



Adsorption of Xylenol Orange on *Kigelia Africana* and *Melia Azedarach* Fruits Based Adsorbents from Aqueous Solution

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Abstract - Two types of low cost adsorbents were prepared from fruits of *Kigelia africana* (KA) and *Melia azedarach* (MA) trees. Adsorption of xylenol orange dye on these adsorbents was studied varying the initial concentration, solution pH, contact time and adsorbent dose. Equilibrium was achieved within the first 15 minutes contact time in both the cases. Adsorption data of xylenol orange on KA and MA adsorbents generally followed Temkin model at lower solution pH (3, 7) and Freundlich model at higher solution pH (9) values. KA and MA adsorbents showed comparable adsorption efficiency for xylenol orange with that of a commercial activated carbon. Amount of xylenol orange adsorbed at equilibrium (q_e) remained almost the same till pH 7 and decreased on increasing pH of the solution to 9. It is observed from the adsorption studies that these two plant waste based low cost adsorbents have significant dye removal capacity in the pH range 3 – 7.

Key words: Xylenol orange, adsorption, *Kigelia Africana*, *Melia azedarach*

INTRODUCTION

Colour is the first and visible contaminant in water [1] and the presence of dyes in water interferes with the light absorption and this further affects the bacterial growth [2]. A variety of low cost absorbent materials such as rice husk [3], chitin [4], inorganic and organic industrial wastes [5], banana and orange peel [6], neem saw dust [7], agricultural waste [8], silica gel [9] and waste sugarcane bagasse, saw dust, charcoal [10] and peanut hull [11] were utilized for the removal of dyes from aqueous solution. Polymer matrix and neem husk carbon were used as adsorbents [12] and [13] for the removal of xylenol orange from aqueous solution. Xylenol orange, [3,3-bis-N, N, bis-(carboxymethyl) aminomethyl-o-cresolsulfonephthalein] (Figure 1) is an excellent complexometric indicator and potentiometric reagent used for the determination of many metal ions in the laboratory. Effluents from xylenol orange

manufacturing industries and laboratories pollute water bodies. Xylenol orange present in the water bodies further attracts heavy metals and causes various ailments to both humans and aquatic animals. Careful examination of the literature reveals that not much work is reported on the adsorption of xylenol orange on low cost adsorbents from aqueous solution and hence the present study was undertaken. The main objective of this study is to investigate the suitability of KA and MA based adsorbent materials in the removal of xylenol orange dye from aqueous solution at different pH values.

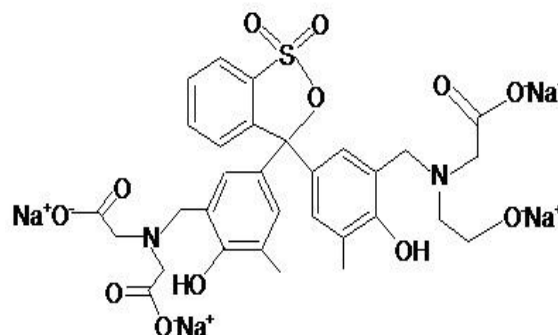


Figure 1: Structure of Xylenol orange

MATERIALS AND METHODS

Adsorbents

MA fruit based adsorbents: About 5kg of matured fallen fruits of MA tree were collected from a park situated in Mohali, Punjab (India). Fruit pulp was removed by crushing and seed kernels were washed thoroughly with water. Air dried seed kernels were powdered in a mechanical mill and 100g of seed powder was mixed with 100ml of 1N H₂SO₄. This mixture was heated on a stirrer cum water bath for 6 hours maintained at 80°C. Later, this acid activated sample was filtered, washed repeatedly with tap water and finally with distilled water. Sulphate ions free MA powder was further dried in an electric oven for 6 hours

at 100°C. Cooled sample was labeled as MA fruits based adsorbent and was stored in an air tight container. 25g of this MA adsorbent was further mixed with 50ml of 0.1N KOH solution and shaken for 30 minutes in a mechanical stirrer. After 30 minutes, the slurry obtained was washed repeatedly with tap water till solid material was free from OH⁻ and finally with distilled water. KOH treated MA adsorbent (will be addressed as base treated MA adsorbent) was dried in electric oven at 100°C for 6 hours, cooled and stored in an air tight container for further use.

