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Preparation and characterizations of microwave assisted activated carbons from industrial waste lignin for Cu(II) sorption

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ABSTRACT

Industrial waste lignin was used to prepare activated carbons by zinc chloride activation by using different impregnation methods (with and without microwave treatment) at 500–800 °C. Effect of impregnation ratio was also studied. The textural properties of the samples were investigated by means of SEM, cryogenic N₂ adsorption, whereas, surface chemistry was probed through FTIR and modified Boehm's titration method. Textural properties and surface chemistry of activated carbons were found to be strongly depending on the activation temperature, impregnation ratio and impregnation method. BET surface area, total pore volume, micropore volume and micropore area increased with increase in activation temperature up to 600 °C and then decreased on further increase in temperature. Maximum surface area of 1172.2 m²/g, total pore volume 0.640 cm³/g, and total oxygen surface functional groups 3.14 meq/g was observed in case of microwave treated sample at activation temperature 600 °C and impregnation ratio 1:1.5 whereas, for the sample obtained by simple impregnated method the above said values are 917.5 m²/g, 0.506 cm³/g and 2.66 meq/g respectively, using same precursor and conditions. The adsorption of Cu²⁺ from aqueous solution on samples could be favorably described by Langmuir isotherm, and the adsorption kinetics was well fitted in pseudo-second-order model. Results revealed usefulness of microwave treatment in influencing BET surface area, micropore surface area and type and extent of surface oxygen functional groups and ultimately greater uptake capacity.

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1. Introduction

Activated carbons (ACs) are an amorphous form of carbon characterized by high internal porosity and consequently high adsorbability. It has wide applications like removal of organic, inorganic pollutants from drinking water and as catalyst support [1]. Growing environmental issues demand for locally prepared low cost activated carbons (ACs).

Adsorption capacity of activated carbon strongly depends on its porosity and surface area. Textural property of ACs depends on method of preparation and starting material [2]. Generally, two methods are used for the preparation ACs via, physical and chemical activation. During physical activation, the raw material is carbonized first at high temperature and then it is activated by CO₂ or steam under pressure to increase porosity and surface area of ACs. In chemical activation both carbonization and activation takes place simultaneously, in which raw material is first impregnated with activating chemical and then carbonized at desired

temperature that varies according to activating chemical used [1].

According to Gigis and El-Hendawy [3] chemical activation inflicts the physical and chemical modification on the original structure by penetrating particle swelling and partial dissolution of biomass, bond cleavage and reformation of new polymeric structure resistant to thermal decomposition. ACs with high surface area and porosity can be prepared from many ligno-cellulosic materials such as coal, coconut shell [2,4] wood, agricultural waste [5,6] sawdust, cashew nut shell [7], hazelnut shell [8], and jackfruit peel waste [9]. Researcher's interest is growing in use of other low cost and abundantly available ligno-cellulosic material as a precursor for the preparation of ACs [10–13]. Adsorption capacity of prepared ACs especially for metal ion depends on number of acidic/polar oxygen functional groups present on its surface. Different oxidizing post treatments can be conducted on ACs to increase surface functional groups. Yin et al. [14] recently reported several techniques to modify surface functional groups for enhancing the capability and selectivity for adsorption from aqueous medium.

Application of microwave heating technology for regeneration of ACs from industrial waste is investigated with good results [15–20]. Main difference between microwave and conventional heating is, the way of heat generated. In conventional technique

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heat transfer takes place by conduction but in microwave heating microwave radiation supply energy directly to carbon skeleton at molecular level. The microwave energy is directly converted into heat by dipole–dipole rotation and friction within matrix. In the recent past, microwave energy has been widely used in several applications for both research and industrial processes. Microwave energy changes several properties of carbonaceous material [21,22]. Nabais and Carrott [16] studied the modification in surface chemistry of activated carbon fiber by microwave heating very effectively.

Paper industries invariably produce lignin material as a recurring waste material in huge quantities and its disposal is a general problem. Several utilization techniques are under investigation but they mostly lack in wholesome utilization aspect. Many of the black liquors can be easily treated to obtain solid lignin mass. In addition, variety of raw materials used during the pulping process and the type of pulping process influence the finally available chemical nature of solid lignin. As a result, different sources and type of pulping method provides a different kind of lignin material [23]. Scientists have worked on variety of raw materials, variety of activating chemicals and variety of treatments like heat or microwave but mostly they involve cellulosic materials or ligno-cellulosic materials. Reporting adsorption studies on variety of organic molecules and metal ions [24]. In a present case, cellulosic material is practically absent in a raw material therefore it provides predominantly phenylpropane type of organic aromatic skeleton. Its degradative carbonization is likely to provide some stabilized structure with a polarity to exhibit weak ion exchange type of activity and thus giving rise to ability to uptake metal ion to the resultant carbonaceous material.

Recently many workers [1,24–31] reported use of the Kraft lignin for the preparation of highly porous activated carbon having surface area ranging from 500 to 2000 m²/g and total pore volume from 0.2 to 1.3 cm³/g. All workers have concluded that the surface area and pore volume are strongly depend on the activating chemical used, impregnation ratio of lignin to activating chemical and activation temperature. We chose the Cu(II) as a common representative metallic contaminant as an adsorbent to determine effect of microwave treatment on adsorption capacity of prepared ACs, as several workers have used Cu(II) ions as a adsorbate on ACs prepared from lignin [24] and from other biomaterials and fly ash [32–44].

Since most of the reports involve use of cellulosic material in production of ACs, present work focuses on production of ACs from purified industrial waste lignin obtained from pulp and paper industry, which is practically free from carbohydrate material. It devotes to examine effect of microwave treatment on the surface properties as well as on adsorption capacity of prepared ACs to remove Cu(II) ion from aqueous solution.

2. Experimental

2.1. Material used and procedure

All reagents used were of analytical grade supplied by Merck India. Black liquor obtained from Kraft pulping process was supplied by Simplex paper mills Gondia (M.S.) India. It was acidified by dilute hydrochloric acid and allowed to precipitate. After filtration, lignin was washed with plenty of water to remove water-soluble impurities, and then dried in oven for 12 h at 80 °C. Dried lignin was dissolved in 1,4-dioxane and filtered to remove insoluble impurities. Solvent from filtrate was recovered through vacuum distillation technique and a pure lignin was obtained as a residue. It was then used for the preparation of activated carbons (ACs).

