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Removal of naphthalene from aqueous system using unripe orange peel as adsorbent: effects of operating variables

C.N. Owabor[a,*], S.E. Agarry[b], D. Jato[a]

[a]*Department of Chemical Engineering, University of Benin, Benin City*
Tel. + 23 480 3410 1218; email:owabor4you@yahoo.com
[b]*Department of Chemical Engineering, Ladoke Akintola University, Ogbomoso, Nigeria*
email: sam_agarry@yahoo.com

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ABSTRACT

The adsorption of naphthalene from aqueous solution onto unripe orange peel has been investigated. The experiments were conducted using a batch reactor system. The influence of different experimental parameters such as pH, initial naphthalene concentration, particle size, adsorbent dosage and contact time on naphthalene removal was considered. Results of the batch adsorption experiment showed that equilibrium adsorption was attained in 180 min. The removal efficiency increased with an increase in adsorbent dosage, contact time and concentration but decreased with an increase in the particle size. The adsorption capacity of the unripe orange peel for an initial 100 mg/l of naphthalene was maximum at an optimum pH of 6, with an orange peel loading of 7.5 g. This study satisfactorily demonstrated that unripe orange peel which is an environmental pollutant could be used to adsorb polycyclic aromatic hydrocarbons and achieve environmental cleanliness.

Keywords: Adsorption; Agricultural waste; Adsorbent loading; Low density materials; Sorption capacity

1. Introduction

There is increasing knowledge on the mutagenic, carcinogenic and toxicological effects of polycyclic aromatic hydrocarbon compounds. Pollution especially from polycyclic aromatic hydrocarbons (PAHs) has increased rapidly, mostly in the Niger Delta area of Nigeria since industrial revolution. Due to their mobility in natural ecosystem and their persistence in nature, it has becomes imperative to remove them from the environment. The state of the environment has become pathetic due to the infertility and poor quality of our farm produce, poor quality of natural water and air caused by the various activities of our industries.

Humans are exposed to these organic pollutant (PAH) through breathing air containing PAHs in the work place of cooking, asphalt production plants, smoking cigarette, coming in contact with air, water, or soil near hazardous waste sites, eating of contaminated cereals, flour, bread, vegetables, fruits, meats, and processed food and drinking contaminated water or cowís milk. Additional contributions from tobacco smoking and the use of unvented heating sources can increase PAH

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*Corresponding author.

concentrations in indoor air, in certain cases PAHs can increase to very high levels [1–3].

The process of adsorption is well established and it is a powerful technique for adsorbing these hazardous compounds [4–8]. A variety of carbonaceous raw materials are used for the preparation of activated carbon. The common starting materials for decolourizing activated carbon are lignin, lignite, peat, wood, sawdust, etc. [9,10]. These materials are generally mixed with alkali metal sulfate, carbonate or phosphate or zinc chloride and then calcined at 500–900 °C. A good number of activated carbon used for vapour or gas adsorption are made from nutshells (mostly coconut shell), rice hull, peat, refinery residue, or coal. Several approaches have been studied and developed for the effective removal of organic pollutant using agricultural byproducts as adsorbents such as soya bean, hulls, cotton seed hull, walnut hull [8–15]. The orange peel is also one of such agricultural byproduct. It is a cheap and cost effective way of adsorbing organic pollutants from industrial effluent. This capability may be as a result of some adsorptive properties such as cellulose and hemicelluloses which it contains [16,17].

It has been observed that the modification of these agricultural byproducts as adsorbent such as the orange peel tends to increase the active sites and also made them readily available for sorption [18,19].

This research work is aimed at determining the effectiveness of unripe orange peel in adsorbing naphthalene from the environment and investigating the adsorption behaviour of naphthalene from aqueous solution.

2. Materials and methods

2.1. Materials

The unripe oranges used as adsorbent were collected from an orange tree located at the Faculty of Social Science, University of Benin, Benin City. The unripe peel was sun dried and grinded. Naphthalene (laboratory grade) was obtained from Griftin and George Loughborough, England and used as the representative PAHs in this study.

Ethanol which was used to dissolve the naphthalene and subsequently diluted with distilled water was obtained from Alconi Nigeria Limited, Amuwo Odofin Industrial Estate, Lagos, Nigeria. Freshly prepared hydrochloric acid and sodium hydroxide were used to adjust the pH of the sample solution during experiment.

