

Removal of Phenol from Water by Carbon Adsorbents Prepared by Pyrolysis of Sorghum and Millet Straws in Ortho Phosphoric Acid

¹A.O. Lawal, ²J.A. Lori and ¹D. Tom Toker

¹Department of Applied Science, College of Science & Technology, Kaduna Polytechnic, P.M.B. 2021, Kaduna, Nigeria

²Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria

Abstract: The aim of this study is to determine the suitability of sorghum and millet straws as precursors for carbon adsorbents with capabilities for removing phenol from contaminated water. Phenol compounds react with chlorine in water to produce chlorophenols which have very low threshold odour concentrations in domestic water supply. Activated carbon adsorbents were prepared from millet and sorghum straws by chemical activation with phosphoric acid and used for the removal of aqueous phenol. The abilities of the carbon adsorbents to remove phenol from contaminated water were determined by aqueous phase phenol adsorption. Equilibrium concentrations of phenol were monitored, using Cole UV7504 Spectrophotometer at a wavelength of 269 nm. The adsorption data fitted the Freundlich isotherm and indicated multilayer adsorption of aqueous phenol on the carbon beds. The maximum adsorption capacities of the granular activated carbon from the cellulosic precursors were 80.36 and 82.34 mg/g of carbon from millet and sorghum straws respectively. The results suggest the suitability of the carbon adsorbents in community water detoxification protocols to remove phenol.

Key words: Activated carbon, chemical activation, millet, phenol, sorghum, straws

INTRODUCTION

Wastes from agricultural biomass have been converted into activated carbon for use as adsorbent for environmental application (Barkauskas *et al.*, 2004; Lua *et al.*, 2004; Lori *et al.*, 2007). Agricultural residues like sugarcane bagasse, wood, corn cob, corn straw, coconut shells, palm kernel shells, walnut shells, grape seeds, rice straw, rice husks, wheat straw can be pyrolysed into porous char or activated carbon materials, which are versatile adsorbents of major importance in a wide range of applications, including industrial and domestic uses (Imagawa *et al.*, 2000; Guo *et al.*, 2000; Yun *et al.*, 2001; Zanzi *et al.*, 2001; Garcia-Perez *et al.*, 2002; Hayashi *et al.*, 2002; Baquero *et al.*, 2003; Su *et al.*, 2003; Barkauskas *et al.*, 2004; Lua *et al.*, 2004; Lori *et al.*, 2008a; Lori *et al.*, 2008b). The large surface area, good thermal stability, hydrophobic nature and porosity of activated carbon result in a high capacity for adsorbing chemicals from gases or liquids (Hayashi *et al.*, 2000; Zanzi *et al.*, 2001; Barata-Rodrigues *et al.*, 2003). In the mineral category, activated carbon has been made from peat, lignite soft and hard coals, tars, asphalt and petroleum residues (Baksi *et al.*, 2003). Hamerlinck *et al.* (1994) defines activated carbon as a crude form of graphite with a

random or amorphous structure, which is highly porous with large internal surface area and exhibit a broad range of pore sizes from visible cracks, crevices and slits of molecular dimensions. Studies have shown that activated carbon from agricultural wastes have higher adsorptive capacity (Rao *et al.*, 2005; Mohan *et al.*, 2006). The major applications of activated carbon include water treatment (to remove taste, odour and trace metals), waste water treatment, solvent recovery, chemical separation, catalysis and air filters. Special emphasis on the preparation of activated carbon from agricultural byproducts has been given due to the growing interest in low-cost activated carbon. Phenol is considered to have toxic effects on human health even when present in small concentration. Ingestion of water contaminated with phenol causes protein degeneration and tissue erosion of the central nervous system and also damages the kidney, liver and pancreas (Gokturk and Kaluc, 2008). The main objective of this study therefore, is to investigate the aqueous phase adsorption of phenol on activated carbon prepared from millet and sorghum straws.

MATERIALS AND METHODS

Dry straws of sorghum and millet were collected from Rigasa farm center (non industrial area) in Kaduna State (Nigeria), in February 2008 after harvest. The straws

were cut into pieces of approximately 3 cm to obtain samples for milling. The chopped straw samples were milled with Christy and Morns miller, and sieved into a particle size of 1180 μm as recommended by Lori *et al.* (2007).

