RESEARCH ARTICLE

PHENOL ADSORPTION USING ACTIVATED CARBON PREPARED FROM DEGRADATION OF INDUSTRIAL WASTE LIGNIN.

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Abstract

Phenol and phenolic compounds are the common water pollutants in the effluents from various industries and even in the small amounts are undesirable for human health. In this research work adsorption of phenol on the activated carbon prepared from thermal degradation of industrial waste lignin was studied. The industrial waste lignin was subjected to thermal degradation at temperature of 500°C in N₂ atmosphere in presence of ZnCl₂ catalyst. The major product obtained after degradation is the activated carbon. The activated carbon obtained was characterized with proximate analysis, CHN analysis, FTIR, SEM and surface textural properties. The surface morphology of the AC reveals that it posses high porosity and surface area, hence it can be utilized for adsorption purpose. The adsorption capacity of the prepared AC for phenol was studied with various parameters such as effect of contact time, adsorbent dose, pH and initial concentration. The maximum adsorption for phenol is found to be 19.3050mg/g. To describe the equilibrium isotherms, Langmuir and Freundlich models were applied. Although adsorption equilibrium data was found to follow Freundlich model, it was better fitted in Langmuir model. The scope of this work suggests that the AC obtained from industrial waste lignin can be utilized as a low cost adsorbent for the removal of phenol from aqueous solution.

Introduction:

Phenol and phenolic compounds are common contaminants in the effluents from industries such as plastics, leather, paint, textile and petrochemical[1]. Such contaminated water in human body causes protein degeneration, tissue erosion, paralysis of central nervous system and the repeated exposure to low levels of phenol in water causes health effects such as damage to liver, kidney and pancreas[2]. Also, phenol is a strong eye and respiratory irritants. Phenolic compounds are harmful to organism at low concentrations and many of them have been classified as hazardous pollutants[3]. As phenol and phenolic compounds are harmful, there is a need for its removal in order to prevent the environmental pollution. The commonly used methods for the treatment of aqueous solutions containing phenol includes stripping, solvent extraction, oxidation, ion exchange, biodegradation and adsorption[4]. Among these, adsorption onto the activated carbon is the most widely used method for the removal of dissolved organics from waters.

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In order to scavenge organic species like phenol from aqueous solutions, activated carbon could be one of the potential adsorbent. Activated carbon [5-6] is the commonly used adsorbent for removal of dyes and phenolic compounds. Activated carbons are the amorphous form of carbon characterized by high surface areas, micropore volumes, large adsorption capacities, fast adsorption kinetics and relative ease of regeneration [7] It has wide applications like removal of organic, inorganic pollutants from drinking water and as catalyst support. 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 [8]. However commercially available activated carbons are very expensive. Therefore there is a need to produce low cost and effective carbons for water pollution control.

Recently a lot of work has been published on the production of AC by using agricultural waste products such as onion skin, flour waste, paddy husk, paddy straw, waste slurry[9,10], fly ash[11], lignite[12], pine bark, peat and lignin [13-20] etc for adsorption studies. Some researchers have reviewed the application of low-cost adsorbents for removal of organic compound like phenol from contaminated waters [21,22]. 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 carbon [23].

Pulp and paper industries uses enormous quantity of wood material and the lignin thus removed is considered as a recurring waste material in huge quantities and its disposal is a matter of environmental concern. A considerable research work has been reported for its partial utilization e.g. hydrogenation, alkali fusion, polymer blending, wood adhesive, carbon fibers etc. As lignin is a three dimensional branched polymer with aromatic phenolic units, it degrades slowly and leads to the formation of a carbonaceous residue 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 with chemical activating agent (ZnCl₂). The pyrocatalytic degradation has produced the activated carbon with high surface area. Therefore the activated carbon obtained from thermal degradation of industrial waste lignin has been used for the adsorption studies of Phenol.

Materials and Method:-

Adsorbent:-
In this present 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 and then purified. The pyrocatalytic degradation of pure lignin was carried out in presence of activating agent ZnCl₂.

Preparation of Activated Carbon:-
80 g of pure lignin is impregnated with 80 g of ZnCl₂ in 250 ml round bottom flask along with thermocouple, distilling head and condensers in N₂ atmosphere at 500°C. It was heated strongly for 5 hrs. At the bottom of the flask, a carbonaceous residue (activated carbon) was left. After cooling, it was scratched out from the flask and the AC 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 AC weighed 46.60 g.

