

Synthesis, Characterization and Adsorption Properties of Carbonaceous Residue (Coke) Obtained from Industrial Waste Lignin for Removal of Cu (II)

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Abstract: *Pulp and paper industries produce a large amount of waste lignin which creates a disposal problem. A few works has been carried out for its utilization to some extent, one of the methods of its maximum and efficient utilization is thermal degradation. In this research work the industrial waste lignin was subjected to thermal degradation at temperature of 500^oC in N₂ atmosphere without catalyst and in presence of catalyst ZnCl₂. The major product obtained after degradation is the carbonaceous residue (coke). The cokes obtained in both the cases were characterized with proximate analysis, CHN analysis, FTIR, SEM and surface textural properties. The proximate and CHN analysis of coke showed about 60% of carbon content. FTIR spectra of the cokes showed that many peaks present in lignin are lost during thermal degradation and there is flattening of remaining peaks. The surface morphology of the cokes reveals that they posses high porosity and surface area, hence it can be utilized for adsorption of heavy metal ions. In the present study, adsorption studies of Cu²⁺ ions on the prepared cokes were carried out. The adsorption studies of Cu²⁺ ions were carried out through various parameters such as pH, adsorbent dosage and contact time. It was observed that the coke obtained from degradation of lignin in presence of activating agent ZnCl₂ showed better adsorption capacity than the coke obtained in absence of activating agent. The adsorption data was fitted well into the Langmuir and Freundlich isotherm equation.*

Keywords: *Lignin, thermal degradation, activating agent, carbonaceous residue, adsorption*

1. INTRODUCTION

Rapid increase in urbanization and industrialization increases the mining of metals to meet the demands of industries. It causes major pollution, resulting the presence of heavy metals and organic species in industrial effluents. Some of the industries such as metal plating, mining operations, tanneries, radiator manufacturing, smelting, alloy industries and storage batteries manufacturers [1] have the existence of heavy metal contamination in their waste waters. Thus industrial activities have been releasing large amounts of toxic metals into the environment. As a result of this, living things are constantly exposed to heavy metals at an increasing rate. A number of treatment processes have been applied for the removal of these heavy metal ions such as precipitation, membrane separation, ion exchange, adsorption and reverse osmosis [2-4]. In waste water treatment, the process of adsorption has an edge over the processes due to its sludge free and clean operation.

In order to scavenge metal ions and other organic species from aqueous solutions, activated carbon could be one of the potential adsorbent. Activated carbon [5] is the commonly used adsorbent for removal of dyes and phenolic compounds. Activated carbons are the amorphous form of carbon characterized by high internal porosity and consequently high adsorptivity. Adsorption capacity of activated carbon mainly depends on its porosity and surface area. The textural property of activated carbon depends on the method of preparation and starting material [6]. However commercially available activated carbons are very expensive. Therefore there is a need to produce low cost and effective carbons for water pollution control. Thus interest has arisen in the use of agricultural waste products [7] such as onion skin, flour waste, paddy husk, paddy straw, waste slurry, fly ash, peat and lignin etc. for adsorption studies.

Some researchers have reviewed the application of low-cost adsorbents for heavy metal removal from contaminated waters [8-10]. Researcher's interest is growing in use of other low cost and abundantly

available lingo-cellulosic material as a precursor for the preparation of activated carbons [11-14]. The adsorption capacity of prepared activated carbon especially for metal ions depends on number of acidic/ polar oxygen functional groups present on its surface. Different oxidizing post treatments can be conducted on activated carbon to increase surface functional groups. Some recent results reported several techniques to modify surface functional groups for enhancing the capability and selectivity for adsorption from aqueous medium [15].

Enormous quantity of wood material is used by pulp and paper industries and the lignin thus removed is a recurring waste material in huge quantities and its disposal is a matter of environmental concern. A considerable research work has been reported for partial utilization e.g. hydrogenation, alkali fusion, polymer blending, wood adhesive, carbon fibers [16] etc. As lignin is a three dimensional branched polymer with aromatic phenolic units, it degrades slowly and leads to the formation of coke as a major degradation product. Thus one of the potential applications of lignin is as a precursor for the preparation of activated carbon. The surface textural properties and morphology of the activated carbon produced depends upon the various reaction conditions. The chemical activation enhances the surface characteristics of the activated carbon.

In the present research work, the industrial waste lignin was subjected to high energy degradation in N₂ atmosphere without and with chemical activating agent (ZnCl₂). The pyrocatalytic degradation has produced coke with high surface area and various micropores and mesopores. Therefore it was thought to utilize this coke for the adsorption of metal ions. The coke obtained from thermal degradation of industrial waste lignin has been used for the adsorption studies of Cu²⁺ ions.