2.2. Methods

2.2.1. Preparation of standard solution

Naphthalene (100 mg) of was measured using the analytical weighing balance. Ethanol (500 ml) of was used to dissolve the 100 mg of naphthalene measured. Subsequently the solution was diluted with 500 ml of distilled water to make it up to 1 l. The mixture was thereafter stirred properly to obtain a homogenous solution.

2.2.2. Preparation of adsorbent

The collected unripe oranges were thoroughly washed extensively in running tap water to remove dirt and other particulate matter. The washed oranges were dried, peeled and sun dried, and thereafter grinded using the blender machine to the desired particle size and stored in an air tight container.

2.2.3. Effect of varying initial naphthalene concentration.

Naphthalene solutions varying from 20 to 100 mg/l were prepared from standard solution in a 100 ml conical flask. A blank solution was also prepared. Two grams of adsorbent were added to each sample solution. These solutions were agitated using an orbital shaking machine (TZ-82 vapour bathing constant temperature vibrator; B.Bran Scientific and Instrument Company England) for 3 h. After the shaking operation, the solutions were filtered and the filtrates were analyzed to determine the concentration adsorbed using the UV spectrophotometer at 226 nm [20].

2.2.4. Effect of varying adsorbent dosage on naphthalene adsorption.

Fifty milliliter of 100 mg/l of naphthalene solution was prepared from standard solution in a 100 ml conical flask. The solution of same concentration was prepared in six different places. 2 g, 4 g, 6 g, 8 g, 10 g and 12 g of adsorbent were added to the six different samples. The resulting solutions were agitated using the orbital shaking machine for 3 h. The solutions were filtered and the filtrate analyzed to determine the concentration of naphthalene adsorbed [20].

2.2.5. Effect of pH variation on adsorption

The effect of pH on naphthalene adsorption was studied by varying the pH of the sample solutions [20–22]. Fifty millilitre of 100 mg/l of naphthalene solution was prepared in a 100 ml conical flask. The solution of same concentration was prepared in six different places. Two grams of adsorbent dosage was added to the solution of each sample. The pH of these solutions were adjusted with 0.05 N HCl and 0.05 N NaOH to values from 2 to 12 and measured using a digital pH meter (Jenway 3505). The solutions were agitated using the orbital shaking machine for 3 h and thereafter filtered. The filtrates were analyzed using the UV spectrophotometer to determine the concentration of naphthalene adsorbed.

2.2.6. *Effect of contact time on naphthalene adsorption*

Fifty millilitre of 100 mg/l solution was prepared from standard solution in a 100 ml conical flask. The solution of same concentration was prepared in nine different places. Two grams of adsorbent dosage was added to the solution of each sample. These solutions were agitated using the orbital shaking machine. The duration of contact for the nine samples in the shaking machine was at 20 min interval. After the shaking operations, the solutions were filtered and the filtrates were analyzed using the UV spectrophotometer to determine the concentration of naphthalene adsorbed [20].

3. Results and discussion

The potential of unripe orange peels for use as an adsorbent has been exploited in this study. The results of the effect of operating variables on the adsorptive capability of this low density material are presented below.

The dependency of naphthalene sorption on dosage was studied by varying the amount of adsorbent from 0 g to 12 g while keeping the parameters (pH, contact time, temperature, and concentration) constant. From Fig. 1 showing the percent naphthalene removal, result indicates that the removal efficiency of the adsorbent generally increases with increasing dosage. This is expected due to the fact that the higher the dose of the adsorbent in the solution, the greater the availability of the surface area and also the greater the availability of the active sites for the ions [23]. Consequently, with an increase in the surface area, there tends to be the creation of more accessibility of the adsorbent for the molecules of the mobile phase (naphthalene solution). However, beyond a dosage of 7.5 g, it was observed that there was no further increase in adsorption. This suggest that at a dose of 7.5 g of adsorbent, maximum adsorption sets in and the number of free ions remains constant even with further increase in the dose of the adsorbent.