KA fruit based adsorbents: KA belongs to bignoniaceous family. Mature ripe fruits were collected from Punjab Engineering College campus, Chandigarh. Fruits were washed with water, cut in to small pieces and air dried in the open for a few days. Further dried in an electric oven at 110°C for 72 hours and powdered in a mechanical mill. 100g of powdered material was taken in a 500ml beaker. 250ml of 1:1 H₂SO₄ (v/v) was added. The mixture of fruit powder and sulphuric acid was stirred well and heated on an electric oven maintained at 80°C for 24 hours. Contents of the beaker were stirred once in an hour. The slurry was filtered and the solid material obtained was washed thoroughly with tap water and finally with distilled water. Dried KA fruit powder material was stored in air tight container for further use.

Chemicals and Reagents

All chemicals used in these investigations were purchased from Ranbaxy India Limited except xylenol orange which was procured from Aldrich, India. Solution pH was adjusted using NaOH and HCl solution. A stock solution of 1000mg/L was prepared (90% content, Aldrich India) and was employed in the preparation of working standards.

Analysis of xylenol orange

Analysis of xylenol orange was carried out with visible spectrophotometer (Spectronic 20 D⁺ of Bosch & Lamb) at 3 different solution pH values. Readings were taken at 488nm for xylenol orange with solution pH 3, 502nm for pH 7 and 508nm for pH 9, as maximum adsorption occurred at these wavelengths.

Equilibrium adsorption studies

Equilibrium adsorption experiments were performed in duplicate by adding 0.1g of adsorbent to labeled 250ml reagent bottles. Xylenol orange solutions of various initial concentrations (C₀), pH 5 ± 0.1, were equilibrated at 25 ± 0.5°C by shaking the capped bottles for 30 minutes on a horizontal thermo stated water bath cum shaker (Popular Instruments, Ambala, India) at 100rpm. Preliminary experiments had indicated that equilibrium could be reached within first 15 minutes. At the end of this period, equilibrium concentration C_e of the dye in the supernatant liquid was determined using spectrophotometer.

Initial dye concentration studies

Xylenol orange dye solutions (50ml) having different initial concentrations were taken in a series of 250ml stoppered conical flasks and 0.01g of adsorbent samples was added and the suspensions were shaken in a thermo stated water bath for an hour. After an hour, a portion of the clear supernatant liquid was withdrawn and analyzed for the equilibrium concentration of xylenol orange in solution.

Contact time studies

50ml of xylenol orange dye solution (20mg/L) was taken in 250ml reagent bottle and the solution was adjusted to pH 5 and 100mg of MA or KA based adsorbents were added to it. This adsorbent adsorbate slurry was stirred well and allowed to equilibrate in a thermo stated water bath for varying period of time interval. The temperature of the water bath was maintained at 25±2°C and the clear liquid was drawn after the stipulated time period and analyzed for xylenol orange dye concentration with Spectronic 20 D⁺ spectrophotometer.

Adsorption dose studies

50, 100, 150 and 200mg of adsorbent samples were added to 50ml of pH adjusted xylenol orange solutions taken in 250ml reagent bottles. Adsorbent adsorbate suspensions were kept in a thermo stated water bath cum shaker well beyond the equilibrium. Thereafter, clear supernatant solutions were drawn and analyzed for xylenol orange concentration with Spectronic 20 D⁺ spectrophotometer.

Determination of zero point of charge (pH_{ZPC})

5 gm of adsorbent sample was taken in a 250 ml stoppered conical flask and 100ml of CO₂ free demineralized water was added. The suspensions were shaken occasionally for 24 hours. The pH of supernatants obtained by centrifugation was assayed using microprocessor based pH meter (Century model 931, India).

RESULTS AND DISCUSSION

Figure 2 and 3 illustrate matured *Kigelia Africana* and *Melia Azedarach* trees with fruits respectively. *Kigelia Africana* and *Melia Azedarach* fruits based adsorbents were characterized by FTIR, SEM and surface studies. Elemental composition of KAFP adsorbent material is presented in table 1. FTIR figures of KA and MA adsorbents are given in figures 4 and 5 respectively. SEM figure of MA adsorbent sample was shown in figure 6. Surface areas of MA and base treated MA adsorbents were found to be 132.3 and 156.4 m²/g respectively. Zero point charge of MA and base treated MA (pH_{ZPC}) were 3.7 and 4.2 respectively.