Adsorbate:-
The stock solution of Phenol concentration 1000mg/l was prepared. The concentration of phenol in solutions was determined spectrophotometrically at 270 nm. Different concentration of phenol solutions were prepared ranging from 100 to 200mg/l from its stock solution.

Characterization of pure lignin and the Activated Carbon obtained from thermal degradation of lignin in N₂ atmosphere in presence of ZnCl₂:

Proximate Analysis:-
Proximate analysis of pure lignin and the AC obtained by thermal degradation was carried out by standard method to find out the percentage of moisture, volatile matter, ash and fixed carbon.
CHN (Elemental) Analysis:
The elemental analysis of pure lignin and the prepared AC 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.

FTIR Analysis:
The Infra Red Spectrum of pure lignin and the AC obtained from thermal degradation of lignin in N2 atmosphere has been recorded by using FTIR-Schimadzu 100 and Perkin Elmer using KBr pellets. The spectra were compared according to the assignments [24,25] given to the peaks so as to see the structural changes occurred in lignin during thermal degradation.

SEM Analysis:
The surface morphology of lignin and the AC obtained from thermal degradation of lignin 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.

Surface Textural properties:
Specific surface area (textural properties) of the prepared AC was determined at 770K from nitrogen adsorption experiment conducted on Smart Sorb 93 Surface area analyzer. The sample was duly degassed at 300°C for 2 hrs under vacuum prior to its surface characterization. Then the sample was dipped in liquid nitrogen having temperature (-196°C). 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.

Optimization of various parameters for maximum uptake of Phenol on the Activated Carbon obtained by thermal degradation of lignin:

Optimization of adsorbent dose:
To optimize the adsorbent dose for maximum uptake, studies were carried out for uptake of phenol on the AC. 0.25g, 0.5g, 0.75g, 1g, 1.25g, 1.5g and 2g of AC were agitated with 100ml phenol solution for 60 minutes separately with intermittent stirring. The solutions were filtered and phenol concentrations in aqueous solutions were determined by measuring the absorbance at 269.4 nm using UV visible spectrophotometer. (See Table 3).

Optimization of pH:
To select the pH range for maximum uptake, studies were carried out for phenol at different pH ranging from 2-10. 1g of the AC was agitated with 100 ml of phenol solution maintained at different pH range for 60 minutes with intermittent stirring. The solutions were filtered and the phenol concentrations in aqueous solutions were determined by using UV visible spectrophotometer. (See Table 4).

Optimization of contact time:
To optimize the contact time for maximum uptake, adsorption studies were carried out for phenol at different contact time from 1 hr to 6 hrs. 1g of AC was agitated with 100 ml of phenol solution for different contact time with intermittent stirring. The solutions were filtered and the phenol concentrations in aqueous solutions were determined by using UV visible spectrophotometer (See Table 5).

Adsorption experiments of Phenol:
Adsorption isotherms of phenol were obtained using the adsorbent. These adsorption isotherms were used to determine the maximum adsorption capacity of the AC obtained from thermal degradation of lignin. Batch adsorption experiments were performed using phenol with different initial concentration ranging from 100mg/l to 200mg/l. Adsorption studies were performed by shaking a fixed mass of adsorbent (1g) in fixed volume of phenol solution (100ml) separately for 3 hrs. These experiments were performed at pH 7.
Adsorption capacity of adsorbent for Phenol ($q_e$, mg/g) was calculated by mass balance

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

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

**Results and Discussion:-**

**Characterization of pure lignin and the Activated Carbon obtained from thermal degradation of lignin in N$_2$ atmosphere in presence of ZnCl$_2$.**

**Proximate Analysis:-**

Proximate analysis of pure lignin and the prepared AC shows difference in percentage of moisture, volatile matter, ash and fixed carbon. The results showed that the percentage of fixed carbon is high in the AC obtained in presence of ZnCl$_2$ as compared to pure lignin.

**Table 1:-** Proximate analysis of lignin and prepared Activated Carbon (with ZnCl$_2$ catalyst)

| Sample                  | Proximate analysis (%) |
|-------------------------|------------------------|
|                         | Moisture   | Volatile Matter | Ash   | Fixed Carbon |
| Pure lignin             | 4.20       | 42.68           | 9.02  | 44.10        |
| Activated Carbon        | 1.98       | 22.8            | 15.13 | 60.08        |
| (Lignin+ZnCl$_2$)       |            |                 |       |              |

**CHN (Elemental) Analysis:-**

The elemental analysis of pure lignin and the prepared AC was carried out. Higher carbon content in the prepared AC 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, liquid tar and the solid carbonaceous residue left behind with high carbon content. However, the low hydrogen and low oxygen content in AC may be due to breaking of molecular chain.

