbon

Metakaolin

Sugar industrial effluent

Tamarind nut carbon

ABSTRACT

Studies on reduction of chemical oxygen demand (COD) in effluent from sugar industry have been carried out by employing different adsorbents optimizing various parameters, such as initial concentration of adsorbate, pH, adsorbent dosage and contact time. Experimental studies were carried out in batches using metakaolin, tamarind nut carbon and dates nut carbon as adsorbents by keeping initial adsorbent dosage at 1 g l^{-1} , agitation time over a range of 30–240 min, adsorbent dosage at $100\text{--}800 \text{ mg l}^{-1}$ by varying the pH range from 4 to 10. Characterization of these adsorbents were done using techniques such as Fourier transforms infra red spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM). The experimental adsorption data fitted well to Langmuir and Freundlich adsorption isotherms. The isotherms of the adsorbents indicate appreciable adsorption capacity. Higher COD removal was observed at neutral pH conditions. Studies reveal that maximum reduction efficiency of COD takes place using metakaolin as an adsorbent at a dosage of 500 mg l^{-1} in a contact time of 180 min at pH 7 and it could be used as an efficient adsorbent for treating sugar industrial effluent.

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1. Introduction

Effluents from sugar industries induce environmental pollution. India, being one of the major producers of sugar in the world, is prone to large volume of wastes from sugar industries. The by-products namely bagasse, molasses, distillery wastes and press mud are some of the major objectionable wastes generated by the sugar industries [1].

Activated carbon is one of the major adsorbents used for treatment of sugar industry wastes to reduce chemical oxygen demand (COD) [2,3]. Ideal adsorbents must obey the following characteristics – a solid, with high surface area, high porosity, inertness – stability to withstand chemical, thermal and climatic changes, cost effective and good physicochemical properties similar to that of commercial activated carbon. An adsorbent possessing the above properties, would be considered as a good adsorbent in water and wastewater treatments [4,5].

The adsorbents may be classified under four major headings based on their origins namely agricultural wastes, industrial by-products, natural materials and commercial and synthetic activated carbons. When comparing the cost of the above categories with the available literature [6–12] it is of the order: natural minerals ($0.04\text{--}0.12 \text{ US\$/kg}$) < agricultural wastes ($\sim 0.25 \text{ US\$/kg}$) < industrial by-products ($\sim 1 \text{ US\$/kg}$) < commercial synthetic carbons ($20\text{--}22$

$\text{US\$/kg}$). Many researches have been done to identify a low cost substitute for activated carbon for the treatment of industrial effluents to reduce COD. The low-cost adsorbents can be viable alternatives to activated carbon for the treatment of wastewater. It is important to note that the adsorption capacities may vary, depending on the characteristics of the individual adsorbent, surface modification and the initial concentration of the adsorbate. In general, technical applicability and cost-effectiveness are the key factors that play major roles in the selection of the most suitable adsorbent to treat effluent.

To achieve an economically effective effluent treatment of wastewater, various low-cost materials have been investigated worldwide, such as in India [13], Thailand [14], Nigeria [15], Italy [16] and USA [17]. Further, it has been reported that wool [18], soya cake [19], sawdust [20], maple saw dust [21], distillery sludge [22], cocoa shell [23], sugar beet pulp [24] and zeolite [25] could be used as possible adsorbents in conjunction with Cr(VI) to treat the effluents for reduction of COD with high efficacy. Common materials such as sawdust, fly ash, bagasse pith, controlled burnt wood charcoal, etc., have been used for the treatment of industry wastes [26,27]. Kaolin based adsorbents have been studied to treat other industrial effluents [28,29]. However, metakaolin has not been studied as an adsorbent for the treatment of wastewater from sugar industry, so far.

Further, use of adsorbents for COD reduction has the advantage of easy sludge disposal when compared to conventional precipitation technique. In the present study metakaolin (natural materials) and carbon derived from tamarind and dates nuts (agricultural

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Table 1
Physico-chemical properties of effluent from sugar industry.