Figure 2: Kigelia African tree



Figure 3: Melia Azedarach tree

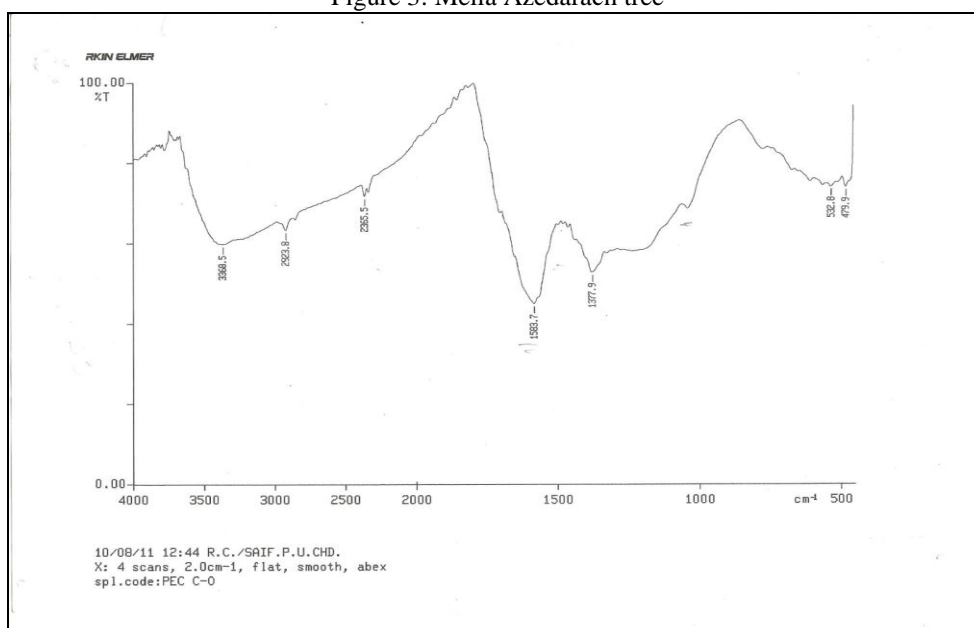


Figure 4: FTIR spectrum of KA adsorbent

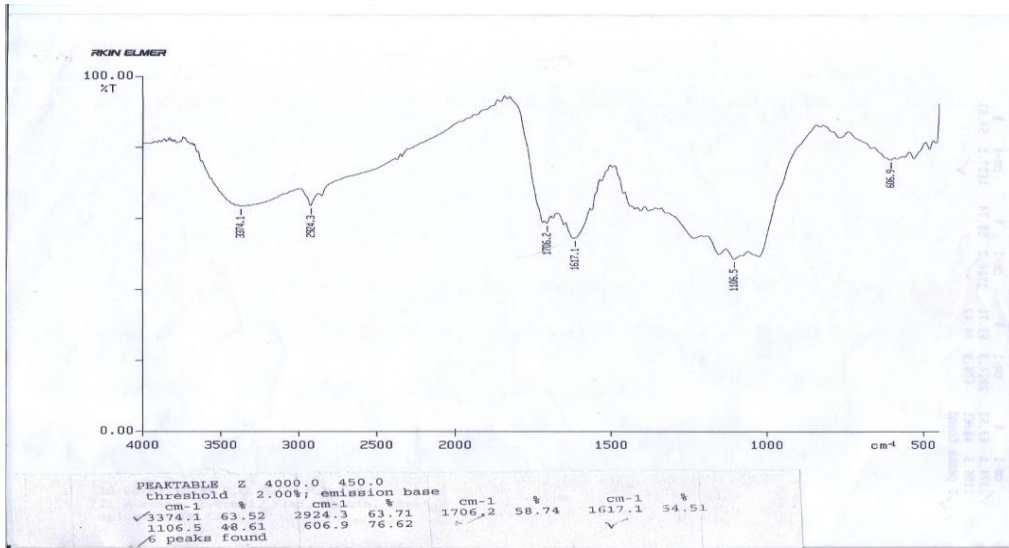


Figure 5: FTIR spectrum of MA adsorbent