2. MATERIALS AND METHOD

In the present research work, the kraft lignin used has been procured in the form of black liquor from Simplex Paper Mills, Gondia, Maharashtra. The solid lignin was precipitated from black liquor by acidification with dilute HCl. The pyrocatalytic degradation of lignin was carried out in absence and in presence of activating agent ZnCl₂ separately.

2.1. Preparation of Coke (Without Catalyst)

The experiment was conducted in 250 ml round bottom flask fitted with thermocouple, distilling head and condensers in N₂ atmosphere at 500^oC. Pure lignin (80 g) was heated strongly in the round bottom flask for 5 hrs. After complete degradation a carbonaceous residue (coke) has been observed in the flask. The coke was allowed to cool to the ambient temperature in the presence of continuous flow of N₂ gas.

After recovery, the coke obtained was crushed and sieved to get a particle size of 300 microns then it was treated with dilute HCl followed by plenty of distilled water and dried in oven at 110^oC for 1 hr. The coke weighed 42 g. The coke obtained from degradation of lignin in absence of activating agent is hereafter referred as C_N.

2.2. Preparation of Coke (with catalyst ZnCl₂)

80 g of pure lignin is impregnated with 80 g of ZnCl₂ in 250 ml round bottom flask along with the assembly discussed earlier. It was heated strongly for 5 hrs. At the bottom of the flask, a carbonaceous residue (coke) was left. After cooling, it was scratched out from the flask and the coke obtained was crushed and sieved to get a particle size of 300 microns. Then it was washed with dilute HCl several times followed by plenty of distilled water to remove any traces of ZnCl₂ used during thermal degradation. The coke weighed 46.60 g. The coke obtained from degradation of lignin in presence of activating agent (ZnCl₂) is hereafter referred as C_{NZ}.

2.3. Characterization of Pure Lignin and the Cokes Obtained from Thermal Degradation of Lignin

2.3.1. Proximate Analysis

Proximate analysis of pure lignin and both the cokes obtained by thermal degradation was carried out by standard method to find out the percentage of moisture, volatile matter, ash and fixed carbon.

2.3.2. CHN (Elemental) Analysis

The elemental analysis of pure lignin and the cokes was carried to find out the percentage of carbon, hydrogen and nitrogen present. The Elemental Analyzer (Carlo Erba Model 1108) was used for the analysis. The % of oxygen was calculated by difference.

2.3.3. FTIR Analysis

The Infra Red Spectrum of pure lignin and the cokes obtained from thermal degradation of lignin in N₂ atmosphere (with and without catalysts) has been recorded by using FTIR-Schimidzu 100 and Perkin Elmer using KBr pellets. All the spectra were compared according to the assignments [17, 18] given to the peaks so as to see the structural changes occurred in lignin during thermal degradation.

2.3.4. SEM Analysis

The surface morphology of lignin and the cokes obtained from thermal degradation of lignin (with and without catalysts) was studied by SEM. The SEM images were recorded with Scanning Electron Microscope (JEOL; JSM-6380A) equipped with an electron probe analyzer system (accelerating voltage 30KV). The sample was coated with palladium in order to have good conductivity.

2.3.5. Surface Textural Properties

Specific surface area (textural properties) of all cokes was determined at 77⁰K from nitrogen adsorption experiment conducted on Smart Sorb 93 Surface area analyzer. All samples were duly degassed at 300⁰C for 2 hrs under vacuum prior to its surface characterization. Then the sample was dipped in liquid nitrogen having temperature (-196⁰C). In this flow, gas gets adsorbed on the surface and forms a monolayer on the surface. The adsorbed nitrogen is allowed to desorb by bringing the samples at room temperature. The desorbed nitrogen is proportional to the surface area and so measured to calculate surface area.

2.4. Optimization of various parameters for maximum uptake of Cu²⁺ ions on the cokes (C_N and C_{NZ})

2.4.1. Optimization of Adsorbent Dose

To optimize the coke dose for maximum uptake, studies were carried out for uptake of Cu⁺² ions on both the cokes C_N and C_{NZ}. 0.25g, 0.5g, 0.75g, 1g, 1.25g, 1.5g and 2g of C_N and C_{NZ} coke were agitated with 100ml standard copper solution for 60 minutes separately with intermittent stirring. The solutions were filtered through sintered glass funnel and analyzed for the amount of Cu⁺² ions adsorbed. The quantitative estimation of Cu⁺² ions adsorbed was performed on Atomic Absorption Spectrophotometer, GBC 932. (See **Table 4**).

2.4.2. Optimization of pH

From the optimization of coke dose, it is observed that C_{NZ} showed maximum uptake of Cu⁺² ions as compared to C_N therefore further uptake studies were carried out only with C_{NZ}.