2.1.1. Preparation of microwave treated activated carbons (ACM)

Microwave treated activated carbons were prepared according to procedure given by Yagmur et al. [6]. Purified lignin was mixed with zinc chloride (activating agent) to the desired lignin/zinc chloride ratio ranging from 1:1 to 1:2 (w/w) as shown in Table 1 and appropriate volume of water to prepare uniform semisolid paste, which was placed in 250 ml round bottomed flask. The flask-containing sample was properly fitted in modified microwave oven (Kenstar model, 2.45 GHz, with an arrangement to attach adapter and condenser on outside) and immediately subjected to microwave treatment for 4 min. Immediately after microwave treatment the contents in the flask were removed and subjected to heat treatment in a programmable furnace in identical manner as given below.

2.1.2. Activated carbon by simple method (ACS)

Another sample impregnated with zinc chloride for 48 h at room temperature was not subjected to microwave energy treatment.

All samples those, which were treated with and without microwave treatment, were carbonized in a closed stainless steel reactor placed in programmable furnace under self-generated environment. Each sample was held for 1 h in furnace at desired temperature as shown in Table 1. After cooling, the degraded carbonaceous residue was removed, washed successively with dilute hydrochloric acid and plenty of hot water. Then it was filtered, dried in oven at 105 °C for 24 h.

2.2. Characterization of activated carbons

Proximate and elemental analysis were carried out by using American standard for testing material (ASTM) methods and elemental analyzer (Carlo Erba model 1108) respectively.

Surface chemistry was analyzed by modified procedure based on Boehm's method similar to that of recently reported by Toles et al. [45] was used to quantify total and individual polar/acidic oxygen functional groups (TOFG) on the surface of derived carbons. They involve carbonyl, phenol, lactones and carboxyl's groups and quantified by means of titrating a carbon sample with a series of base solutions of different strengths.

Chemical characterization of functional groups in bulk phase and on surface of the samples was studied by a Fourier transform infrared spectrometer (FTIR-100, Shimadzu) in the range 4000–400 cm^{−1}, using pellets with samples dispersed in KBr.

The surface morphologies of the resultant samples were imaged by using a scanning electron microscope Model (JEOL JSM-6380A).

Textural characteristics were determined by N₂ adsorption at −196 °C on automatic apparatus (ASAP 2000, Micromeritics), and the samples were degassed at 300 °C for 2 h under vacuum before the measurements. The specific surface areas (*S*_{BET}) were estimated by the Brunauere–Emmette–Teller (BET) equation [46], and the total pore volume (*V*_{tot}) was calculated by the adsorption data at *P*/*P*₀ = 0.995. The micropore volume (*V*_{mic}) and mesopore volume (*V*_{mes}) were obtained by applying BJH method. External surface area (*A*_{ext}) is the surface area associated to the non-microporous structure (macroporous and mesoporous).

2.3. Equilibrium metal ion adsorption experiments

To study the effect of microwave treatment on the adsorption capacity of prepared ACs, Cu(II) ion was selected as representative metal adsorbate.

The stock solution of 1000 mg/L of Cu(II) was prepared by dissolving 2.6826 g of CuCl₂·2H₂O in 1000 ml of deionized water which was used in entire experiments after appropriate dilutions.

Effect of pH of solution on adsorption capacity of Cu(II) ion was first determined by contacting 0.1 g of ACs with 100 ml (50 mg/L)

Table 1
Activation conditions and surface characteristics of prepared ACs.

Sample ID	Activation conditions			Yield (%)	BJH						
	T (°C)	Lignin/ZnCl ₂ (w/w)	Impregnation time		S_{BET} (m ² /g)	A_{micro} (m ² /g)	A_{ext} (m ² /g)	V_{micro} (cm ³ /g)	V_{meso} (cm ³ /g)	V_{total} (cm ³ /g)	Average pore diameter (Å)
ACM(1:1)500	500	1/1	4 min	66.51	604.4	502.4	102.1	0.222	0.116	0.335	23.16
ACM(1:1)600	600	1/1	4 min	58.97	993.7	855.1	138.6	0.384	0.165	0.559	21.02
ACM(1:1)700	700	1/1	4 min	58.28	757.2	615.7	141.5	0.269	0.134	0.401	21.14
ACM(1:1)800	800	1/1	4 min	47.26	519.6	447.1	72.4	0.197	0.096	0.288	26.15
ACM(1:1.5)600	600	1/1.5	4 min	60.73	1164	1002	162.4	0.457	0.174	0.640	20.82
ACM(1:2)600	600	1/2	4 min	61.43	1105	969.2	136.1	0.431	0.254	0.695	21.04
ACS(1:1.5)600	600	1/1.5	48 h	60.49	921.2	702.2	218.5	0.329	0.155	0.506	22.48

S_{BET} : specific surface area obtained by BET equation, A_{micro} , A_{ext} : micropore area, external surface area, V_{mic} , V_{meso} , V_{total} : micropore volume, mesopore volume, total pore volume.

solution in 250 ml conical flask at different pH. Stoppered conical flask was then shaken on orbital shaker for 24 h at 28 °C. Amount of Cu(II) ion untaken by ACs was then analyzed using atomic absorption spectroscopy (AAS) (SensAA Dual GBC) after appropriate dilution (using 1% nitric acid).

Adsorption kinetic experiments were performed by contacting 0.1 g ACs with 100 ml Cu(II) ion solution of initial concentration ranging from 20 to 100 mg/L at 28 °C and pH 6. The stoppered conical flasks mounted on orbital shaking machine were withdrawn after contact time of 5, 10, 15, 20, 25, 30, 45, 60, 75, 100, 125, 150, 200, 300, 400, 500, 600, 1200 min and subsequently adsorbent was separated from solution by centrifugation at 4000 rpm for 10 min and concentration at equilibrium was immediately analyzed on AAS.