**Table 2:-** Elemental analysis of lignin and prepared Activated Carbon (with ZnCl$_2$ catalyst)

| Sample                  | Elemental analysis (%) |
|-------------------------|------------------------|
|                         | Carbon | Hydrogen | Nitrogen | Oxygen (arithmetically) |
| Pure lignin             | 58.9   | 8.2      | 0.1      | 32.8                    |
| Activated Carbon        | 69.11  | 3.3      | 0        | 27.59                   |
| (Lignin+ZnCl$_2$)       |         |          |          |                         |

**FTIR Analysis:-**

During thermal degradation, the changes occured in lignin were assessed through IR studies. These studies of AC showed the structural changes occurred during the thermal treatments. The comparative study of IR showed almost flattening of maximum peaks in the AC obtained on thermal degradation of lignin. After carbonization, all the peaks related to C-OH, CH, CH$_3$, CH$_2$, CO and C=O groups were considerably reduced in the prepared AC.

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 1508.81cm$^{-1}$, 1458.39cm$^{-1}$ and 1426.41cm$^{-1}$ 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.
Figure 1: FTIR spectra of pure lignin.

Fig. 2 shows the FTIR spectra of activated carbon obtained from thermal degradation of lignin with ZnCl₂ catalyst. The FTIR spectra for this AC 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 AC, low absorption occurred in the region 800-1000 cm⁻¹ suggests a lower content of substituted aliphatic groups on the aromatic ring.

Figure 2: FTIR spectra of AC from lignin with ZnCl₂ catalyst.

From the above results, lignin and AC prepared from lignin in presence of catalyst showed a shift in wave numbers. The intensity of the transmittance due to hydrogen bonded OH stretching has been decreased in the AC 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 AC, this shows that CH₃ groups were removed from substituted aromatic ring during thermal degradation. The intensity of band that appears at 2927 cm⁻¹ corresponding to aliphatic CH stretch decreased to a great extent or disappeared in the AC. 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 AC formed a network of fused rings.

SEM Analysis:
To study the effect of lignin degradation process, the surface morphology of the AC was recorded. SEM observations of the AC obtained from thermal degradation of lignin revealed its complex and porous surface texture. The SEM image shows a highly porous morphology of AC 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 AC. The SEM image of prepared AC 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 AC from purified lignin](image1) ![SEM image of AC with ZnCl₂ catalyst](image2)

Figure 3: 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 phenol removal from aqueous solution.

**Surface Textural Properties:**
The N₂ adsorption isotherm at -196°C of the AC obtained from thermal degradation of lignin was carried out. The surface area of the prepared AC obtained on thermal degradation at 500°C with the impregnation ratio of lignin to ZnCl₂ catalyst as 1:1 was found to be 819.82 m²/g. AC with ZnCl₂ as activating agent has the surface area as large as those of commercial activated carbon. ZnCl₂ worked as dehydration reagent and restricted the formation of tar and promoted the charring and aromatization of carbon up to carbonization temperature 500°C. This can be the reason for the higher yield and more surface area of the AC prepared by ZnCl₂ activation.

**Optimization of various parameters for maximum uptake of Phenol on the coke obtained by thermal degradation of lignin:**

**Optimization of adsorbent dose:**
The effect of adsorbent dose on the removal of phenol by AC was studied for the initial concentration. The uptake studies have been carried out by varying the adsorbent dose, ranging from 0.25 to 2g/100ml for the time interval of 60 mins. Table 3 shows the effect of adsorbent dosage on the removal of phenol by the AC obtained from industrial waste lignin. The maximum removal of phenol was obtained for the adsorbent dose 1g/100ml. The % removal of phenol was 78.48%. However it was observed that after this dose, there was no significant change in the % removal of phenol. It may be due to the availability of the exchangeable sites or surface area on the adsorbents. So 10g/l was considered as the optimum dose for the uptake studies. As the quantity of adsorbent increases, the number of adsorbent particles increases and more exchangeable sites are available, so more phenol is attached to the vacant sites.