To select the pH range for maximum uptake, studies were carried out for Cu⁺² ions at different pH

1-6. 1g of C_{NZ} coke was agitated with 100 ml of Cu⁺² ion solution maintained at different pH range for 60 minutes with intermittent stirring. The solutions were then filtered through sintered glass funnel and analyzed for the amount of Cu⁺² ions adsorbed which was quantitatively determined by the difference between the initial and final concentration of Cu⁺² ions solution by AAS(See **Table 5**).

2.4.3. Optimization of Contact Time

To select the contact time for maximum uptake, adsorption studies were carried out for Cu⁺² ions at different contact time from 1 hr to 6 hrs. 1g of C_{NZ} coke was agitated with 100 ml of above Cu⁺² ion solution for different contact time with intermittent stirring. The solutions were then filtered through sintered glass funnel and analyzed for the amount of Cu⁺² ions adsorbed which was quantitatively determined by the difference between the initial and final concentration of Cu⁺² ions solution by AAS(See **Table 6**).

2.4.4. Adsorption Experiments of Cu⁺² Ions on Coke Obtained from Thermal Degradation of Lignin in Presence of ZnCl₂ (C_{NZ})

Adsorption isotherms of Cu⁺² ions were obtained using C_{NZ} adsorbent. These adsorption isotherms were used to determine the maximum adsorption capacity of C_{NZ}. Batch adsorption experiments were performed using metal ion solution with different initial concentration ranging from 50mg/l to 100mg/l. Adsorption studies were performed by shaking a fixed mass of adsorbent (1g) in fixed

volume of metal ion solution (100ml) for 3 hrs. These experiments were performed at pH 6 for Cu^{+2} ions.

Adsorption capacities for metal ions (q_e , mg/g) of adsorbent (C_{NZ}) was calculated by mass balance

$$q_e = \frac{(C_0 - C_e)V}{m}$$

where, C_0 and C_e is the initial and final concentration of metal ion in solution(mg/l), V is the volume (l) of metal ion solution for adsorption experiments and m is the adsorbent mass(g) respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of Cokes Obtained from Thermal Degradation of Industrial Waste Lignin in N_2 Atmosphere (With and Without Catalysts)

3.1.1. Proximate Analysis

Proximate analysis of pure lignin and both the prepared cokes shows difference in percentage of moisture, volatile matter, ash and fixed carbon. The results showed that the percentage of fixed carbon is highest in the coke obtained in presence of ZnCl_2 as compared to other coke.

Table1. Proximate analysis of lignin and prepared cokes (with and without catalyst)

Sample	Proximate analysis (%)			
	Moisture	Volatile Matter	Ash	Fixed Carbon
Pure lignin	4.20	42.68	9.02	44.10
Coke				
Lignin only	3.99	26.6	21.99	47.42
Lignin+ ZnCl_2	1.98	22.8	15.13	60.08

3.1.2. CHN (Elemental) Analysis

The elemental analysis of pure lignin and the prepared cokes was carried out. The percentage of carbon is more in the coke prepared in presence of ZnCl_2 as compared to the coke prepared without catalyst. Higher carbon content indicates that aromatic structure becomes dominant after degradation in the presence of catalyst used. It can be explained as, due to thermal degradation, the organic substances have degraded into volatile gases and liquid tar and the solid carbonaceous residue left behind with high carbon content. However, the low hydrogen and low oxygen content in the cokes may be due to breaking of molecular chain.

Table2. Elemental analysis of lignin and prepared cokes (with and without catalyst)

Sample	Elemental analysis (%)			
	Carbon	Hydrogen	Nitrogen	Oxygen (arithmetically)
Pure lignin	58.9	8.2	0.1	32.8
Coke				
Lignin only	60.82	3.4	1.022	34.75
Lignin+ ZnCl_2	69.11	3.3	0	27.59

3.1.3. FTIR Analysis

The changes in lignin during thermal degradation were assessed through IR studies. These studies of coke showed the structural changes occurred during the thermal treatments. The comparative study of IR showed almost flattening of maximum peaks in the cokes obtained on thermal degradation of lignin. After carbonization, all the peaks related to C-OH, CH, CH_2 , CH_3 , CO and C=O groups were considerably reduced in the prepared cokes.