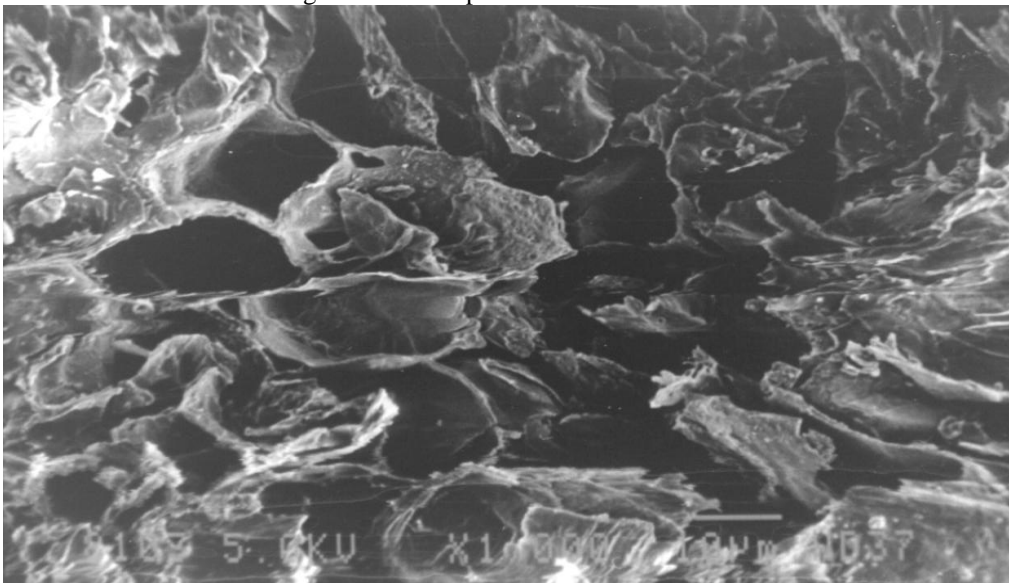


Figure 6: SEM f of MA adsorbent

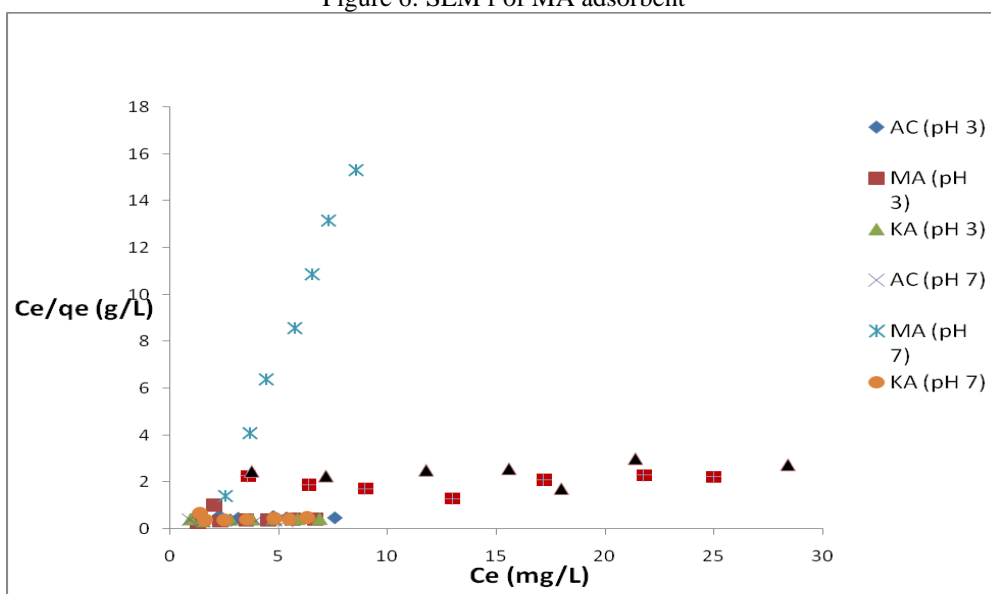


Figure 7: Linear Langmuir plots for the adsorption of xylene orange on various adsorbents at different solution pH conditions