Adsorption equilibrium isotherm on prepared ACs and commercial activated carbon (CAC) were determined by contacting 0.1 g sample with 100 ml solution of metal ion concentration ranging from 5 to 400 mg/L under the identical conditions for predetermined minimum contact time required to attain equilibrium. All experiments were conducted in duplicate and average values are reported. The difference between replicate was not more than 2%. A blank without sorbent was also maintained to avoid any drift in result due to sorption on the wall of conical flask.

3. Results and discussion

3.1. Surface textural properties

Fig. 1 shows the N₂ adsorption isotherms at −196 °C of simple and microwave treated ACs prepared by zinc chloride activation at different temperatures. According to the IUPAC classification [46] all isotherms exhibits features intermediate between those of type I and II showing significant increase in the adsorption at low P/P_0 values (<0.1), a broad knee and long plateau up to $P/P_0 \approx 1.0$ and extended to small tail. Pointing to porous network formed by micropores, mesopores and relatively small external surface area. Kriaa et al. [24] reported a similar trend for surface development with the activation temperature (200–500 °C) in the preparation of activated carbon derived from Kraft lignin by phosphoric acid activation with maximum BET surface area of 463.5 m²/g obtained at 500 °C.

The N₂ uptake reaches maximum when the activation temperature increases up to 600 °C, and increasing the temperature to 700 °C results in significant decrease of N₂ uptake over the entire pressure range. A further rise in the carbonization temperature to 800 °C does not affect N₂ uptake. On increasing impregnation ratio from 1:1 to 1:2 at 600 °C carbonization temperature in microwave treated sample, the N₂ uptake increases up to impregnation ratio

1:1.5 on further increasing ratio significant decrease in N₂ uptake is observed. Whereas, at impregnation ratio 1:1.5 the sample treated by simple method and carbonized at 600 °C shows significantly lesser uptake of N₂ than all other microwave treated samples carbonized at 600 °C.

Table 1 reports the yields and various textural parameters calculated from N₂ adsorption isotherm at −196 °C and variation of these parameters with the activation temperature are shown in Fig. 2. The yield decreases from 66.51% at 500 °C to 47.26% at 800 °C with increasing temperature. This could be due to progressive loss of carbon at higher temperature. Change in impregnation ratio does not affect the yield % significantly for the samples carbonized at 600 °C, the % yield remains nearly same.

As shown in Table 1, the BET surface area increases with increase of carbonization temperature. It reaches maximum value of 993.7 m²/g at 600 °C, and then decreases on further heating. The noticeable increase of surface area with rise in temperature up to 600 °C may correspond to evolution of compounds produced from cross-linking reaction [47]. At the temperature above 600 °C, the

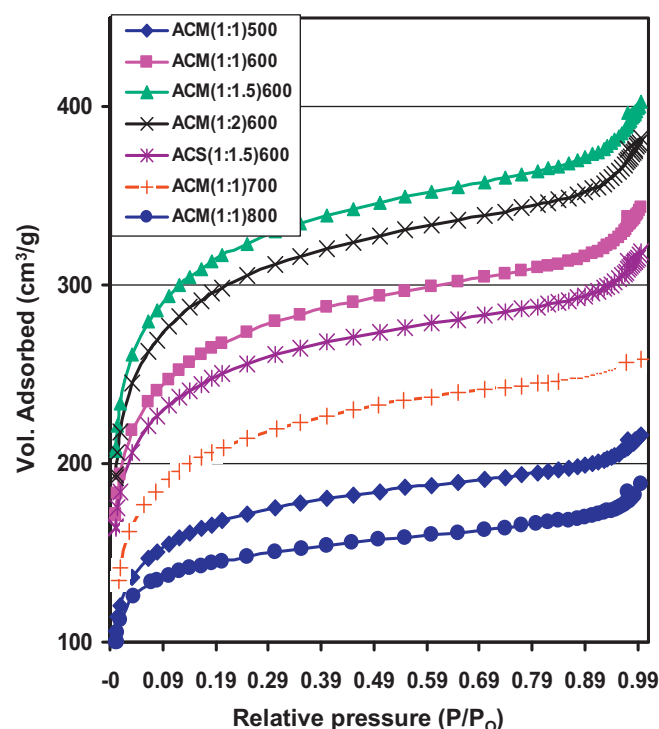


Fig. 1. Nitrogen adsorption isotherm for prepared ACs.

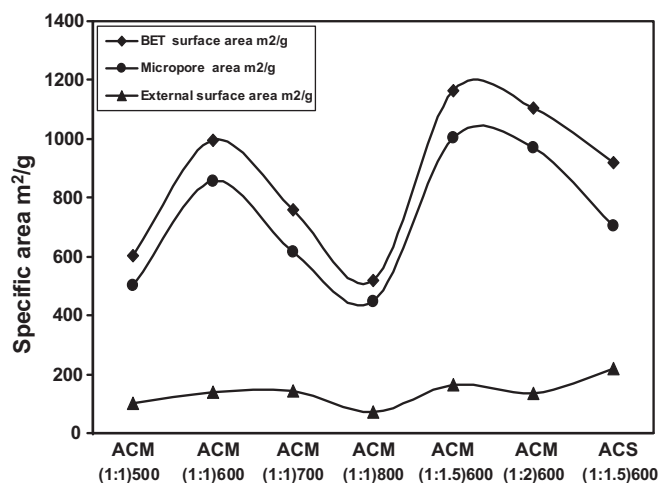


Fig. 2. BET surface area, micropore area and external surface area of prepared ACs.

carbon structure shrinks and the surface area decreases as given in Table 2 this can be explained on the basis of the fact that the removal of carbon atom at high extent of burn-off results in the elimination of pore walls leading to a decrease in surface area [36]. It ultimately forms a denser carbon material with reduced porosity. This may be due to expansion of molten zinc chloride.