Fig.1. shows the FTIR spectra of pure lignin, the first peak at 3413.44 cm^{-1} is assigned to OH stretching vibration of hydroxyl group of the lignin. A symmetric stretch for CH_3 of methoxyl group appeared at 2840 cm^{-1} . The absorbance at 2927.39 cm^{-1} arises from C-H stretching in methyl and methylene group. A peak at 1713.83 cm^{-1} assigned to carbonyl stretching—unconjugated ketone and carboxyl groups. The peak at 1508.81 cm^{-1} , 1458.39 cm^{-1} and 1426.41 cm^{-1} corresponds to aromatic skeletal vibrations, β -O-4 ether bond band at 1119.78 cm^{-1} , Carbonyl stretching at 1713.83 cm^{-1} . A small peak at 1035 cm^{-1} may be due to aromatic CH in plane deformation, guaiacyl type and C-O stretching for primary alcohol.

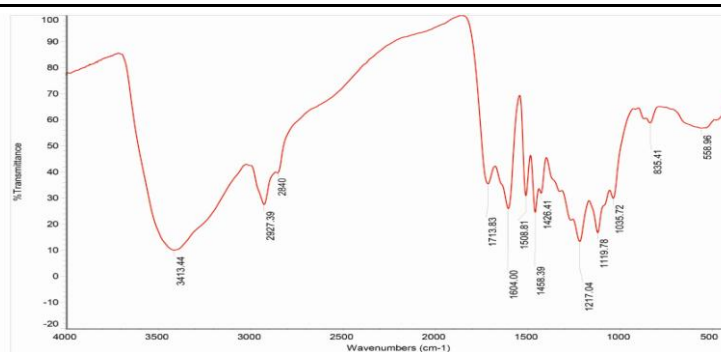


Fig1. FTIR spectra of pure lignin

Fig.2. shows the FTIR spectra of coke obtained from thermal degradation of lignin without catalyst. The spectra shows that many peaks present in lignin are lost, few peaks are shifted and there is a flattening of remaining peaks present. The peaks at 3447.53 cm⁻¹ and 1613 cm⁻¹ may be assigned to –OH stretching and aromatic skeletal vibrations respectively. Carbonyl group in the pure lignin is found to be lost during the coke formation. It may be due to the thermal cleavage that leads to the loss of carbon dioxide during thermal degradation.

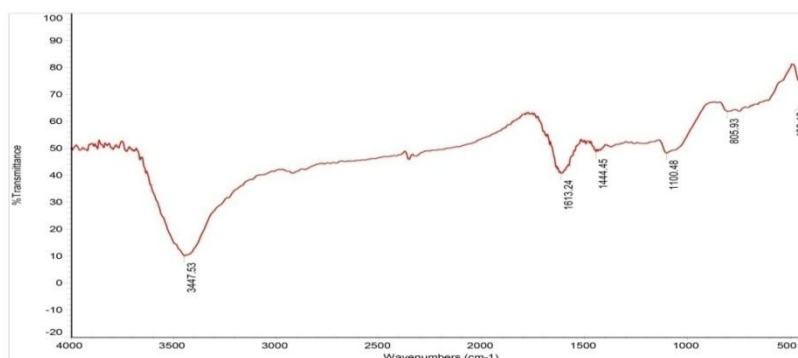


Fig2. FTIR spectra of coke from lignin without catalyst

Fig.3. shows the FTIR spectra of coke obtained from thermal degradation of lignin with ZnCl₂ catalyst. The FTIR spectra for this coke showed the peak at 3426.71 cm⁻¹ mainly due to –OH stretching and the peak at 1615.73 cm⁻¹ resulting from C=C stretching vibration in aromatic ring. A new peak at 1064 cm⁻¹ may be due to the superposition of signals corresponding to oxygen functional groups like ether, phenol and lactones. For this coke, low absorption occurred in the region 800-1000cm⁻¹ suggests a lower content of substituted aliphatic groups on the aromatic ring.

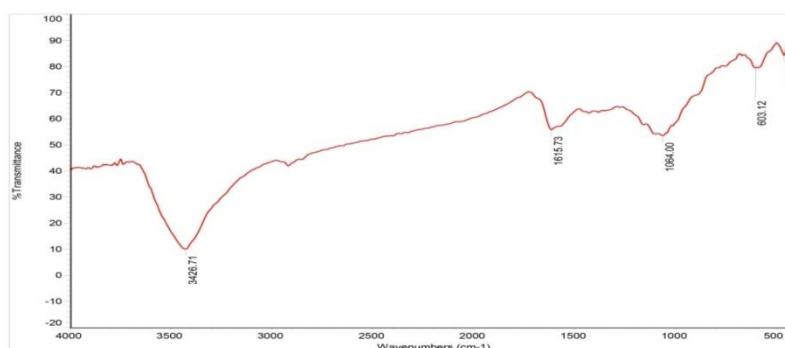


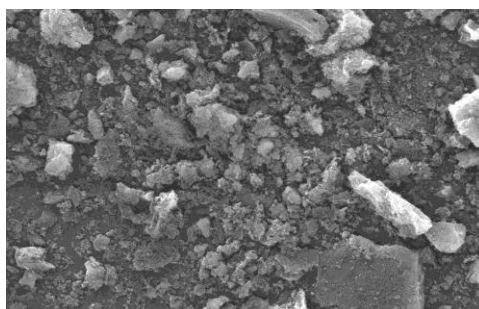
Fig3. FTIR spectra of coke from lignin with ZnCl₂ catalyst