Parameters	Characteristic value*
Colour	Blackish grey
pH	6.7
Alkalinity	882
Chlorides	522
Sulphate	271
Dissolved solids	2432
Suspended solids	447
DO	Nil
BOD	2987
COD	6820

* All values are in mg l^{-1} except pH and colour.

wastes), which are belonging to low cost category, have been investigated as the possible adsorbents for the reduction of COD from sugar industrial effluents. Characterizations of adsorbents were done through Fourier transforms infra red spectroscopy (FTIR), scanning electron microscope (SEM) and X-ray diffraction (XRD) analysis. Several parameters like contact time, adsorbent dosage and pH were optimized and the adsorption data were fitted in Langmuir and Freundlich isotherm adsorption isotherms.

2. Materials and methods

2.1. Effluent sample

Effluent collected from Dharani Sugar Mills, Vasudevanallur, Tamilnadu, India was used in the present studies. The effluent samples were analyzed for physicochemical characteristics and results are listed in Table 1.

2.2. Preparation of adsorbents

Metakaolin, a pozzolana, was prepared by heating kaolin clay to a temperature of 600–800 °C. Kaolin, a fine white clay mineral, consists of alternate layers of silica and alumina in tetrahedral and octahedral co-ordinations having a specific surface area of $15 \text{ m}^2 \text{ g}^{-1}$ was used. Metakaolin was washed in distilled water, filtered, dried and used as adsorbent.

Dried tamarind and date nuts were crushed mechanically and soaked in 1 N H_2SO_4 for few hours. The nuts were separated from the fruit remains stuck on the surface of the nut shell. The nuts were then washed thoroughly with distilled water to remove the excess acid. It was dried in hot air oven initially and then heated in a muffle furnace for about 4–5 h at 120 °C in nitrogen atmosphere. Then it was crushed and sieved to get a very fine carbon powder and were used as adsorbents.

2.3. Characterization of adsorbents

The adsorbents were characterized using FTIR (PerkinElmer, UK, Model: Paragon 500). FTIR spectrum was recorded in the range 4000–450 cm^{-1} . XRD pattern of the adsorbents were recorded in order to study its nature using JEOL-JDX, X-ray diffractometer. The powdered samples of adsorbents were also subjected to SEM analysis using Hitachi S-3000H to study the morphological characteristics.

2.4. Batch studies

The performance of the prepared adsorbents was evaluated through batch process with varying dosages. The adsorbents in varying proportions (100–800 mg l^{-1}) were mixed with 100 ml of sugar industrial effluent. The mixtures were taken in 250 ml conical

flask and shaken using rotary spinner. After a definite interval of time, the adsorbent was separated by filtration. The filtered samples were tested for COD at regular intervals by using standard reflux method [30]. The adsorption equilibrium study was also conducted at different pH conditions varying from 4 to 10. The absorption time with the effluent was varied from 30 to 240 min. The COD was determined intermittently till it attains steady state equilibrium. All the studies were carried out at ambient temperature 32 ± 1 °C.

3. Results and discussion

3.1. FTIR

FTIR spectra of the adsorbent materials viz., metakaolin, tamarind nut carbon and dates nut carbon recorded between wave number 4000 and 450 cm^{-1} are presented in Fig. 1a–c, respectively. FTIR spectra of metakaolin (Fig. 1a) show three large regions where the main vibration and deformation bands of Si–Al, Ca and OH are concentrated. Vibrational and deformation bands of occult water (O–H) appeared through a broad transmittance reflection around $\sim 3437 \text{ cm}^{-1}$ region. Vibrational bands corresponding to calcium silicates are present around ~ 1010 and 930 cm^{-1} . Further, a secondary vibrational region of calcite appears around ~ 2930 and 2850 cm^{-1} [31]. C-vibrational bands (C–O) are observed around $\sim 1500\text{--}700 \text{ cm}^{-1}$ region [32]. Reflections around $1100\text{--}400 \text{ cm}^{-1}$