**Table 3:** Effect of adsorbent dose on removal of Phenol

| Sr. No. | Quantity of AC per 100 ml of phenol solution (g) | % Uptake |
|---------|-----------------------------------------------|----------|
| 1       | 0.25                                          | 58.24    |
| 2       | 0.5                                           | 65.64    |
| 3       | 0.75                                          | 70.12    |
| 4       | 1                                             | 78.48    |
| 5       | 1.25                                          | 83.74    |
| 6       | 1.5                                           | 87.20    |
| 7       | 2                                             | 91.47    |
Effect of pH:
The uptake capacity is largely dependent on pH of aqueous solution. The removal of phenol under similar conditions was studied at different pH. The % adsorption increases with pH to attain a maximum at pH 6-7. The effect of variation of pH on removal of phenol by the AC obtained from thermal degradation of industrial waste lignin in presence of ZnCl₂ has been summarized below:

Table 4: Effect of pH on removal of Phenol

| Sr. No. | pH | % Uptake |
|--------|----|----------|
| 1      | 2  | 42.32    |
| 2      | 3  | 49.85    |
| 3      | 4  | 51.26    |
| 4      | 5  | 54.62    |
| 5      | 6  | 59.8     |
| 6      | 7  | 65.8     |
| 7      | 8  | 67.61    |
| 8      | 9  | 71.28    |
| 9      | 10 | 74.13    |

Effect of contact time and initial phenol concentration:
For a fixed concentration of phenol solution and a fixed adsorbent mass, the removal of phenol 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: 80.43 % for phenol. 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, later the removal rate of phenol was not increased significantly resulted from saturation of adsorbent surfaces with phenol, it indicates the possible monolayer formation on the outer surface of adsorbent. Effect of contact time for removal of phenol is tabulated in Table 5.

**Table 5:** Effect of contact time on removal of Phenol by AC

| Sr. No. | contact time (in hrs) | % uptake  |
|---------|-----------------------|-----------|
| 1       | 1                     | 69.48     |
| 2       | 2                     | 74.55     |
| 3       | 3                     | 80.43     |
| 4       | 4                     | 84.14     |
| 5       | 5                     | 89.58     |
| 6       | 6                     | 93.8      |

![Figure 6: Effect of contact time on removal of Phenol](image)

**Adsorption isotherms for Phenol:**

The analysis of equilibrium data for the adsorption of phenol on the AC obtained on degradation of industrial waste lignin was carried out with the Freundlich and Langmuir isotherm model. Figure 7 shows the adsorption isotherms of Freundlich model and Figure 8 shows the adsorption isotherms of Langmuir model.

The parameters of the two models were calculated and summarized from the plots of $1/q_e$ versus $1/C_e$ and Log $q_e$ versus Log $C_e$ (see Table 6). 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. From the Langmuir isotherm model, it has been observed that the adsorption capacity ($\theta_0^0$) of the AC for phenol is 19.305 mg/g.

The linear plots of $1/q_e$ versus $1/C_e$ suggests the applicability of Langmuir model, showing the formation of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The essential characteristic of Langmuir isotherm is expressed in terms of dimensionless equilibrium parameter, $R$. The values of $R$ lie between 0 and 1 showing favorable adsorption of organic species on the adsorbent.

**Table 6:** Freundlich and Langmuir Constants for Adsorption of Phenol.

| Sr. No | Organic species | Freundlich constants | $R^2$ | Langmuir constants | $R^2$ |
|-------|-----------------|----------------------|-------|--------------------|-------|
|       |                 | $1/n$                | $K_f$ | $b$                | $\theta_0^0$ |   |
| 1     | Phenol          | 0.2835               | 7.7125| 0.3650             | 19.305 | 0.9707 |

The essential characteristic of Langmuir isotherm may be expressed in terms of dimensionless equilibrium parameter, the values of $R$ for phenol lie between 0 and 1 showing favorable uptake of the dye on the adsorbent (see Table 7).
Table 7: Equilibrium parameter (R) at different initial concentration of Phenol

| Sr. No. | Initial Concentration (mg/l) | Equilibrium parameter (R) |
|---------|-------------------------------|---------------------------|
| 1.      | 100                           | 0.0519                    |
| 2.      | 120                           | 0.0436                    |
| 3.      | 140                           | 0.0376                    |
| 4.      | 160                           | 0.0331                    |
| 5.      | 180                           | 0.0295                    |
| 6.      | 200                           | 0.0266                    |

Thus this study investigated the feasibility of lignin derived activated carbon as a new, low cost and efficient adsorbent for phenol adsorption. The chemical activation of lignin with ZnCl$_2$ activating agent is a suitable method for the preparation of AC with high surface area.

Conclusions: Activated carbon obtained from industrial waste lignin can be successfully used as a low cost adsorbent for removal of phenol. 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 phenol. Thus utilization of the lignin in this way is promising and minimizes the disposal problems and converts the waste into useful raw materials.
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