From the above results lignin and cokes prepared from lignin in presence and absence of catalysts showed a shift in wave numbers. The intensity of the transmittance due to hydrogen bonded OH stretching has been decreased for both the cokes as compared to pure lignin. The decrease may be due to the loss of phenolic or alcoholic groups during degradation. The peak due to symmetric CH₃ stretch of O-CH₃ groups appeared at 2840 cm⁻¹ in pure lignin disappeared from both cokes, this shows that CH₃ groups were removed from substituted aromatic ring during thermal degradation. The intensity of band that appears at 2927cm⁻¹ corresponding to aliphatic CH stretch decreased to a great extent or

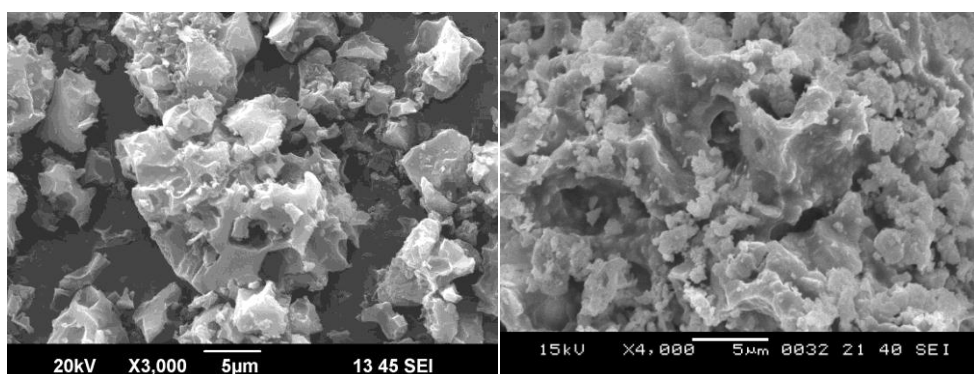
disappeared in both cokes. The shifts in the bands suggest the formation of fused ring systems such as substituted naphthalene, anthracene or phenanthrene. Thus the extent of aromatic substitution decreases during thermal degradation and the coke formed a network of fused rings.

3.1.4. SEM Analysis

To study the effect of lignin degradation process, the surface morphology of the cokes (with and without catalyst) was recorded. SEM observations of the cokes obtained from thermal degradation of lignin revealed its complex and porous surface texture. The SEM images shows a highly porous morphology of coke with pores of more or less different shapes and sizes and a variety of crevices on the external surface which shows smoother surface with irregular, heterogeneous and grainy surface. These may contribute to the relatively high surface area of the coke. The SEM images of prepared cokes from lignin showed 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 purified lignin



SEM image of Coke without catalyst SEM image of Coke with $ZnCl_2$ catalyst

Fig4. SEM images

Researchers suggest that the mentioned pores represent active sites of the adsorption process. Moreover, remarkably porous material having a high specific surface area should be able to play an important role in heavy metal and organic species removal from aqueous solution.

3.1.5. Surface Textural Properties

The N_2 adsorption isotherm at $-196^\circ C$ of both the cokes obtained from thermal degradation of lignin (with and without catalyst) was carried out. **Table 3.** reports the surface area of the cokes obtained on thermal degradation at $500^\circ C$ carbonization temperature with the impregnation ratio of lignin to $ZnCl_2$ catalyst as 1:1

Table3. Surface characteristics of prepared cokes

Sample (Coke)	Carbonization Temperature($^\circ C$)	S_{BET} (m^2/g)
Only lignin	$500^\circ C$	486
Lignin + $ZnCl_2$	$500^\circ C$	819.82

The maximum surface area which could be achieved in the present experimental condition is by the coke prepared with $ZnCl_2$ activation which is $819.82 m^2/g$. This surface area is much larger than that of coke prepared from lignin in absence of catalyst. $ZnCl_2$ coke has the surface area as large as those of commercial activated carbon.

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ZnCl₂ worked as dehydration reagent and restricted the formation of tar and promoted the charring and aromatization of carbon upto carbonization temperature 500⁰C. This can be the reason for the higher yield and more surface area of the coke prepared by ZnCl₂ activation.