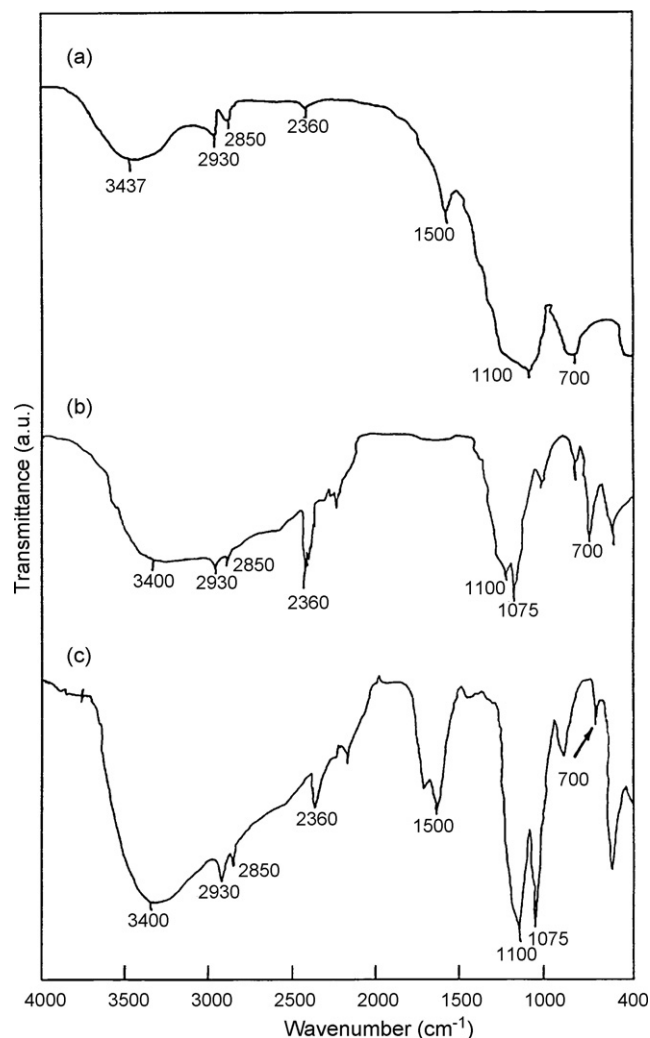


Fig. 1. FTIR spectra of (a) metakaolin; (b) tamarind nut carbon and (c) dates nut carbon.

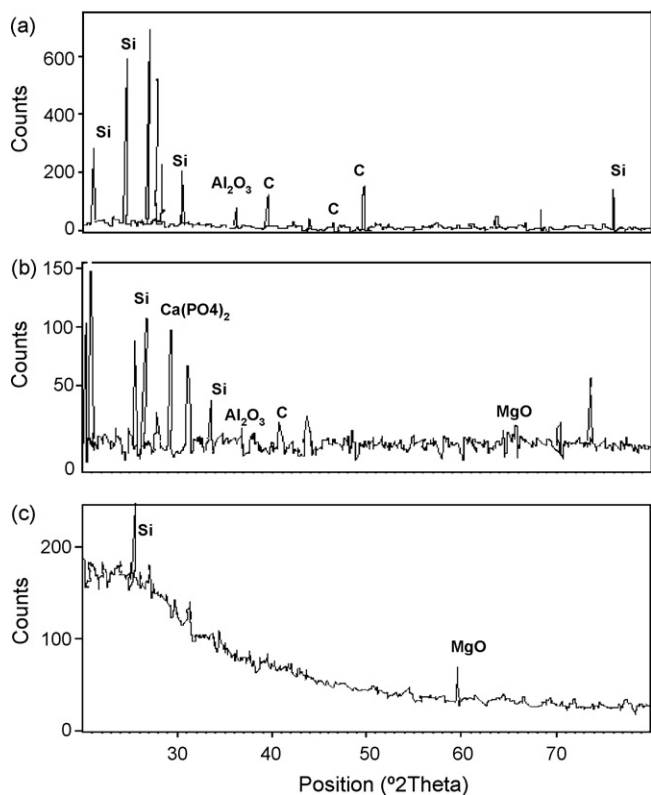


Fig. 2. XRD patterns of (a) metakaolin; (b) tamarind nut carbon and (c) dates nut carbon. Silicate: Si; calcite: C; calcium phosphate hydrate: $\text{Ca}(\text{PO}_4)_2$; aluminates: Al_2O_3 ; magnesia: MgO.

are assignable to vibrational bands of Si (Si–O and Si–O–Si) and Al (Al–O and Al–O–Al).