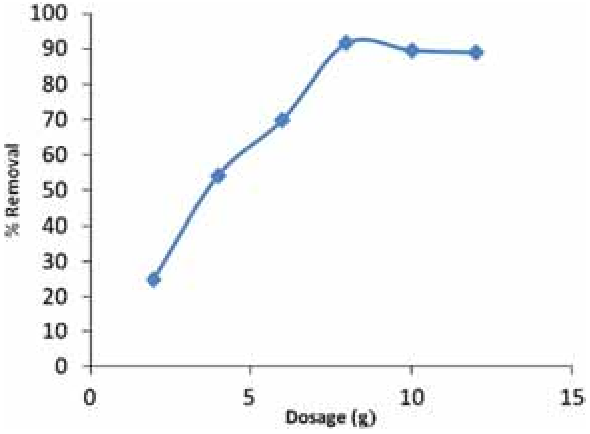

Fig. 1. Effect of adsorbent dosage on the removal of naphthalene from aqueous medium.

Fig. 2 shows the adsorption capacity with varying particle sizes of the adsorbent. The amount of naphthalene adsorbed or the percentage removed decreased with an increase in the particle size. This can be attributed to the fact that the amount of naphthalene adsorbed depends on the accessibility of the mobile phase. A large surface area can be provided by using a finely divided adsorbent. This is a basic requirement for a useful adsorbent as the large surface area provides it with the preferential ability to take up adsorbate.

The influence on adsorption by pH was studied over the pH range 2.0–12.0 as shown in Fig. 3. There is a significant difference in adsorption due to the influence of pH. The adsorption capacity of naphthalene increases with increasing pH but peaks at pH 6. Further increase in the pH evidently results in a decrease in the percentage removal. This observation are consistent with literature report of [22].

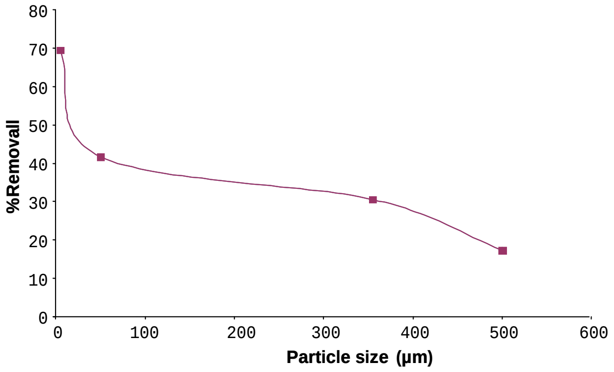

Fig. 2. Effect of particle size variation on the removal of naphthalene from aqueous medium.

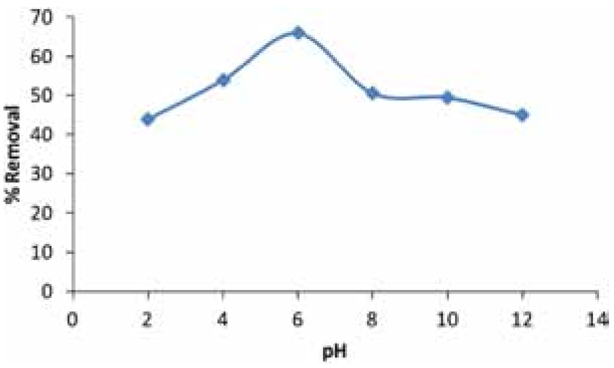

Fig. 3: Effect of pH on the removal of naphthalene from aqueous medium.

At lower pH, the adsorbent is positively charged due to protonation and naphthalene ions exist as anions thus leading to an electrostatic attraction between the adsorbate and adsorbent. The surface of the adsorbent becomes surrounded by hydronium ions which enhance the naphthalene interaction with the binding sites of the adsorbent by greater attractive forces.

However, as pH increases however, deprotonation begins thereby resulting to decreased adsorption capacity. The decrease in the percentage removal of naphthalene may be may also be attributed to the presence of excess $OH^{-\cdot}$ ions competing with the naphthalene anions for the adsorption sites since the effluent naphthalene solution is basic.

The removal efficiency of naphthalene generally increased with increasing sorption time (Fig. 4). Adsorption capacity sharply increases with increase in time and attains equilibrium in 180 min. The adsorption capacity remains constant for sorption time greater than 180 min. These results can be associated with the fact that an increase in the adsorption time allows time for sufficient adsorption reaction. The increase of contact time favours the diffusion of naphthalene ions to the surface of the adsorbent. Result shows that there was a sharp increase in the removal efficiency at the onset and as contact progresses, but it however remains nearly constant afterwards. This indicates that the surface binding sites are made readily available for naphthalene uptake at the initial time after which the adsorbent capacity got exhausted on attaining equilibrium [24].