3.2. Optimization of Various Parameters for Maximum Uptake of Cu²⁺ Ions on the Cokes (C_N and C_{NZ})

3.2.1. Effect of Adsorbent dose on uptake of Cu²⁺ Ions

Table 4. shows the results obtained for Cu²⁺ ions uptake using different doses of coke obtained from thermal degradation in N₂ atmosphere (C_N and C_{NZ})

Table 4. Uptake of Cu²⁺ ions on coke (C_N and C_{NZ})

Initial concentration of Cu²⁺ solution = 40 ppm

Sr. No.	Quantity of coke per 100 ml solution (g)	Residual concentration of Cu ²⁺ after uptake (ppm) on C _N	Uptake % on C _N	Residual concentration of Cu ²⁺ after uptake (ppm) on C _{NZ}	Uptake % on C _{NZ}
1	0.25	14.3	64.25	11.9	70.25
2	0.5	12.28	69.3	9.94	75.15
3	0.75	8.8	78	4.5	88.77
4	1	7.84	80.42	3.28	91.8
5	1.25	6.8	83	3.02	92.47
6	1.5	5.68	85.82	2.44	93.92
7	2	5.32	86.7	2.36	94.12

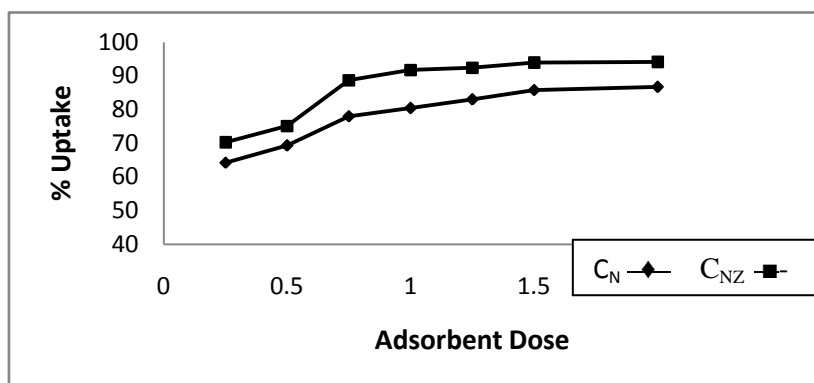


Fig 5. Comparison between adsorption capacity of C_N and C_{NZ} for Cu²⁺ ions

From the above results it is observed that the uptake capacity of C_{NZ} is more as compared to C_N. This may be due to the process of chemical activation which enhances porosity of the coke formed. The ZnCl₂ activation is accompanied by increase in the surface area and total pore volume [19-22]. The softening or partial fusion which lignin undergoes at relatively low temperature (180-280⁰C) may favour ZnCl₂ diffusion throughout the matrix. Also when resolidification takes place at temperature above the melting point of ZnCl₂ (293⁰C), a microporous structure has already developed through devolatilization allowing melt of ZnCl₂ to migrate through this microporous net. Thus ZnCl₂ activation increases microporosity of carbon residue and subsequently shows greater uptake capacity.

3.2.2. Effect of pH on uptake of Cu²⁺ ions using coke (C_{NZ})

The uptake studies of Cu²⁺ ions on the cokes obtained from thermal degradation of industrial waste lignin in presence of ZnCl₂, at different pH has been summarized below:

The uptake capacity is largely dependent on pH of the metal solution. The adsorption of Cu²⁺ ions under similar conditions was studied at different pH. For the Cu²⁺ ions the % adsorption increases with pH to attain a maximum at pH 6 [23]. It may be due to high H⁺ ion concentration, which reverses the process of adsorption.

Table5. Uptake studies of Cu^{+2} ions on coke (C_{NZ}) at different pHConc. of Cu^{+2} solution = 40 ppmQuantity of coke per 100ml solution (C_{NZ}) = 1g

Sr. No.	pH	% Uptake of Cu^{2+} ions on C_{NZ}
1	1	49.75
2	2	55.37
3	3	63.25
4	4	71.65
5	5	84.90
6	6	85.45