FTIR spectra of tamarind nut carbon and date nut carbon are depicted in Fig. 1b and c, respectively. Basically, these nuts comprises of polysaccharides, crude proteins, ether extracts, fibers and small percentage of elements like Na, K, Ca, Mg, P and Si. Upon calcination organic matters escapes and the metal elements forms various ash products like silicates, calcites, phosphates etc. These facts are well reflected in the FTIR spectra. Both the spectra have similarity in their FTIR reflections which can be broadly segregated into four zones. The reflections observed in the region $1200\text{--}800\text{ cm}^{-1}$ are assigned to burnt residues of polysaccharides [33]. The absorption peak around $1110\text{--}1000\text{ cm}^{-1}$ arises from the asymmetric stretching of phosphate group [34,35]. The absorption bands at 2360 cm^{-1} can be attributed to CO_2 of FTIR environment.

Vibration and deformation bands of moisture (O–H) appeared over a broad transmittance reflection around $\sim 3400\text{ cm}^{-1}$ region. Vibration bands corresponding to calcium silicates are present around ~ 1010 and 930 cm^{-1} . Further, a secondary vibration region of calcite appears around ~ 2930 and 2850 cm^{-1} [36]. C-vibration bands (C–O) are observed around $\sim 1500\text{--}700\text{ cm}^{-1}$ region [31]. Reflections around $1100\text{--}400\text{ cm}^{-1}$ are assignable to vibration bands of Si (Si–O and Si–O–Si) and P (P–O and P–O–P).

3.2. X-ray diffraction

Fig. 2a–c shows the XRD patterns obtained for three absorbents investigated viz., (a) metakaolin (b) tamarind nut carbon (c) dates nut carbon, respectively. It can be seen from the XRD profile of metakaolin that the intensity of the reflections are significantly high indicating highly crystalline nature of the sample. The peak signatures corresponding to silicates, calcites and aluminates are also present in the spectrum (marked in the figure). The orderly crystalline characteristic of the sample could be beneficial to be an efficient absorbent as the regular crystalline pattern would entrap the organic species at large volume. This fact is well reflected from the experimental results. In the case of the carbon made out of tamarind nuts (Fig. 2b) also the XRD peaks are of high intensity indicating highly crystalline nature of the sample. The peak signatures for calcite and silicates could be seen. However, in the case of dates nut carbon (Fig. 2c) the degree of crystallinity is low as could be evident from the broad spectrum of XRD reflection. Further, dates nut carbon sample exhibits few resolved peak signatures corresponding to silicates. The low order of crystallinity makes it to be a poor absorbent and this fact is supported from the experimental data.

3.3. SEM

Scanning electron micrograph images of the absorbents were obtained in order to understand its surface morphological characteristics. Figs. 3–5 illustrate SEM images of metakaolin, tamarind nut carbon and dates nut carbon particles before (a) and after (b) usage as adsorbent. The samples were exposed for 300 h of adsorption in the effluents. Over the adsorption period, it can be seen that, the morphology of the particles had undergone remarkable physical disintegration. The primary particles of metakaolin (Fig. 3a) present in a more integrated and clumsy form while the other two (Figs. 4a and 5a) are of flakes like morphology with inscribed cracks on it. Metakaolin particles had disintegrated to a larger degree (Fig. 3b) after the usage as adsorbent thereby increasing the active surface area. As it is evidenced from the appearance of micro and sub-micro pores which are potential features for an efficient adsorbent. This fact is ratified from the superior adsorbing performance exerted by