Pyrolysis of millet and sorghum straws: 0.5 g each of millet and sorghum straws were separately weighed on mettler P.E 160 electronic weighing balance in ten labeled porcelain crucibles covered with lids in each case. The straws were impregnated with 4.0 cm³ of phosphoric acid. Immediately after impregnation each of the samples was placed in Laboratory Thermal Equipment (LTE) oven and heated at 110°C for an hour to remove moisture. The samples were removed from the oven with protective gloves and placed carefully on an improvised crucible rack fabricated with a metal. The crucible racks with the crucibles covered with lids were transferred gently to muffle furnace at 450°C for previously determined residence times of 32 and 36 min for sorghum and millet straws respectively. During carbonization, once the residence time was attained, the crucible rack with the carbonized samples was gently removed with the aid of two strips of iron rod. The crucible racks with the samples were placed gently on a cold iron plate to ensure rapid cooling. Each of the crucibles with lids containing the carbonized samples was removed from the crucible rack and then kept in the desiccator for 24 h at room temperature of 27°C. The activated carbons were crushed into granules in the crucible with glass-rod. The granular activated carbons were washed with de-ionized water and then filtered into 250 cm³ conical flasks to remove ash and residual H₃PO₄ from the activated carbon. Blue litmus papers were dipped into the filtrates to ascertain neutralities of the activated carbon. The washed activated carbons were collected from the filter paper and dried in LTE oven at 110°C for an hour. The activated carbons were stored in air tight packages to prevent adsorption from air.

Adsorption studies: Adsorption experiments were carried out in eight 250 cm³ Erlenmeyer flasks with stopper. 0.3g of activated carbon was dispensed into each of the flasks and 25 cm³ of 1000 mg/dm³ phenol solutions were added and corked. In each case, the flask was agitated at room temperature of 27°C using Griffin flask shaker set at moderate speed for 5, 10, 15, 20, 25, 35, 45 and 55 min, respectively. The solutions were centrifuged for 30 min, using a Gallenkamp centrifuge. The concentrations of phenol in the supernatant solutions were monitored at a wavelength of 269 nm using Cole UV 7504 spectrophotometer. Standard solutions of 2, 4, 6, 8 and 10 mg/dm³ phenol were used for calibration.

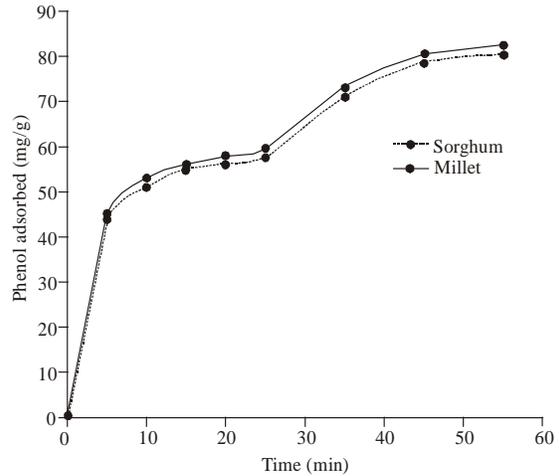


Fig. 1: Adsorption of phenol on activated carbon from millet and sorghum straws at different contact times

The concentrations of phenol retained on the adsorbents were calculated from Eq. (1).

$$q = \frac{(C_o - C_t)V}{W_s} \quad (\text{Gokturk and Kaluc, 2008})$$

- C_o = initial concentration of phenol (mg/dm³)
- C_t = concentration of phenol at time (t) (mg/dm³)
- V = volume of solution (dm³)
- W_s = mass of activated carbon (g)

The adsorption data was correlated with the Freundlich adsorption model (Eq. 2).

$$\ln q_e = \ln K + \left(\frac{1}{n}\right) C_e \quad (2)$$

- q_e = amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium in mg/g
- K = Freundlich constant representing the adsorption capacity in mg/g
- n = constant depicting adsorption intensity
- C_e = final concentration of adsorbate at equilibrium

RESULTS

The adsorption profile of phenol on activated carbon adsorbents prepared from millet and sorghum straws is shown in Fig. 1. The isotherms indicate similar phenol adsorption profile on activated carbon from millet and sorghum straws. However, the amount of phenol adsorbed per unit weight of the activated carbon was higher for activated carbon from sorghum straw.