Hayashi et al. [1] reported similar results for the surface development with the activation temperature (500–900 °C) in the preparation of activated carbon derived from kraft lignin by zinc chloride activation having maximum BET surface area $\approx 1100 \text{ m}^2/\text{g}$ obtained at 600 °C. It was shown that carbonization temperature 600 °C for ZnCl_2 and H_3PO_4 produced ACs having nearly the same surface area those of commercial activated carbon. It is worthy to note that the present results are quit comparable with that of Gonzalez-Serrano et al. [28] who prepared activated carbon from Kraft lignin having high surface area $\approx 1800 \text{ m}^2/\text{g}$ and micropore volume $1.039 \text{ cm}^3/\text{g}$ at 500 °C carbonization temperature with impregnation ratio of lignin to zinc chloride 1:2.3.

Micropore volume (V_{mic}), micropore area (A_{mic}) and total pore volume (V_{tot}) with activation temperature follow same trend, which was obtained for BET surface area. This indicates that rise in activation temperature produces a progressive porosity development of ACs, and 600 °C be the best temperature in the range studied.

The influence of zinc chloride to lignin ratio on the surface area was also determined. The BET surface areas were 993.7, 1164.4 and $1105.3 \text{ m}^2/\text{g}$ for the ratio 1:1, 1:1.5 and 1:2 respectively. As amount of zinc chloride increases from 1:1 to 1:1.5 the surface area raises and again slightly drops down on increasing ratio up to 1:2. The surface area was maximum ($1164.4 \text{ m}^2/\text{g}$) for the sample activated at ratio 1:1.5 and carbonized at 600 °C.

Microwave treatment shows positive effect on all textural properties over simple treated sample. The ACM(1:1.5)600 obtained by microwave treatment and carbonized at 600 °C shows higher

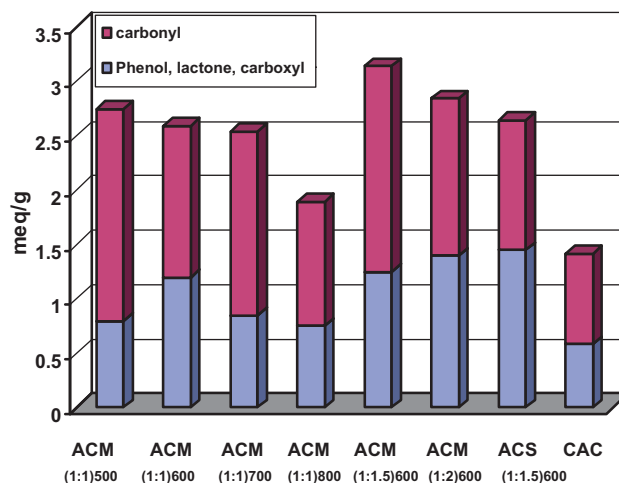


Fig. 3. TOFG determined by modified Boehm's method for ACs prepared by microwave and simple impregnation method at different temperature and impregnation ratio from lignin.

BET surface area ($1164.36 \text{ m}^2/\text{g}$) and micropore area ($1001.93 \text{ m}^2/\text{g}$) than the ACS(1:1.5)600 obtained by simple treatment and carbonized at 600 °C, which shows BET surface area ($917.53 \text{ m}^2/\text{g}$) and micropore area ($702.74 \text{ m}^2/\text{g}$) respectively. Microwave treatment play effective role in improving the surface characteristics of prepared AC. This could be due to fact that microwave selectively interacts with a polar molten zinc chloride making it expand and diffuse through the carbon matrix to the greater extent than which is possible in conventional method. The micropore volume, external surface area, Single point surface area and average pore diameter also found to be higher in case of microwave treated sample.

Yagmur et al. [6] reported a similar trend for surface development with the activation temperature (250–700 °C) in the preparation of activation carbon derived from waste tea by phosphoric acid activation by using microwave treatment. With maximum BET surface area of $1157 \text{ m}^2/\text{g}$ obtained at 350 °C for the sample activated at the impregnation ratio 1:3 (waste tea to phosphoric acid).

3.2. Total oxygen surface functional groups

The total and individual content of surface oxygen functional groups (TOFG) of all prepared ACs determined by modified Boehm's method are illustrated in Fig. 3. During studies on effect of carbonization temperature on TOFG content, we found that amount of TOFG decreases with increasing carbonization temperature. This loss of TOFG may be due to instability of carboxylic and other groups at higher temperatures. However, the content of sodium hydroxide titrable groups i.e. phenol, lactones and carbonyls are found to be more in ACM(1:1)500 than ACM(1:1)600.

Effect of impregnation ratio on content of TOFG shows that, total amount of TOFG is more at impregnation ratio of (1:1.5) 3.14 meq/g

Table 2

Proximate and elemental analysis of lignin, and ACM(1:1.5)600 and ACS(1:1.5)600.

Sample	Proximate analysis (%)				Elemental analysis (%)			
	Moisture	volatile	Fixed carbon	Ash	C	H	N	O ^a
Lignin	3.96	45.1	42.8	8.74	8.74	7.1	0.1	33.5
ACM(1:1.5)600 ^b	–	17.68	68.74	13.58	79.0	4.6	–	16.4
ACS(1:1.5)600 ^b	–	16.09	70.12	13.79	80.9	4.3	–	14.8
CAC ^b	–	22.36	73.83	4.81	89.9	0.8	0.6	8.7

^a Determined from the difference.

^b On dry basis.