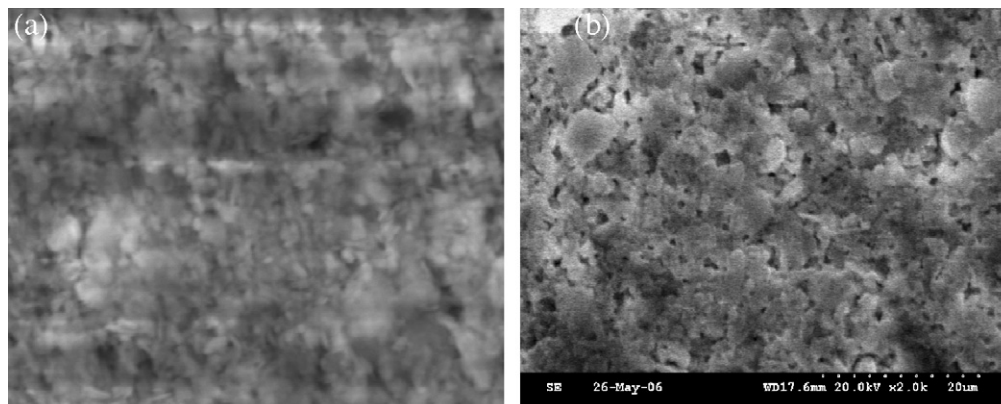


Fig. 3. SEM images of metakaolin particles (a) before and (b) after usage as adsorbent.

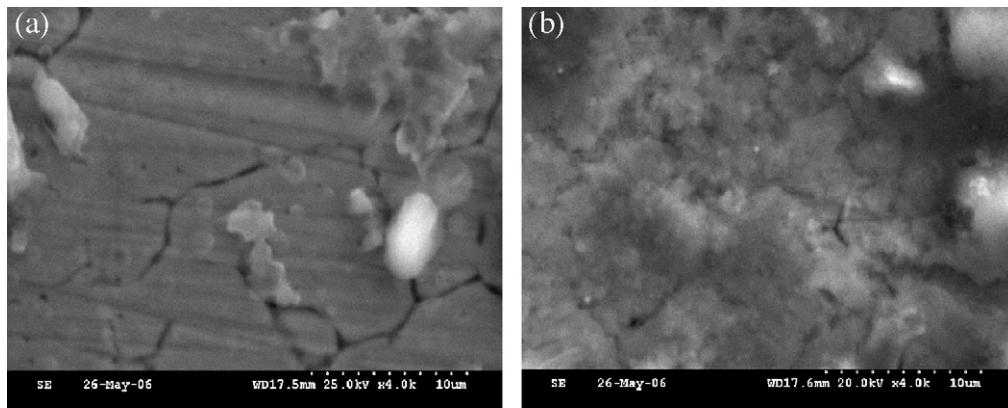


Fig. 4. SEM images of tamarind nut carbon particles (a) before and (b) after usage as adsorbent.

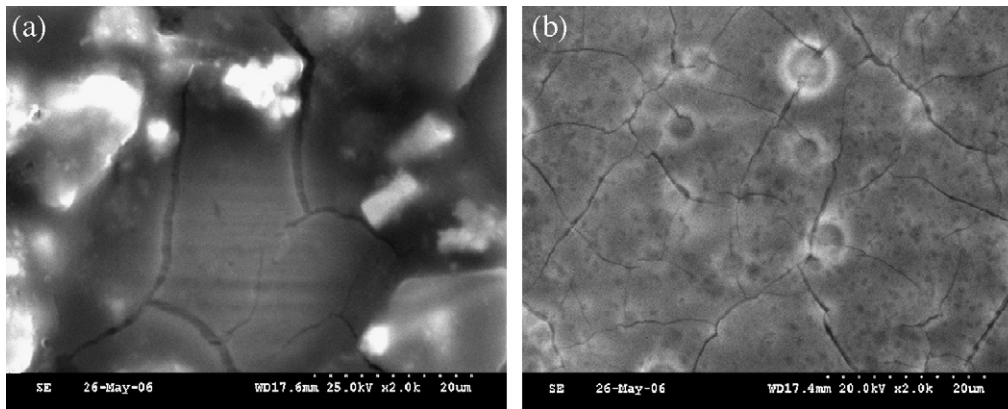


Fig. 5. SEM images of dates nut carbon particles (a) before and (b) after usage as adsorbent.

this material (Table 2) than the other. Conversely, the morphology of dates nut carbon (Fig. 5b) convincingly depict that the order of disintegration is lesser than tamarind nut carbon (Fig. 4b) after usage as adsorbent. Undeniably the flakes had cleaved further; however, absolute disintegration is scarce. These observations are well supplemented by the poor adsorption performance exhibited by these materials over the tested 300 h of operation.