The result of this batch experimental study showed that the adsorption capacity increases to the point of saturation of the adsorbent with an increase in concentration (Fig. 5). The increase was relatively less at higher concentration. This indicates that there exists a reduction in the immediate solute adsorption as the concentration is increased owing to the lack of available sites required for the high initial naphthalene concentration.

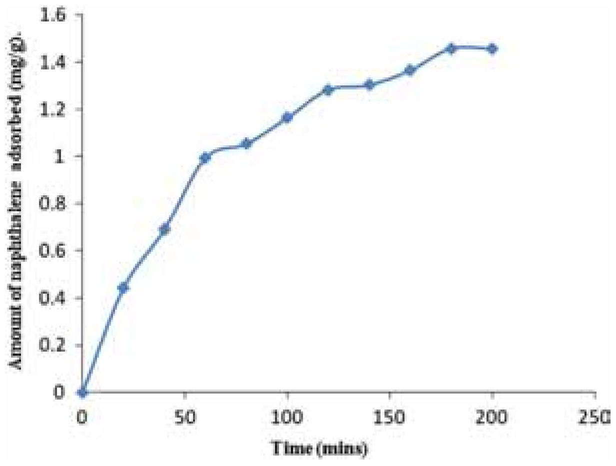

Fig. 4. Effect of contact time on the removal of naphthalene from aqueous medium.

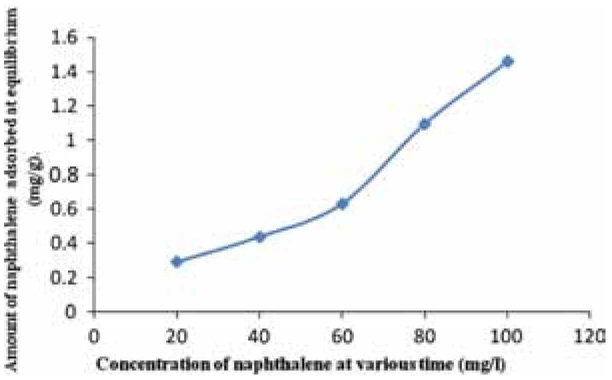

Fig. 5. Effect of concentration on the removal of naphthalene from aqueous medium.

4. Conclusion

The effectiveness of unripe orange peel for removing naphthalene has been examined in this study. The results obtained showed that the use of unripe orange peel for naphthalene removal from an aqueous stream is technically feasible. The peels have been shown to serve as excellent adsorbent with high efficacy. They are eco-friendly due to the fact that being composed entirely of agricultural wastes, their utilization, serves as a means of reduction of the waste from our environment. The cheap and ready availability of the peels makes it a very suitable alternative source of low density adsorbents that should be exploited.

References

[1] K. Boki, S. Kadota, M. Takahashi and M. Kitakouji, Uptake of polycyclic aromatic hydrocarbons by insoluble dietary fibre. J. Health Sci., 53 (1)(2007) 99–106.

[2] Y. Liu, L. Chen, Z. Jianfu, H. Qinghui, Z. Zhiliang and G. Hongwen, Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments of rivers and an estuary in shinghai China. Environ. Poll., 154 (2) (2008) 298–305.

[3] W. Guo, Y. Pei, Z. Yang and H. Chen, Historical changes in polycyclic aromatic hydrocarbons (PAHs) input in lake Baiyangdian related to regional socio-economic development. J. Hazard. Mater., 187 (1–3) (2011) 441–449.

[4] K.D. Biney, *Mass Transfer and Separation Process*, Prentice Hall of India Limited, 611-641.

[5] Y. Dudal, A.R. Jacobson, R. Samson and L. Deschenes, Modeling the dynamics of pentachlorophenol bioavailability in column experiments. Water Res., 38 (14–15) (2004) 3149–3154.

[6] A.G. Ahangar, Sorption of PAHs in the soil environment with emphasis on the role of soil organic matter: A review. World Appl. Sci., 11 (7) (2010) 759–765.

[7] C.N. Owabor, S.E. Ogbeide and A.A. Susu, Adsorption and desorption kinetics of naphthalene, anthracene and pyrene in soil matrix. Petrol. Sci. Technol., 28 (5) (2010) 504–514.