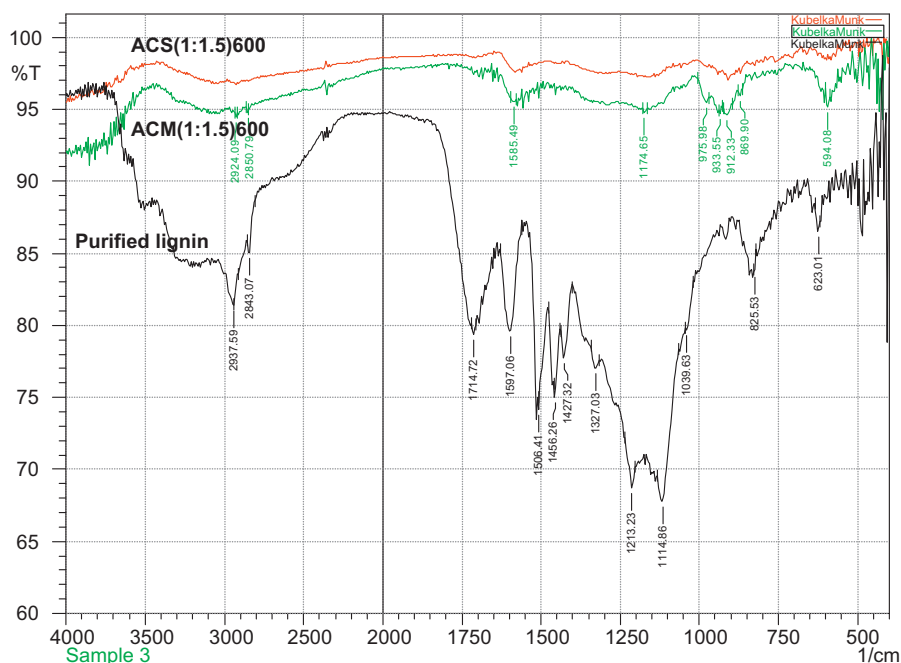


Fig. 4. FT-IR spectra of purified lignin, ACM(1:1.5)600 and ACS(1:1.5)600.

than the (1:1) when ratio increases up (1:2) it again shows slight decrease. Only content of carbonyl groups found to vary considerably with changing impregnation ratio while amount of aqueous sodium hydroxide titrable groups remained unchanged or slightly changed.

At the same impregnation ratio (1:1.5) microwave treated sample ACM(1:1.5)600 shows comparatively higher TOFG (3.14 meq/g) than ACS(1:1.5)600 (2.66 meq/g), but the total amount of aqueous sodium hydroxide titrable groups i.e. phenol, lactones and carbonyl is more in ACS(1:1.5)600 than microwave treated sample.

3.3. Proximate and elemental analysis

Elemental analyses does not show significant difference in ACM(1:1.5)600 and ACS(1:1.5)600 but slight change in percentage volatile and fixed carbon may be due to the structural changes in ACM(1:1.5)600 and ACS(1:1.5)600.

Table 2 shows proximate and elemental analysis of lignin and prepared ACs. Results show that fixed carbon content increases in lignin and prepared ACs in the same order from 42.8% for lignin to 68.74% for ACM(1:1.5)600 and 70.12% for ACS(1:1.5)600. Higher carbon content indicates that aromatic structure becomes dominant after degradation in the presence of zinc chloride. Whereas hydrogen percentage decreases from (7.1%) for lignin to (4.6%) for ACM(1:1.5)600 and (4.3%) for ACS(1:1.5)600. Volatile matter decreased whereas fixed carbon increased. At high temperature, due to pyrolysis, organic substances must have degraded into volatile gases and liquid tar, leaving behind material with higher carbon content as well as lower hydrogen content due to rupture of molecular chain.

The yield (%) of the prepared activated carbons based on initial weight of lignin is given in Table 1. Results show that (%) char yield decreases with increasing carbonization temperature.

3.4. FTIR analysis

Fig. 4 shows the FTIR spectra of purified lignin, ACM(1:1.5)600 and ACS(1:1.5)600. The first peak at 3400 cm^{-1} is ascribed to OH

stretching vibration of hydroxyl group of the lignin. The absorbance at 2923 cm^{-1} arises from C–H stretching and small absorbance at 1506 , 1456 , 1427 , and 1327 cm^{-1} corresponds to aromatic skeletal vibrations, β -O-4 ether bond band at 1114 cm^{-1} . Methoxy group band at 2937 , 2843 , 1456 , and 1427 cm^{-1} , the C=C vibration of aromatic ring at 1514 cm^{-1} , the band at 1600 cm^{-1} which is characteristic of quinoid structure and carbonyl group at 1664 and 1720 cm^{-1} .

After carbonization the all peaks related to C–OH, CH, CH_2 , CH_3 , CO and C=O groups were considerably reduced in prepared ACs. Whereas in ACM(1:1.5)600 comparatively more peak intensity is observed than ACS(1:1.5)600. In the light of action of molten zinc chloride with the organic mass particularly in the presence of microwave irradiation, it is reasonable to accept that after carbonization at same temperature the microwave treated sample developed comparatively more surface functionality which is in agreement with TOFG analysis discussed earlier (in Section 3.2). FTIR spectra for the ACs developed by both the methods shows absorption band between 500 and 850 cm^{-1} that may be assigned to aromatic substitution by aliphatic groups. For ACS(1:1.5)600 low absorption occurred in this region, this result suggests a lower content of substituted aliphatic groups in the aromatic ring in the latter. The bands between 950 and 1300 cm^{-1} is due to super position of signals corresponding to oxygen functional groups like ether, phenol and lactones. The bands between 1400 and 1750 cm^{-1} are preferentially assigned to carboxylic groups, quinones, ketones, lactones, diketones and keto-ester and ketoenol. The ACM(1:1.5)600 and ACS(1:1.5)600 also show a intense peak between 1550 cm^{-1} and 1650 cm^{-1} resulting from C=C stretching vibration in aromatic ring enhanced by polar functional groups.