3.4. Effect of contact time

In any batch adsorption system, contact time plays a vital role in the reduction of COD. The absorption increases with increase in time and reaches saturation according to its capability. Table 2 depicts the reduction efficiency of COD of different adsorbents with respect to contact time ranging from 30 to 240 min at 1 g l^{-1} of adsorbent concentration. The efficiency of COD reduction for the three adsorbents are of the order metakaolin > tamarind nut > dates nuts. It is observed that the removal of COD from the sugar industrial effluent increases gradually with increase in contact time and ceases after certain span of time and is shown in Fig. 6. Among the three investigated adsorbents, the maximum efficiency (79%)

of COD reduction was observed with metakaolin in 180 min. In the case of tamarind nut carbon, the maximum efficiency of COD reduction was 74% in 180 min of contact time. Dates nut carbon, depicts maximum efficiency as 73% in 150 min. The superior performance exerted by metakaolin may be attributed to the orderly crystalline nature of the material and the clumsy morphological characteristics with micro inter-granular orientation enable better absorption behaviour. On the other hand, the flakes like morphology with adorned cracks of tamarind nut carbon and dates nut carbon do no good.

Table 2
Effect of contact time on COD reduction efficiency of different adsorbents at a dosage of 1 g l^{-1} .

Adsorbent	Time (min)							
	30	60	90	120	150	180	210	240
Metakaolin	20	40	45	52	69	79	79	79
Tamarind nut carbon	15	35	40	48	66	74	73	74
Dates nut carbon	15	33	39	45	73	70	73	73

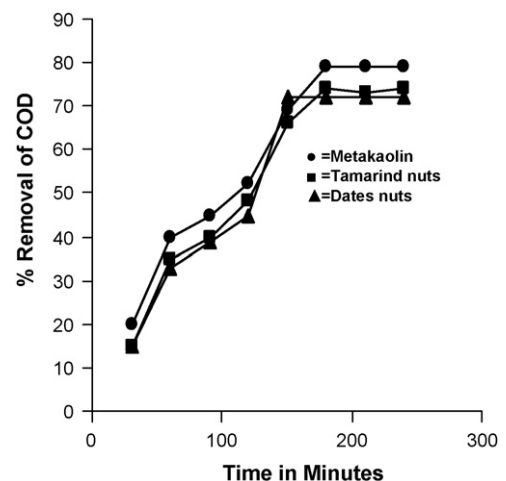


Fig. 6. Effect of contact time on COD removal.

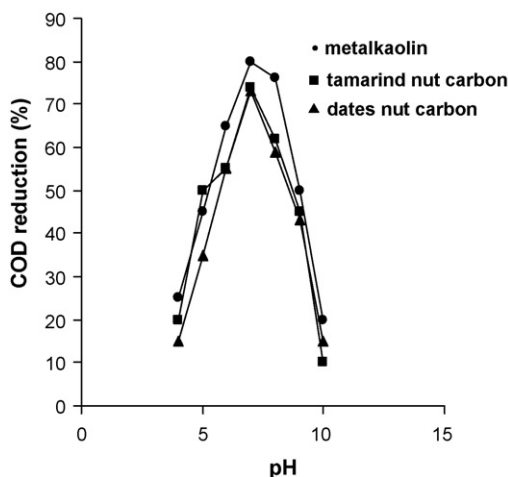


Fig. 7. Effect of pH on COD removal.