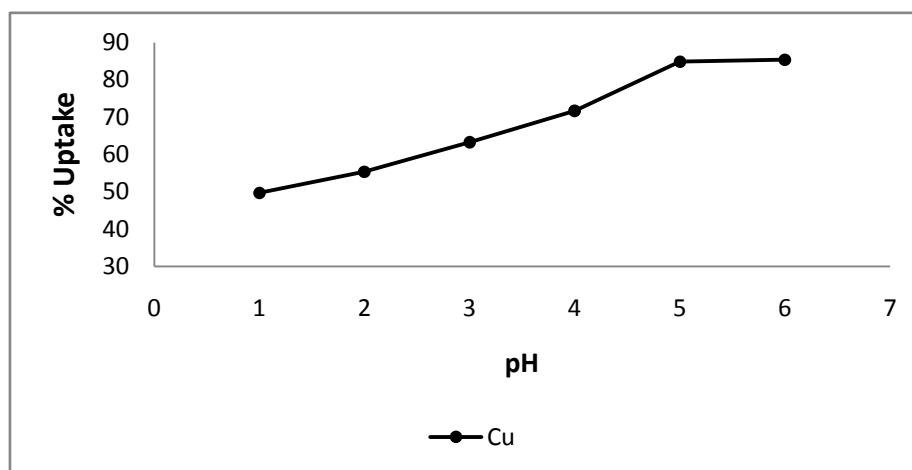
**Fig6.** Effect of pH on uptake of Cu^{2+} ions on coke C_{NZ}

Fig.6. showed that the maximum uptake of Cu^{+2} ions occurred at pH 6, so pH 6 was considered as the optimum condition.

3.2.3. Effect of contact time on uptake of Cu^{+2} ions using coke (C_{NZ})

For a fixed concentration of heavy metals and a fixed adsorbent mass, the retention of heavy metals increased with increasing contact time. It was observed that the adsorption rate initially increased rapidly, and that the optimal removal efficiencies were reached within about 3 hrs: 91.85 % for Cu^{+2} ions. The removal efficiencies reached a steady value with increasing contact time after equilibrium had been reached. This may be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high, later the uptake rate of metal ions was decreased significantly resulted from saturation of adsorbent surfaces with heavy metals followed by adsorption and desorption processes that occur after saturation, it indicates the possible monolayer formation of metal ions on the outer surface [23].

Table6. Uptake studies of various metal ions on coke (C_{NZ}) for different contact timeConc. of Cu^{+2} solution = 40 ppmQuantity of coke per 100ml solution C_{NZ} = 1g

Sr. No.	Contact Time (hrs)	% Uptake of Cu^{2+} ions on C_{NZ}
1	1	84
2	2	86.7
3	3	91.85
4	4	93.10
5	5	94.05
6	6	94.9

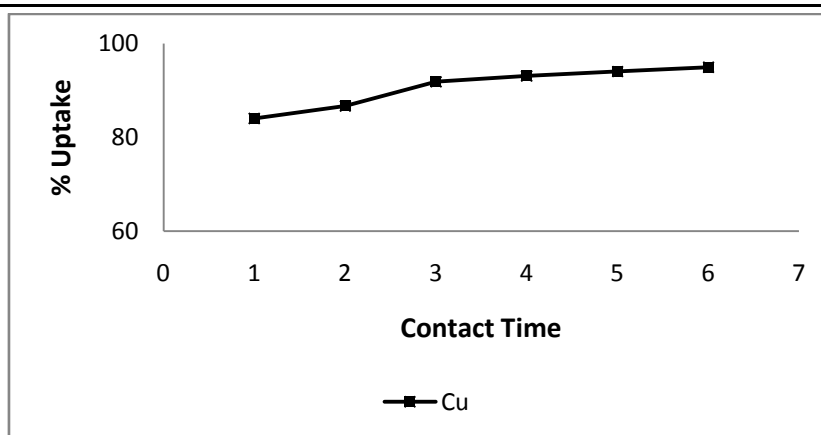


Fig7. Effect of contact time on uptake of Cu^{2+} ions on coke C_{NZ}

The effect of contact time on uptake capacity of coke showed that the significant adsorption takes place at contact time of 3 hrs. Hence for further studies the optimized contact time was 3hrs.

Adsorption Isotherms

The equilibrium relationship between adsorbent and adsorbate are described by adsorption isotherms which is usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. Most often biosorption equilibria are described with adsorption isotherms of Langmuir or Freundlich types. Since the adsorption isotherms are important to describe how adsorbates will interact with adsorbents and so are critical for design purposes, therefore, the correlation of equilibrium data using an equation is essential for practical adsorption operation. When the sorption data of the metal ions investigated on prepared coke were plotted logarithmically, they all fitted the Freundlich adsorption isotherm.

The adsorption data was fitted to the linear form of Freundlich equation (1)

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

Where, K_f and $1/n$ are Freundlich constants related to the adsorption capacity and adsorption intensity respectively. The value of $1/n$ which is less than 1 indicates that the metal ions are favourably adsorbed by the prepared coke. A smaller value of $1/n$ indicates better adsorption mechanism and formation of relatively stronger bond between adsorbate and adsorbent.