3.5. Surface morphology

To study the effect of microwave treatment on the surface morphology of ACs the SEM images of ACM(1:1.5)600 and ACS(1:1.5)600 were recorded as shown in Fig. 5(A) and (B) respectively. The lignin used in this work was in the powder form and individual particles of lignin were polygonal in shape with multiple

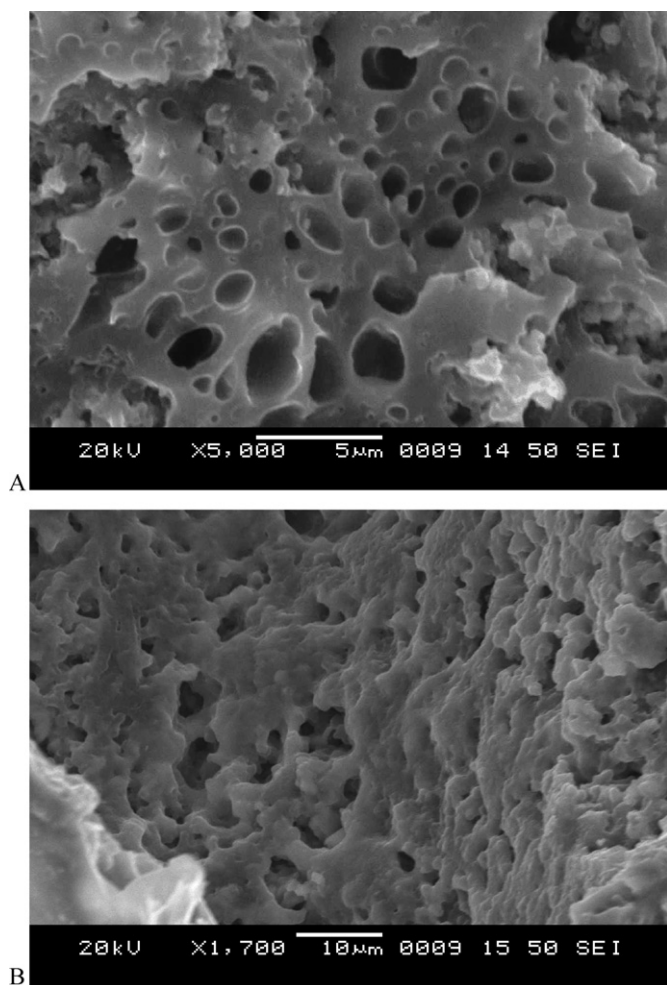


Fig. 5. SEM micrograph of (A) ACM(1:1.5)600 and (B) ACS(1:1.5)600.

conchoidal fracture surface [48] but SEM images of prepared ACs from lignin show that the lignin particle has been softened, melted and diffused into the mass of matrix with number of pores on its surface. These vesicles, micropores and mesopores might have been the result of volatile gases released from the softened lignin matrix during carbonization. SEM image of ACM(1:1.5)600 Fig. 5(A) shows porous surface with number of large and small holes on its surface, cracks, crevices and fair different from Fig. 5(B) which shows smoother surface with irregular, heterogeneous and grainy surface.

3.6. Metal ion adsorption study

One AC from each category viz. ACM(1:1.5)600 and ACS(1:1.5)600 was chosen to know the benefit of microwave treatment over conventional treatment in the formation of ACs. ACM(1:1.5)600 was presumed to be the optimized one from microwave treatment ACs as indicated by greater TOFG and better surface characteristics as discussed in Section 3.2.

Firstly the effect of pH on adsorption capacity of metal ion was studied by contacting the solution of equal concentration (50 mg/L) at different pH ranging from 1 to 7 with ACM(1:1.5)600 and ACS(1:1.5)600 as a pH of solution play important role in efficiency of adsorption of metal ion. Comparison of both the ACs indicated minor difference and nature of curve is very similar as shown in Fig. 6.

However small difference may be due to the change in extent and type of surface functional groups as depicted in Fig. 3 and also

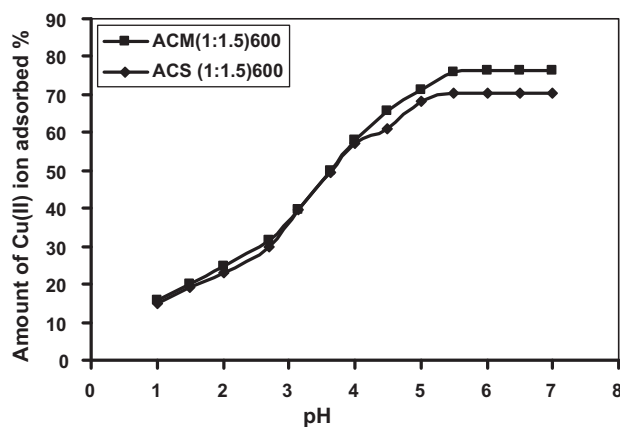


Fig. 6. Effect of pH on adsorption of Cu(II) ion on ACs. $C_0 = 50$ mg/lit, $t = 24$ h, $T = 28^\circ\text{C}$, carbon dose = 1 g/L.

small changes in nature of matrix of ACs (Fig. 5). Adsorption of Cu(II) ion increases gradually from pH 1 to 5.0 then it shows some what constant adsorption at pH 5.5 onward. Nearly about 75% of Cu(II) ion is adsorbed from solution at pH 5.5. Such adsorption trend is attributed to the competition between Cu(II) and proton for the binding site on carbon surface. At low pH an excess of proton compete with Cu(II) resulting in low level of adsorption. The pH dependent of adsorption suggests that Cu(II) ion adsorbed, at least partly according to ion-exchange mechanism [49,50]. However, precipitation of Cu(II) ion occurred at higher pH. Thus to achieve higher adsorption efficiency and to avoid precipitation, all experiments were conducted at pH 6.0

3.6.1. Adsorption kinetics

For kinetic studies only ACM(1:1.5)600 was selected due to its apparent superiority over ACS(1:1.5)600. Kinetic experiments were carried out at various initial concentrations, ranging from 20 to 100 mg/L and at different contact time to determine time required to attain equilibrium. From Fig. 7, it is concluded that rate of metal ion adsorption increases sharply at short contact time and slowed gradually as equilibrium was approached. This behavior may be due to the, availability of initial large number of vacant surface active sites for adsorption and sorption rate is very fast thus rapidly increases the amount of adsorbate accumulated on the carbon surface mainly within the first 3 h of adsorption. Afterward the filling of vacant sites becomes difficult due to repulsive forces between metal ion adsorbed on solid surface and metal ion from solution [51]. According to Liu and Huang [52], two steps adsorption characteristics may be due to the heterogeneity of the surface binding sites on sorbents. Explaining that different binding site had different binding affinities to metal ion and resulted in different binding rates. In order to investigate the mechanism of Cu(II) adsorption on prepared ACs pseudo-first-order, Hameed et al. [53], and pseudo-second-order, Ho and McKay [54], kinetic model were used. The pseudo-first-order rate equation is