3.5. Effect of concentration

Table 3 presents the effect of concentration of adsorbents (varied from 100 to 800 mg l⁻¹) on reduction efficiency of COD at the optimum contact time. It has been observed that there is an increase in reduction efficiency of COD with increase in concentration of the adsorbent in all the cases. The reduction efficiency of COD reaches a maximum value and remains unchanged thereafter irrespective of increase in adsorbent concentration. The reduction efficiency of COD with metakaolin increases from 25% to 78% with the increase in adsorbent concentration from 100 to 500 mg l⁻¹ while tamarind nut carbon exhibited 25–74% reduction efficiency with the concentration variation from 100 to 600 mg l⁻¹. Dates nut carbon shows least reduction efficiency as 15% at 100 mg l⁻¹ and a maximum of 72% at 600 mg l⁻¹ of adsorbent concentration. The superior performance of metakaolin (78%) at 500 mg l⁻¹ is attributed to the increased availability of the active sites due to its positive physical feature as is evident from XRD and SEM studies while the physical characteristics of tamarind nut carbon and dates nut carbon are unfavourable.

3.6. Effect of pH

The solution pH plays a significant role in the adsorption. The effect of pH on reduction efficiency of COD in sugar industrial effluent with metakaolin, tamarind nut carbon and dates nut carbon is shown in Fig. 7. The reduction efficiency was measured with varying pH (4–10) at the optimized contact time and concentration of the respective adsorbent. It is evident from Fig. 7 that in all the cases reduction efficiency of COD reaches maxima at neutral pH and falls thereafter. Further, metakaolin demonstrates the highest reduction efficiency of 80% followed by tamarind nut carbon (75%) and dates nut carbon (73%).

Table 3
Effect of concentration on COD reduction efficiency of different adsorbents at an optimum contact time.

Adsorbent	Concentration (mg l ⁻¹)							
	100	200	300	400	500	600	700	800
Metakaolin	25	45	50	55	78	78	77	78
Tamarind nut carbon	25	40	46	52	60	74	74	74
Dates nut carbon	15	32	42	49	58	72	72	72

3.7. Adsorption isotherms

The adsorption data were analyzed and fitted to the Freundlich adsorption isotherm model [37]. The experimental data followed Freundlich adsorption isotherm confirming the adsorption behavior of the investigated materials as potential candidates to use for the reduction of COD from sugar effluents [38]. The adsorption data also confirms to Langmuir isotherm [39] showing that the studied adsorbents exhibit favourable adsorption behaviour [40]. Further, equilibrium constants from Langmuir expression indicates that metakaolin possesses better adsorption characteristics than tamarind nut carbon and dates nuts carbon.

4. Conclusion

An attempt has been made to identify an efficient and low cost adsorbent to treat sugar industrial effluent. Metakaolin, tamarind nut carbon and dates nut carbon are investigated as adsorbents with varying conditions to understand its functionality after initial characterization through FTIR, XRD and SEM analysis. FTIR spectra of metakaolin shows three large regions where the main vibration and deformation bands of Si–O, Si–O–Si, Al–O, Al–O–Al, Ca–O, Ca–O–Ca and OH are concentrated. FTIR spectra of tamarind nut carbon and date nut carbon depict the bands for silicates, calcites, phosphates etc. Further, XRD reflections show that the samples metakaolin and tamarind nut carbon are highly crystalline in nature. However, in the case of dates nut carbon the degree of crystallinity is of low order. The primary particles of metakaolin are present as agglomerated and clumsy form while the other two are of flakes like morphology with inscribed cracks on it. Over the adsorption period, metakaolin particles have disintegrated to a larger degree after the usage as adsorbent thereby increasing the active surface area. The maximum reduction efficiency of COD in sugar industry effluent was obtained using metakaolin as an adsorbent (79%) while; tamarind nut carbon and dates nut carbon show 74% and 73%, respectively. The minimum contact time to get maximum efficiency is found to be 180 min in the case of metakaolin and 150 min for the other adsorbents. The minimum concentration required to derive maximum reduction efficiency of COD at the optimum contact time is determined. The minimum concentration is found to be 500 mg l⁻¹ for metakaolin and 600 mg l⁻¹ for tamarind nut carbon and dates nuts carbon. All the adsorbents show maximum absorption efficiency at neutral pH. Further, the adsorbents obey the Freundlich and Langmuir adsorption isotherms and the equilibrium constant from Langmuir expression indicates that metakaolin possesses better adsorption characteristics than tamarind nut carbon and dates nuts carbon. Hence, it can be concluded that metakaolin derived from natural material could be used as an efficient low cost adsorbent for treating sugar industrial effluent for reduction of COD.

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