Figure 2 and 3 shows the correlation of the phenol adsorption data with the linearized Freundlich adsorption

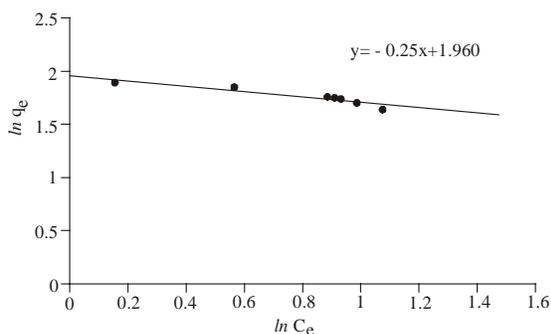


Fig. 2: Freundlich adsorption isotherm for adsorption of phenol on activated carbon from millet straws

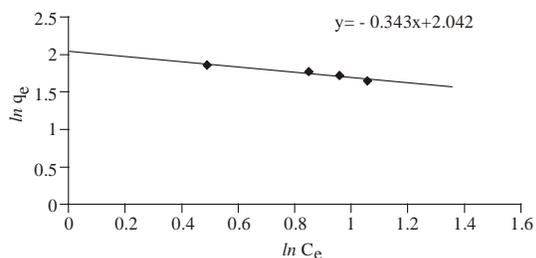


Fig. 3: Freundlich adsorption isotherm for adsorption of phenol on activated carbon from sorghum straw

model. The data fitted the model showing gradual deposition of phenol on the adsorbents.

DISCUSSION

For the adsorption test, phenol was used to establish the adsorptive characteristics of activated carbon sorbents prepared from millet and sorghum straws. In order to establish equilibrium time for optimum adsorption, the adsorption of phenol on the carbon adsorbents was studied as a function of contact time. The adsorption data indicate attainment of adsorption equilibrium was dependent on the time of contact between the phenol molecules and activated carbon granules. The adsorption patterns of phenol on the activated carbon from millet and sorghum straws were similar (Fig. 1) and represent the type IV adsorption isotherm which is typical of carbon which possesses a wide proportion of narrow mesopores. This observation is consistent with the report by Das *et al.* (2004) on removal of volatile organic compound by activated carbon Fiber. The adsorption of phenol on activated carbon from millet straw was moderate between 10-20 minutes and produced a total coverage of the adsorbent surface with about 56.15 mg of phenol per gram of activated carbon (Fig. 1). Rapid adsorption occurred between 25-45 min of the adsorption contact time and resulted into equilibrium at 55 min

contact time, as indicated by the leveling of the curve at 55 min in Fig. 1. The multilayer adsorption resulted in a maximum adsorption capacity of 80.36 mg/g for activated carbon from millet straws. Figure 1 also shows that between 10-25 min the population of phenol molecules on the entire surface of activated carbon from sorghum straw occurred, to yield a surface coverage of 59.72 mg/g. The optimum uptake of phenol by the carbon was achieved at 55 min in a multilayer, to the magnitude of 82.34 mg/g. The phenol adsorption data for the activated carbon from millet and sorghum straws fitted the Freundlich isotherm (Fig. 2 and 3). The linear equations of the isotherm plots were used to deduce the Freundlich constants ($1/n$ and k). From the magnitude of the gradients of the lines in Fig. 2 and 3, it is safe to propose that adsorption intensity of phenol on activated carbon from sorghum straw was less than the adsorption strength of phenol on activated carbon from millet straws. This observation may be related to the surface chemistry of the adsorbent materials which is dependent on the natural variability in the composition of the cellulosic carbon precursors (Haghseresh *et al.*, 2003). The adsorption bond between phenol and activated carbon from millet straw is therefore considered to be stronger than the binding of phenol to activated carbon from sorghum straw. The values of the Freundlich constant ($1/n$) for activated carbon from millet and sorghum straws were 0.25 and 0.343, respectively. The Freundlich phenol adsorption capacities (K) of the activated carbon from millet and sorghum straws were 91.2 and 110.2 mg/g, respectively. These results show that, although activated carbon from millet straw appeared to bind phenol with stronger force, activated carbon from sorghum straws had higher carrying capacity.

CONCLUSION

The maximum adsorption capacities of the granular activated carbon from the cellulosic precursors were 80.36 and 82.34 mg/g of carbon from millet and sorghum straws respectively. The results of this study suggest the suitability of activated carbon from millet and sorghum straws for the removal of phenol from water.

ACKNOWLEDGMENT

We acknowledge the assistance of Mohammed Kabir Shehu (Department of Applied Science, Kaduna Polytechnic) for the UV Spectrophotometric analysis.

REFERENCES

- Barata-Rodrigues, P.M., T.J. May and G.D. Moggridge, 2003. Structured carbon adsorbents from clay, zeolite and mesoporous aluminosilicate templates. Carbon, 41: 2231-2246.