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (1)$$

where, q_t and q_e are amount of solute adsorbed per unit of adsorbent mass at time t and at equilibrium. K_1 is the rate constant for pseudo-first-order kinetic equation. Eq. (1) rearranged in linear form,

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad (2)$$

The pseudo-second-order kinetic equation is

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (3)$$

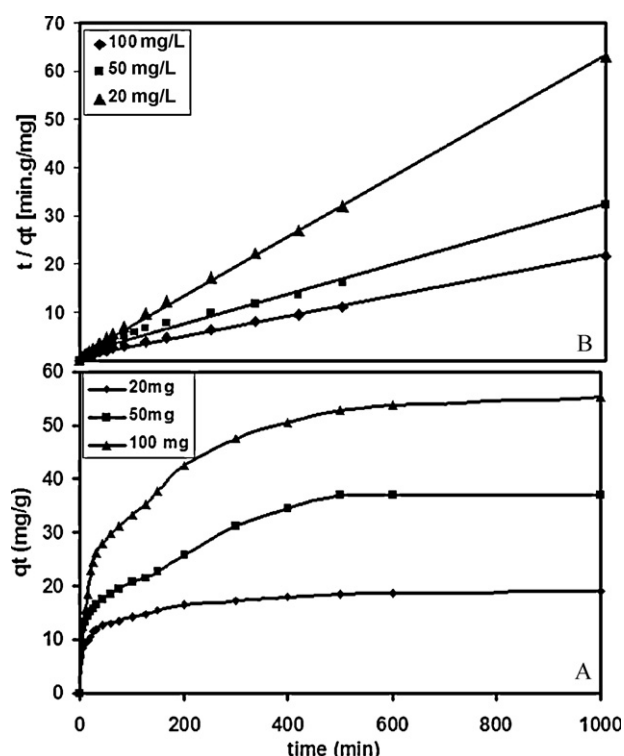


Fig. 7. (A) Adsorption kinetic (B) pseudo-second-order kinetic model plot of Cu(II) ion on ACM(1:1.5)600 at different initial concentration, pH=6, $T=28^\circ\text{C}$, sample dose = 1 g/L.

K_2 is the rate constant for pseudo-second-order kinetic equation. Eq. (3) rearranged in linear form,

$$\frac{t}{q_t} = \frac{1}{K_2(q_e)^2} + \frac{t}{q_e} \quad (4)$$

The applicability of model was verified through the sum of error squares (SSE) [2]. The equilibrium adsorption capacities ($q_{e,cal}$) calculated from pseudo-first-order kinetic model are much lower than obtained from experimental data ($q_{e,exp}$) and bigger error margin of resulted SSE shown in Table 3 indicated that, pseudo-first-order kinetic model is not a good fit for adsorption of Cu(II) on ACM(1:1.5)600. However, experimental kinetic data is better fitted in pseudo-second-order rate model with higher correlation coefficient (R^2) and lower error margin of resulted SSE (Fig. 7(B)). The estimated $q_{e,cal}$ value from model shows good agreement with experimental $q_{e,exp}$ value. The pseudo-second-order model is based on assumption that chemisorptions involving valency forces through sharing or exchange of electron between adsorbate and adsorbent is the rate-limiting step [55]. The experimental model parameter K_2 and $q_{e,cal}$ from Table 3 shows that they markedly depend on metal initial concentration. With increasing metal initial concentration the adsorption rate constant K_2 decreases, this opposite effect of initial concentration on K_2 values have been reported consistently in many works [56,57].

3.6.2. Adsorption isotherm

Distribution of metal ion between the ACs and metal solution when the system is at equilibrium is of importance in determining the maximum sorption capacity of ACs towards the metal. It provides essential physicochemical data for assessing the applicability of adsorption process as a complete unit operation. Fig. 8 shows comparative adsorption isotherm in molar amount of metal ion adsorbed at equilibrium per carbon mass unit (q_e) (mmol/g) and equilibrium metal ion concentration C_e

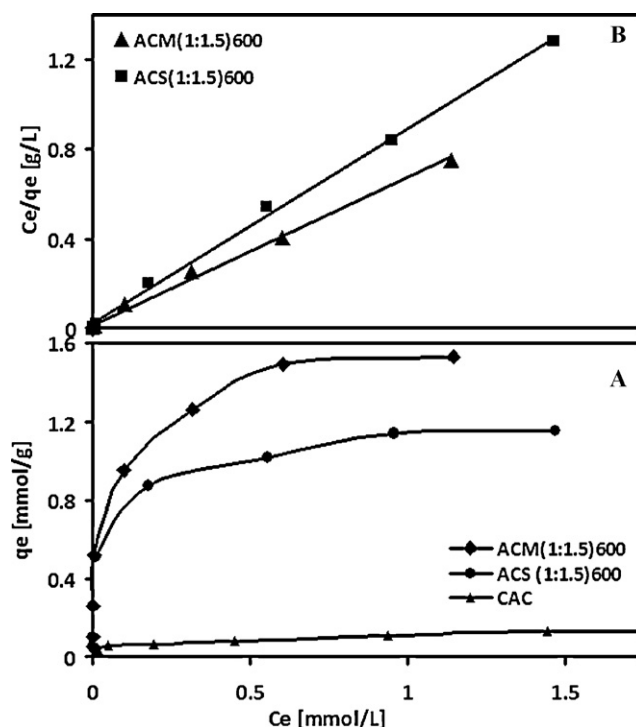


Fig. 8. (A) Adsorption isotherm (B) Langmuir isotherm plot of Cu(II) ion on ACM, ACS and CAC, $C_0 = 10\text{--}500\text{ mg/L}$, pH=6, $T=28^\circ\text{C}$. Sample dose = 1 g/L.

