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APPLICATION OF NANO POROUS CARBON FOR THE UPTAKE OF PHENOL AND 2-CHLOROPHENOL AS BISOLUTE FROM WATER

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ABSTRACT: *Nano porous activated carbon prepared from coir pith using $ZnCl_2$ (ZnCPC) was investigated to find the feasibility of its application for mixture of phenol and 2-chlorophenol in aqueous solution through sequential adsorption/desorption process by HPLC C-18 column. Nano porous carbon was characterized using standard physio-chemical methods, BET surface area, pore diameter, SEM and XRD studies. Adsorption of 2-CP in bisolute systems showed that 2-CP were adsorbed preferentially, but phenol was adsorbed competitively. This result was further confirmed by η_1 and η_2 values obtained from extended Langmuir model. The cost of ZnCPC is economically effective compared to commercial activated carbon.*

Keywords*:* Nano porous activated carbon, Bisolute system, Sequential adsorption/desorption

1. INTRODUCTION

Phenol is present in the surface water of industrial effluents such as coal tar, gasoline, plastic, rubber-proofing, coking, pharmaceutical, petrochemical and steel industries, domestic wastewaters and chemical spillage [1]. Phenol presence in natural water can lead further to the formation of chlorophenols during disinfection and oxidation processes, which are carcinogenic compounds[2]. Chlorophenols are listed as priority environmental pollutants by US EPA because of their higher toxicity, carcinogenicity and recalcitrant properties [3]. Long term ingestion of water containing phenols in the human body causes protein degeneration, tissues erosion and paralysis of the central nervous system, and also damages the kidney, liver and pancreas [4]. The World Health Organization (WHO) guideline for maximum admissible concentration in drinking water is 10 µg/L for 2-chlorophenol (2-CP) and phenol 1mg/L[5]. In India, Coir pith is a lignocellulosic light fluffy biomaterial generated as a byproduct during separation of fiber from ripened coconut husk contains mainly cellulose, lignin and pentosans. The production of coir pith in India is estimated to be about 7.5 million tons annually and this often causes serious disposal problems [6].Usually, the industrial effluents present a mixture of phenols which compete between itself for the active adsorbed sites, that is important for a determination of the phenols selectivity in the solution by adsorbent material. The conventional treatment method available for the treatment of mixture of phenols are sol –gel method [7] and competitive adsorption [8]. Studies of competitive adsorption reveals that different adsorbates compete for adsorption sites characterized by maximum heat of adsorption and minimum free energy of adsorption[9]. Very few adsorbents are reported in literature for the simultaneous adsorption

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of phenol and 2-CP such as hydrophobic FAU zeolites[10], Amberlite XAD-4 and NDA-100[11], granular activated carbon[8], layered hexaniobate [12], montmorillonite modified with hexadecyl trimethylammonium cation [13], polymeric resin MN200[14], CF_2, a pure powdered activated carbon [15] and Duolite ES – 86 [16], respectively. The objective of the work is to explore the feasibility of using the $ZnCl_2$ activated nano porous coir pith carbon as an adsorbent for the removal and recovery of toxic phenol and 2-chlorophenol (2-CP) as binary adsorbate from water using HPLC C-18 column.

2. MATERIAL & METHODS

Coir pith was dried in sunlight for 5 h. The dried coir pith (200 g) was stirred in a boiling solution of anhydrous $ZnCl_2$ (100 g in 1 liter of distilled water) for 1h, then the remaining solution was drained off and dried at 60° C for 12 h. The whole set up was placed in a muffle furnace at 700°C and carbonization was done for 1 h. After cooling the excess zinc chloride present in the carbonized material was leached out by immersing in 1 M HCl solution for 24 h in an oven at 80°C. Then the carbon was repeatedly washed with water to get rid of traces of HCl and $ZnCl_2$.The carbonized material was sieved to 250 to 500 µm size and characterized using physico-chemical methods and used for adsorption studies[6].