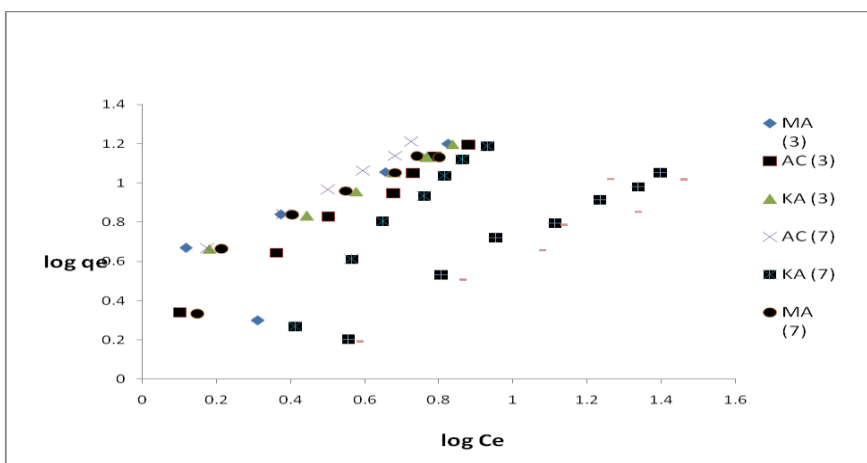


Figure 8: Linear Freundlich plots for the adsorption of xylenol orange on various adsorbents at different solution pH conditions

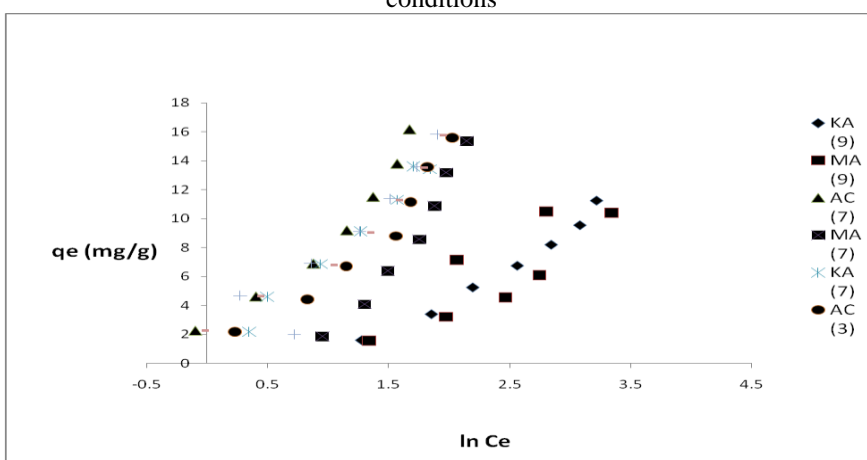


Figure 9: Linear Temkin plots for the adsorption of xylenol orange on various adsorbents at different solution pH

FTIR data of KA and MA adsorbent samples (cf. Table 2) infer the presence of carboxyl, carbonyl surface groups etc. Adsorption of xylenol orange on commercial activated carbon (AC), MA and KA adsorbents at solution pH 3, 7 and 9 was investigated. The adsorption data obtained was analyzed with Langmuir, Freundlich and Temkin adsorption isotherm equations. Linear isotherm plots for all three adsorbents at all three solution pH values are shown in figures 7 – 9. Adsorption isotherm constants calculated from the linear plots are given in Table 3. Adsorption data of xylenol orange dye at solution pH 7 on MA adsorbent fits well in Temkin adsorption isotherm equation. In the case of activated carbon and KA adsorbents, the experimental data fits well in Freundlich and Temkin adsorption model respectively. The results indicate that adsorbent adsorbate interactions exists in the case of xylenol orange adsorption on KA/MA adsorbents. When the initial xylenol orange concentration at solution pH 7 was increased from 10mg/L to 70mg/L, the amount adsorbed on MA adsorbent increased from 1.85mg/g to 15.36mg/g while, it increased from 2.15mg/g to 13.42mg/g in the case of KA adsorbent under similar conditions. Adsorption capacity of these two low cost adsorbents was compared with commercially activated carbon. It was observed that MA and KA showed

comparable adsorption capacity with that of activated carbon.