(mmol/L) for ACM(1:1.5)600, ACS(1:1.5)600 and commercial activated carbon (CAC). Figure shows that ACM(1:1.5)600 had higher adsorption capacity than ACS(1:1.5)600 and both show greater uptake than CAC. This may be due to change in surface structure due to microwave treatment especially micro and mesoporosity as discussed in Sections 3.1 and 3.2. To investigate adsorption process, Langmuir and Freundlich adsorption isotherm are widely applied to experimental equilibrium data, linear form of Langmuir and Freundlich adsorption isotherm are shown in Eqs. (5) and (6) respectively.

$$\frac{C_e}{q_e} = \frac{1}{X_m K} + \frac{C_e}{X_m} \quad (5)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

where, X_m and K are characteristics of Langmuir parameters related to maximum adsorption capacity and intensity of adsorption respectively in Eq. (6). K_F is Freundlich constant and $1/n$ is dimensionless heterogeneity factor relating to nature of adsorbent and nature of species respectively.

The estimated model parameters with correlation coefficient (R^2) shown in Table 4. Compared with Freundlich, Langmuir adsorption isotherm provides better fitting in terms of R^2 (0.99). The value of Langmuir isotherm constant X_m and K calculated from slope and intercept of fitting curve (Fig. 8(B)), shows that maximum adsorption capacity for microwave treated sample i.e. ACM(1:1.5)600 is higher (1.54 mmol/g) than ACS(1:1.5)600 (1.15 mmol/g) and both are much more higher than CAC (0.138 mmol/g). It may be due to higher surface area and more amounts of surface oxygen functional groups being present on surface of ACM(1:1.5)600 than on surface of ACS(1:1.5)600, but the intensity of adsorption K value is somewhat lower for ACM(1:1.5)600 (42.4183 L/mol) than ACS(1:1.5)600 (51.361 L/mol). This indicates that maximum adsorption capacity is less but intensity of adsorption is higher in ACS(1:1.5)600.

Table 3

Comparison of the kinetic parameters for the adsorption of Cu(II) on to the ACM(1:1.5)600.

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-first-order kinetic constant				Pseudo-second-order kinetic constant			
		$q_{e,cal}$ (mg/g)	$K_1 \times 10^3$ (min ⁻¹)	R^2	SSE (%)	$q_{e,cal}$ (mg/g)	$K_2 \times 10^3$ (g/mg min)	R^2	SSE (%)
20	18.99	9.12	6.1	0.991	9.862	19.31	2.158	0.999	0.315
50	37.1	34.17	8.6	0.917	2.938	38.61	0.505	0.988	1.511
100	55.2	36.57	5.3	0.997	18.627	57.14	0.375	0.996	1.942

Table 4

Estimated isotherm parameter estimated form adsorption isotherm of Cu(II) ion on ACM(1:1.5)600, ACS(1:1.5)600 and Commercial AC (CAC).

	Langmuir			Freundlich		
	X_m (mmol/g)	K (L/mol)	R^2	$1/n$	K_f (mmol/g)	R^2
ACM (1:1.5) 600	1.541	42.42	0.998	0.3827	1.929	0.8454
ACS (1:1.5) 600	1.152	51.36	0.996	0.3299	1.309	0.8931
CAC	0.138	7.471	0.983	0.2615	9.226	0.9725

The observed X_m values for ACM(1:1.5)600 and ACS(1:1.5)600 are comparable with those of already reported in literature. Celis et al. [32] reported the X_m value for Cu(II) adsorption on AC prepared from sawdust by using phosphoric acid at 450 °C in self-generated environment was 0.24 mmol/g, whereas, the AC prepared in atmospheric air environment shows maximum adsorption capacity 0.44 mmol/g. ACs prepared in self-generated environment have higher surface area than those prepared in atmospheric air environment and pointed that Cu uptake appears directly correlated with the numbers of surface functionalities. Kriaa et al. [24] reported that, the maximum adsorption capacity (X_m) of natural lignin and AC obtained from kraft lignin and carbonized at 500 °C by H_3PO_4 activation for Cu(II) was approximately 72 and 136 mg/g of adsorbent respectively. They also concluded that the surface structural changes of material play the most important role in the adsorption capacity the Cu ion. They also compared in detail the adsorption affinity and maximum Cu(II) adsorption capacity (X_m) of natural lignin and activated lignin carbonized at 500 °C with those of low cost adsorbents reported in the literature in detail [33–44] and concluded that, both untreated and H_3PO_4 treated lignin shows higher X_m values than the other unconventional adsorbents such as biomass (cassava tuber bark waste, an-aerobically digested sludge) and fly ash materials. Based on present results and on prediction of reported surface complexation model for copper adsorption on activated carbon the carboxyl groups involved in Cu(II) adsorption through the formation of monodentate charged complex ($RCOOCu^+$) where as phenolic group appear to form a hydrated neutral complex ($ROCuOH$) the roll of later could be more for the higher concentrated solution [32,35,48].

4. Conclusions

The surface area and total pore volume reach maxima at 600 °C with lignin to zinc chloride impregnation ratio 1:1.5. Integration of microwave technique to conventional impregnation method has overall shown beneficial effect in terms of porous structure, relatively greater surface area, reduction of time and energy towards effectiveness of impregnation. Besides this, it has clearly shown formation of more number of active surface functional groups than those obtained by conventional thermal process. Also formation of active functional groups on the surface is expected to increase ion exchange or surface complex factor in the sorption process. The adsorption Cu(II) on the samples could be favorably described by Langmuir isotherm, and the adsorption kinetics was found to be well fitted by the pseudo-second-order model. The ACs prepared by microwave treatment show higher capacity for Cu(II) adsorption compared to ACs prepared by simple method. The maximum adsorption capacity for the former ($X_m = 1.541$ mmol/g) is almost

33% higher than those determined for latter ($X_m = 1.152$ mmol/g) which is far higher than determined for CAC ($X_m = 0.138$ mmol/g). The maximum adsorption of Cu(II) on ACs was in agreement with their total contents of acidic/polar oxygen functional groups which is found to be more for ACM(1:1.5)600 than ACS(1:1.5)600. Because of low cost, high availability of industrial waste lignin and high uptake capacity from aqueous medium, demonstrate that, these ACs have great potential to be an economic and effective adsorbent for removal of toxic heavy metal ions from industrial effluents.

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