Procedure

Equilibrium isotherms in two component system Phenol+2-chlorophenol at a constant pH was determined using sequential adsorption/desorption method[17] as follows: To 100 mg of the adsorbent, added 50 ml of 40 mg/L of phenol at pH 2.0, agitated for 2 h. After agitation, the supernatant was removed and analyzed for phenol at 270 nm using HPLC. To the phenol loaded adsorbent, added 50 ml of 120 mg/L of 2-chlorophenol at pH 2.0 and agitated for 2 h. Then the supernatant was analyzed both for phenol and 2-chlorophenol using HPLC at 270 and 273 nm, respectively. The mobile phase was methanol-water-acetic acid in the ratio 60:39:1. The analysis was carried out in an elution gradient mode with 60 % methanol using a flow rate of 1 ml/min at 35 °C [18]. The residual concentrations of phenol and chlorophenol were obtained from calibration curves. The same procedure was repeated for other combinations of phenol and 2-chlorophenol (120 mg/L of P+40 mg/L of 2-CP; 40 mg/L of 2-CP +120 mg/L of P) in two component system.

3. RESULTS AND DISCUSSIONS

The physio-chemical characteristics of $ZnCl_2$ activated coir pith nano porous carbon in comparison with coir pith carbon in the absence of $ZnCl_2$ activation have already been reported [19].

SEM study

In SEM studies, $ZnCl_2$ activated coir pith carbon before adsorption (250 X magnification) revealed honeycomb voids with a large number of pores (Fig.1a). After adsorption the pores were filled by 2- CP (Fig. 1b). Coverage of the surface of the adsorbent due to adsorption of the adsorbate molecule presumably leading to formation of a monolayer of the adsorbate molecule over the adsorbent surface is evident from the formation of white layer (molecular cloud) of uniform thickness and coverage (spread).The preparation of activated carbon from Tectona grandis sawdust with 10% $ZnCl_2$ after mixing and subjected to vaccum drying with 1000 times magnification reveals pores of different size and shapes and there was a scattering of salt particles on the surface of the activated carbon [20].

XRD study

Fig. 2 shows that the XRD pattern of the $ZnCl_2$ activated coir pith carbon is crystalline in nature and shows sharp peaks corresponding to 2θ = 26.56 (d= 3.06056) and 42.0 (d= 2.14006). Measured inter planar distances agreed with the values reported for cellulose in literature [21]. The XRD data of the adsorbate loaded carbons have an evidence of crystalline nature of carbon changing into amorphous nature after adsorption and this suggests that the phenol molecules diffuse into micro pores and macropores.

Batch mode studies

Bisolute sequential adsorption experiments were conducted until a less strongly adsorbed solute desorbed from ZnCPC due to competition.

(i) 40 mg/L of P + 120 mg/L of 2-CP

In this case, phenol was added first and 2-CP was added second to the adsorbent. The phenol which was adsorbed to the extent of 87.54 %, was desorbed up to 43.60 % on the addition of 2-CP solution, while 2-CP adsorption did not change in the presence of phenol. It shows that 2-CP was preferentially adsorbed in comparison with the phenol. The adsorbed quantity of 2-CP (55.87 mg/g) in the presence of phenol is almost the same as that of 2-CP when present as the sole adsorbate (56.07 mg/g)[6,22].

(ii)120 mg/L of 2-CP + 40 mg/L of P

When the order of addition was reversed, i.e. 2-CP first and phenol second, 2-CP, which was adsorbed to the extent of 93.45 % was desorbed up to 9.42 % on the addition of P, while P was adsorbed up to 75.40 % in the presence of 2-CP compared to 87.54 % in the absence of 2-CP. The adsorbed quantity of 2-CP (55.79 mg/g) in the presence of phenol is almost the same as that of 2-CP when present as the sole adsorbate (56.07 mg/g)[6]. In both the cases (i) & (ii) (ie. when the order is reversed), the presence of phenol does not influence the adsorption of 2-CP, whereas presence of 2-CP desorbed P from the P loaded adsorbent. Similarly, the effect of thermally activated carbons were found to be better adsorbers for the bisolute mixture of phenol and 2-chlorophenol compared with chemically activated carbons, but adsorption of phenol was strongly suppressed in the presence of 2-chlorophenol[8].