- Barkauskas, J., S. Tautkus and A. Kareiva, 2004. Residual content of inorganic ions in activated carbons prepared from wood. *J. Anal. Appl. Pyrol.*, 71: 201-212.
- Baksi, S., B. Soumitra and S. Mahajan, 2003. Activated carbon from bamboo, technology development towards commercialization. Proceedings of BAMTECH-2003 March 12-13, Guwahati, India, pp: 1-11.
- Baquero, M.C., L. Giraldo, J.C. Moreno, F. Suarez-Garcia, A. Martinez-Alonso and J.M.D. Tascon, 2003. Activated carbons by pyrolysis of coffee bean husks in presence of phosphoric acid. *J. Anal. Appl. Pyrol.*, 70: 779-784.
- Das D., G. Vivekanand and V. Nishith, 2004. Removal of volatile organic compound by activated carbon fiber. *Carbon*, 42: 2949-2962.
- Garcia-Perez, M., A. Chaala and C. Roy, 2002. Vacuum pyrolysis of sugarcane bagasse. *J. Anal. Appl. Pyrol.*, 65: 111-136.
- Gokturk, S. and S. Kaluc, 2008. Removal of selected organic compounds in aqueous solutions by activated carbon. *J. Environ. Sci. Tech.*, 1(3): 111-123.
- Guo, Y., K. Yu, Z. Wang and H. Xu, 2000. Effects of activation conditions on preparation of porous carbon from rice husk. *Carbon*, 41: 1645-1687.
- Haghseresh, F., S. Noun and E.Q. May, 2003. Effect of carbon surface chemistry and solution pH on the adsorption of binary aromatic solution. *Carbon*, 41: 881-892.
- Hamerlinck, Y., D.H. Mertens and E.F. Vansant, 1994. *Activated Carbon Principle in Separation Technology*, Elsevier New York.
- Hayashi, J., T. Horikawa, I. Takeda, K. Muroyama and F.N. Ani, 2002. Preparing activated carbon from various nutshells by chemical activation with K_2CO_3 . *Carbon*, 40: 2181-2186.
- Hayashi, J., A. Kazehaya, K. Muroyama and A.P. Watkinson, 2000. Preparation of activated carbon from lignin by chemical activation. *Carbon*, 38(13): 1873-1878.
- Imagawa, A., R. Seto, and Y. Nagaosa, 2000. Adsorption of chlorinated hydrocarbons from air and aqueous solutions by carbonized rice husk. *Carbon* 38: 623-641.
- Lori, J.A., A.O. Lawal and E.J. Ekanem, 2007. Proximate and ultimate analyses of bagasse, sorghum and millet straws as precursors for active carbons. *J. Appl. Sci.*, 7(21): 3249-3255.
- Lori, J.A., A.O. Lawal, and E.J. Ekanem, 2008a. Adsorption characteristics of active carbons from pyrolysis of bagasse, sorghum and millet straws in ortho phosphoric acid. *J. Environ. Sci. Tech.*, 1(3): 124-134.
- Lori, J.A., A.O. Lawal and E.J. Ekanem, 2008b. Active carbons from chemically mediated pyrolysis of agricultural wastes: Application in simultaneous removal of binary mixture of benzene and toluene from water. *Int. J. Environ. Res.*, 2(4): 411-418.
- Lua, A.C., T. Yang and J. Guo, 2004. Effects of pyrolysis conditions on the properties of activated carbons prepared from pistachio-nut shells. *J. Anal. Appl. Pyrol.*, 72: 279-287.
- Mohan, D., K.P. Singh and V.K. Singh, 2006. Trivalent chromium removal from waste water using low cost activated carbon fabric cloth. *J. Hazard. Mater.*, 135: 280-295.
- Rao, M.M., A. Ramesh, P. E. Carndra and R.K. Seshaiiah, 2005. Removal of copper and cadmium from aqueous solution by activated carbon derived from *Ceiba Pentandra* hulls. *J. Hazard. Mater.*, B12a: 123-129.
- Su, W., L. Zhou and Y. Zhuo, 2003. Preparation of microporous activated carbon from coconut shells without activating agents. *Carbon*, 41: 861-863.
- Yun, C.H., Y.H. Park and C.R. Park, 2001. Effects of pre-carbonization on porosity development of activated carbons from rice straw. *Carbon*, 39: 559-567.
- Zanzi, R., X. Bai, P. Capdevila and E. Bjornbom, 2001. Pyrolysis of biomass in Presence of steam for preparation of activated carbon, Liquid and gaseous products. 6th World Congress of Chemical Engineering Melbourne, Australia, 23-27 September.