The adsorption data was also investigated by Langmuir adsorption model (equation 2).

$$\frac{1}{q_e} = \frac{1}{\theta^0 b} \times \frac{1}{C_e} + \frac{1}{\theta^0} \quad (2)$$

Where q_e is the amount of metal ions adsorbed per unit weight of the adsorbent (mg/g), C_e is the equilibrium concentration of the metal ions in aqueous solution (mg/L), θ^0 and b are the Langmuir constants related to the adsorption capacity (mg/g) and energy of adsorption and (L/mg) respectively.

The linear plots of $1/q_e$ versus $1/C_e$ suggests the applicability of the above model for the investigated system, showing formation of monolayer coverage of the adsorbate at the outer surface of the adsorbent. Langmuir isothermal adsorption model has been widely used to assume the monolayer and homogeneous adsorption for the whole adsorption process which means that the adsorption can only proceed at fixed amount of definite active sites and there is no steric hindrance and lateral interaction between adsorbates [24, 25]. Freundlich isothermal adsorption model can be used to analyze multilayer adsorption in heterogeneous system where adsorption heat is non uniform distribution and adsorption is the summational result of all the active sites. The parameters of the two models were calculated and summarized from the plots of $1/q_e$ versus $1/C_e$ and $\text{Log } q_e$ versus $\text{Log } C_e$. It can be observed that Langmuir isotherm model described the adsorption with higher R^2 indicating the identical affinity for the adsorbate and no transmigration of the adsorbate on the surface of coke. The values of $1/n$ were discovered to be less than 1 which means the adsorption is favourable.

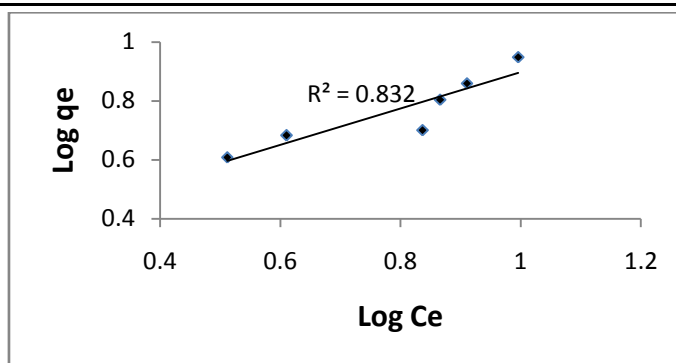


Fig8. Freundlich Isotherm of Cu^{+2} ions

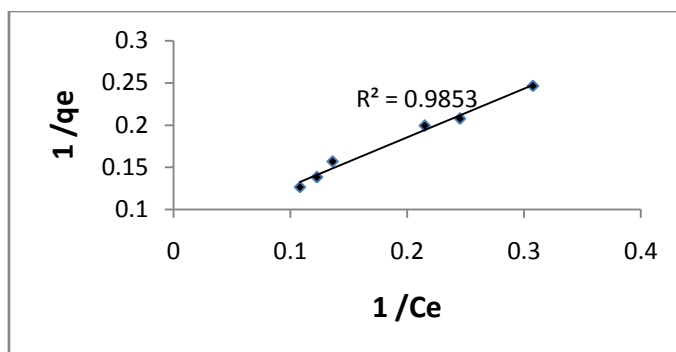


Fig9. Langmuir Isotherm of Cu^{+2} ions

Table7. Freundlich and Langmuir Constants for Adsorption of metal ions

Sr. No	Metal ions	Freundlich constants		R^2	Langmuir constants		R^2
		$1/n$	K_f		b	θ^0	
1	Cu^{+2}	0.616	1.9124	0.832	0.1218	14.245	0.9853

The essential characteristic of Langmuir isotherm may be expressed in terms of dimensionless equilibrium parameter R , using the following equation

$$R = \frac{1}{1 + bC_0}$$

The values of R for all the species lie between 0 and 1 showing favorable uptake of Cu^{2+} ions on the adsorbent.

3. CONCLUSION

The carbonaceous material obtained from industrial waste lignin had been used to investigate the removal of $\text{Cu}(\text{II})$ ions in aqueous solutions. It can be successfully used as a low cost adsorbent for uptake of Cu^{2+} ions. The ZnCl_2 activation increases adsorption capacity of the coke. On appropriate treatment, lignin has potential to become an effective and economical adsorbent for waste water treatment. Lignin can replace the expensive commercially available activated carbon for removal of metals. Therefore the technique for preparation of the carbonaceous material from industrial waste lignin showed its potential to be employed as an effective adsorbent in removal of Copper ions and would be useful for waste water treatment techniques for the removal of other toxic metal ions and other organic species. Thus utilization of the lignin in this way is promising and minimizes the disposal problems and converts the waste into useful raw material.

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