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Modified Langmuir model in bisolute system

In the modified Langmuir model, an interaction term η which is a characteristic of each species and depends on the concentrations of the other components[23]. The modified Langmuir isotherm is written as

$$q_{eq\,i} = \frac{Q^{o}_{i}\, b_i\, (Ceqi/\eta i)}{1 + \sum^{N}_{J=1} b_j\, (C_{eqi}/\eta_j)} \quad (1)$$

where

b_1, b_2 = individual Langmuir adsorption constants of the first and the second solute related to the affinity of the binding sites, respectively, C_{eq1}, C_{eq2} is the unadsorbed concentrations of the first and the second solute, respectively, at equilibrium (mg/L), q_{eq1}, q_{eq2} is the adsorbed quantities of the first and the second solutes per gram at equilibrium, respectively (mg/g), Q^{o}_{1}, Q^{o}_{2} is the individual Langmuir adsorption capacity of the first and the second solutes respectively and η_1, η_2 is the multicomponent Langmuir adsorption capacity of the first and the second solute, respectively. The η values of chlorophenol (η_2) is higher than that of phenol (η_1) in any combination of phenol and 2-chlorophenol. The calculated qe values of Langmuir multicomponent system agreed well with the experimental qe values in P+2-CP system. These results show that the competitive, modified Langmuir isotherm provided a more realistic description of the adsorption process in bisolute system.

4. CONCLUSIONS

The present study shows that $ZnCl_2$ activated carbon developed from an agricultural waste, coir pith, is an effective adsorbent and phenol adsorption was suppressed to a great extent in the presence of 2-CP. Adsorption of 2-CP in bisolute and single solute systems showed that 2-CP was adsorbed preferentially, but phenol was adsorbed competitively. This result was further confirmed by η_1 and η_2 values obtained from extended Langmuir model. Lower solubility, molecular weight, nature and position of the substituent group, greater electron density and lower pKa value are responsible for preferential adsorption of 2-CP over phenol. These results would be useful for designing the removal of phenol/2-chlorophenol from wastewaters in the treatment plants.

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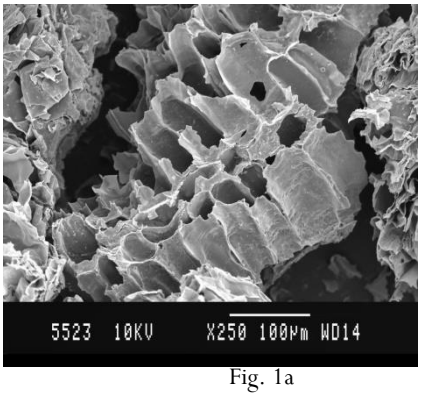

Fig. 1a

SEM Micrograph of ZnCPC before adsorption (250X)

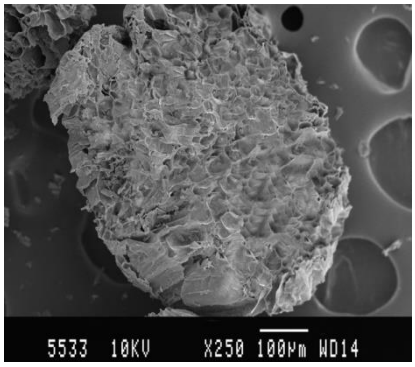

Fig. 1b

SEM Micrograph of ZnCPC after adsorption (250X)

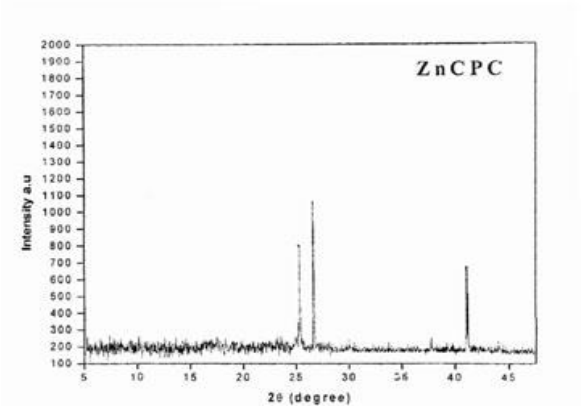

Fig. 2 XRD spectrum of unloaded adsorbent

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