[8] S.X. Liu and J. Kim, Study of asorption kinetics of surfactants onto polyethersulfone membrane surface using QCM-D. Desalination, 247 (1) (2009) 355–361.

[9] A. Amad, M. Rafatullah, Y.Y. Chil and B.M. Siddique, Removal of Cu(II) and Pb(II) ions from aqueous solutions by adsorption on sawdust of meranti wood. Desalination, 247 (2009) 636−646.

[10] S. Hussain, H. Abdul Aziz, M.H. Isa, A. Amad, J.V. Leewen, L. Zou, S. Beecham and M. Umar, Orthophosphate removal from domestic wastewater using limestone and granular activated carbon. Desalination, 27 (1–3) (2011) 265–272.

[11] C. Namasivayam, N. Kanchana and R.T. Yamuna, Waste banana pith as adsorbent for the removal of Rhodamine-B from aqueous solution.î Waste Manage., 19 (1994) 89–95.

[12] C. Namasivayam and K. Kardiverlu, Coirpith as an agricultural waste water product for the treatment of dye waste water. Biores. Technol., 48 (1994) 79–81.

[13] H.W. Haung, Agricultural waste as a metal adsorbent: Sorption of cadmium (II) from aqueous streams. J Environ. Qual., 40(1) (2002) 15–26.

[14] R.W. Gaijwad, Removal of Cd (II) from aqueous solution by activated charcoal derived from coconut shell. Electron. J. Environ Agric. Food Chem. 3(4) (2004) 702–709

[15] N.A. Khan, S. Ibrahim and P. Subramaniam, P, Elimination of heavy metals from wastewater using agricultural waste as adsorbents. Malaysia J. Sci., 23 (2004) 43–51.

[16] F.E. Okieimen, F.I. Ojokoh, C.O. Okieimen and Wuana, Preparation and evaluation of activated carbon from rice husk and rubber seed shell. J. Chem. Soc. Nig. (2004) 191–196.

[17] O.S. Amuda and A.O. Ibrahim, Industrial waste water treatment using natural material as adsorbent. Afr. J. Biotechnol., 916 (2006) 1483–1487.

[18] M. Hanafiah, W.S. Wan Ngah, H. Zakaria and S.C. Ibrahim, Batch study of liquid-phase adsorption of lead ions using Lalang (Imperata cylindrical) leaf powder. J. Biol. Sci., 7 (2) (2007) 222–230.

[19] R. Sivaraj, C. Namasivayan and K. Kadirvelu, Orange peel as an adsorbent in the removal of Acid Violet 17 (acid dye) from aqueous solution. Water Manage., 21 (2001) 105–110.

[20] C.N. Owabor and J.E. Audu, Studies on the adsorption of naphthalene and pyrene from aqueous medium using ripe orange peels as adsorbent. Global J. Pure Appl. Sci., 16 (1) (2010) 131–139.

[21] W.E. Marshall, L.H. Wartall, D.E. Boler, M.M. Johns and C.A. Tolea, enhanced metal adsorption by soyabean hulls modified with citric acidsî Biores. Technol., 69 (1999) 263–268.

[22] M.E. Chukwuedo and F.E. Okieimen, Enhanced metal adsorption by groundnut husks modified with citric acid. J. Chem. Soc. Nig., 33 (2) (2008) 50–53.

[23] A.C. Hari, R.A. Paruchuri, D.A. Sabatini and T.C.G. Kibbey, Effects of pH and cationic and nonionic surfactants on the adsorption of pharmaceuticals to a natural aquifer material. Environ. Sci. Technol., 39 (2005) 2592–2598.

[24] M. Ahmedna, M. Johnson, S.J. Clarke, W.E. Marshall and R.M. Rao, Potential of agricultural by-products based activated carbon for use in raw surge decolorization. J. Sci. Food Agric., 75 (1997) 117–124.

[25] K.B. Payne and T.M. Abdel-Fattah, Adsorption of divalent lead by zeolites and activated carbon: Effects of pH, temperature and ionic strength. J. Environ. Sci. Health, A39 (9) (2004) 2275–2291.

[26] W.H. Cheung and G. Mckay, Kinetics analysis of the sorption of copper(ii) ions on chitosan. J. Chem. Technol. Biotechnol., 78 (2003) 562–571.

[27] E.S. El-Ashtoukhy, N.K. Amin and O. Abdelwahab, Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent. Desalination, 223 (1–3) (2008) 162–173.