Table 1: Elemental composition of KA adsorbent

Compound	% by weight	Compound	% by weight
SO ₃	9.914	WO ₃	0.324
Fe ₂ O ₃	5.610	K ₂ O	0.210
CrO ₃	2.252	Al ₂ O ₃	0.139
CaO	2.11	P ₂ O ₅	0.127
Total			22.71

Table 2: FTIR peak assignments

KA adsorbent		MA adsorbent	
Wavelength (nm)	Functional group	Wavelength (nm)	Functional group
3374 cm ⁻¹	O-H	3390 cm ⁻¹	O-H

2924 cm^{-1}	C-H stretch	2923 cm^{-1}	C-H stretch	1156 cm^{-1}	C-O	532 cm^{-1}	C-H bending of methylene group
1716 cm^{-1}	C=O	1583 cm^{-1}	Asymm C=O stretch of carboxylate	626 cm^{-1}	C-H bending of methylene group	429 cm^{-1}	C-H bending of methylene group
1667 cm^{-1}	C=C stretch	1377 cm^{-1}	symm C=O stretch of carboxylate				

Table 3: Adsorption isotherm constants for the adsorption of xylenol orange on commercial activated carbon, MA and KA fruit based adsorbents from aqueous solution at pH 7.

Adsorbent	Langmuir isotherm constants			Freundlich isotherm constants			Temkin isotherm constants		
	Q (mg/g)	B (g/L)	R ²	1/n	k	R ²	A	B	R ²
Activated carbon	138.89	51.6	0.235	1.0602	2.705	0.993	1.2687	7.468	0.940
MA	0.4254	1.927	0.995	1.7562	0.395	0.983	0.4105	11.45	0.962
KA	93.46	44.74	0.040	1.0833	2.111	0.911	1.0171	7.37	0.981

Freundlich adsorption isotherm model is the best fit for the data obtained for adsorption of xylenol orange on KA and MA adsorbents from aqueous solution at pH 9 (cf. Table 4). This may be due to the non existence of interactions between xylenol orange, an anionic dye with KA/MA adsorbents at this pH. Adsorption amount increased on increasing the initial concentration of the dye from 10 – 70 mg/L from 1.6mg/g to 11.25mg/g and 1.55mg/g to 10.4mg/g for the adsorption of xylenol orange in the case of KA and MA adsorbents respectively. The adsorption of xylenol orange at pH 3 is comparatively more than that observed at two other pH values on all three adsorbent samples. Adsorption at this pH is probably due to the electrostatic attraction between the anionic dye molecules and protonated adsorbent surface.

Table 4: Isotherm constants for the adsorption of xylenol orange on commercial activated carbon, MA and KA fruit based adsorbents from aqueous solution at pH 9.

Adsorbent	Langmuir isotherm constants			Freundlich isotherm constants			Temkin isotherm constants		
	Q (mg/g)	B (g/L)	R ²	1/n	k	R ²	A	B	R ²
MA	66.225	147.43	0.100	0.9641	0.4582	0.932	0.3761	4.393	0.716
KA	71.94	127.55	0.0946	0.9563	0.5384	0.978	0.3426	4.818	0.976

Equilibrium was achieved before first 15 minutes in both the cases. More than 80% removal was achieved with MA adsorbent and the complete removal was possible with KA adsorbent at this pH. The adsorption of xylenol orange on all three adsorbents is comparatively maximum at pH 3 as the surfaces of adsorbents tend to be positively charged and the electrostatic attractions between the positively charged adsorbent surface and the anionic dye is the main reason behind the adsorption. KA and MA adsorbents are acidic in nature and their pH_{ZPC} was found to be 3.2 and 4.5 respectively. This is probably the reason behind the slight decrease in the adsorption beyond pH values higher than pH_{ZPC} .

Table 5: Adsorption isotherm constants for the adsorption of xylenol orange on commercial activated carbon, MA and KA fruit based adsorbents from aqueous solution at pH 3.

Adsorbent	Langmuir isotherm constants			Freundlich isotherm constants			Temkin isotherm constants		
	Q (mg/g)	B (g/L)	R ²	1/n	k	R ²	A	B	R ²
Activated carbon	63.69	37.05	0.4995	1.094	1.7502	0.993	0.8809	7.4058	0.927
MA	40.32	22.94	0.0379	1.0013	2.325	0.673	0.0309	7.7096	0.854
KA	102.041	38.09	0.3367	0.9314	2.645	0.985	1.284	6.5020	0.946

CONCLUSION

Experimental results support that KA and MA fruits based adsorbents have significant adsorption capacity for xylenol orange. Adsorption efficiencies of these two adsorbent materials are comparable with that of commercially available activated carbon. More work is required to investigate the possibilities for getting comparatively more stable xylenol orange impregnated KA and MA fruits based adsorbent materials.

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