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KINETIC AND THERMODYNAMIC STUDIES OF REMOVAL OF 2-NITROPHENOL FROM AQUEOUS SOLUTION USING COWPEA HUSK POWDER TETHERED ON IRON OXIDE.

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ABSTRACT

The uptake of 2-nitrophenol (2NP) from aqueous solution onto cowpea husk powder tethered on iron oxide (CHPI) and pristine cowpea husk powder (CHP) for comparison was investigated under different experimental conditions such as, initial adsorbate concentration, adsorbent dose, contact time, solution pH and temperature using UV-Visible spectrophotometer. Adsorption isotherms were described using the Langmuir and Freundlich models. The experimental data fitted into Freundlich isotherm equation, indicating monolayer adsorption of the adsorbate on the surface of the adsorbent. Kinetic evaluations showed that the adsorption mechanism of the iron tethered cowpea husk powder was well described by the Lagergren pseudo-first-order model with rate constant increasing with initial adsorbate concentration and evaluated to be $9.4x10^{-3}$ $g·mg^{-1}·min^{-1}$ for CHPI and $1.67x10^{-2}$ $g·mg^{-1}·min^{-1}$ for CHP respectively; showing the iron tethered cowpea husk powder as a better adsorbent. The evaluations of enthalpy, entropy and free energy changes revealed that the adsorption processes were spontaneous and endothermic in nature. The study revealed that both adsorbents studied behaved considerably well with an added advantage of convenient adsorbent separation with use of the iron tethered cowpea husk powder.

KEYWORDS: *Adsorption, cowpea husk, iron oxide, magnetic, kinetics, thermodynamic*

INTRODUCTION

There is rapid degradation and pollution of our environment due to increasing pollution, urbanization, and industrial growth. The continuous pollution of freshwater bodies with industrial effluents is the major cause of water scarcity [1]. Due to the high industrial importance of phenols and its derivatives, they have become a major organic pollutant commonly found in industrial wastewaters and effluents. [2, 3] Phenolic compounds are major components of dyes, polymers, drugs, and other organic substances. [4, 5] They are also used as antioxidants and flavoring agents among other beneficial health applications [3]. However, despite the benefits of phenols, they are known to be moderately or highly toxic at low concentrations to plants, fish, and many other organisms.[2] Because of the high solubility and volatility of phenolic compounds, route of exposure in water and wastewater could be nasal, oral, eye or skin and dermal contact.[6] Exposure through any of this route can cause harmful effects, with higher levels of exposure even causing eventual death.

High levels of phenolic compounds in the environment can disrupt the biological ecosystem and nutrient cycling. They top the list of hazardous chemicals that is difficult to be detoxified in the body or broken down by organism [7, 8].

The presence of this phenolic compounds in waste or municipal waters can lead to the formation of substituted compounds during disinfection and oxidation processes [9]. The mutagenic and carcinogenic properties of phenolic compounds have resulted in their categorization as priority pollutants by the US Environmental Protection Agency (EPA). Therefore, a water purity standard lower than 1ppb has been set by EPA for phenols in surface water for both humans and aquatic life [10].

2-Nitrophenol is a water soluble solid which has been used as intermediate in the synthesis of several organophosphorus pesticides and medical products [12]. The vapor phase release of industrial waste results in the wet deposition of nitrophenols from the air to surface water, posing as a major risk to both aquatic organism and humans. Strong pollution of air due to industrial emissions can lead to an increase of nitrophenols concentrations up to 320 ng/dm^3 [13].

Various methods that have been used for the removal of phenols from aqueous solution includes recuperative processes such as adsorption [14-15], membrane separation [16-17], bio-electrochemical treatment [18], electrochemical oxidation [19], ion exchange [20] and solvent extraction [21]. Oxidation with ozonation and incineration, destructive processes, has also been applied [21]. Adsorption process is used majorly for organic and inorganic micropollutants removal from aqueous environments. This is because of cost-effectiveness, ease of operation, and high removal efficiency. [22].

Activated carbon is the most widely used adsorbent for the adsorption of organic pollutant from water [23-25]. Activated carbon has shown strong effectiveness in the removal of organic and in-organic pollutant, However, it high cost, time require for preparation and regeneration is a major limitation [26]. This limitation has stimulated interest in investigating the removal of organic pollutant using low-cost adsorbents. Examples of the cost-effective adsorbents that have been tested are natural zeolite [27], treated waste newspaper [28], and olive mill waste [29]. Unlike traditional adsorbents which are usually removed through screening, a separator can be used to separate a magnetic activated adsorbents from solution even if the solution contains a significant concentration of solids.

It has been reported that agricultural waste as a raw material for adsorption have high adsorption potential with low cost and high availability [30]. Thus, the significance of this study is to propose an ecofriendly and simple method for the treatment of toxic wastes with excellent performance, and good regeneration from treated waters. The research work will also serve as a means of converting agricultural waste into relevant material that will serve the purpose of environmental remediation.

MATERIALS AND METHODS

Sample Source and Preparation of Iron Coated Cowpea Husk

The beans husk was gotten from Obantoko market in Abeokuta, Ogun State, Nigeria. The properly screened beans husk was washed with de-ionized water to remove dirt and other impurities and then dried in an oven at 100°C. The dried beans husk was crushed and converted to a fine powder that can pass through a 100µm mesh and packaged in pre-cleaned container. 10g husk fine powder immersed in 150mL solution of $FeSO_4.7H_2O$ under continuously stirring. 60mL of 5M NaOH solution was drop-wisely added to precipitate the iron oxide on the surface of the cowpea husk powder. The solution was then stirred for 1h. The resulting iron-oxide coated cowpea husk powder was filtered, washed several times with deionized water and dried at 100°C.

Adsorption Procedure

Effect of pH on Adsorption

The effect of solution pH on the adsorption of 2-nitrophenol was studied over different pH range. The pH adjustment was made with 0.1M HCl / 0.1M NaOH solution. 0.1g of a sample of the cowpea husk powder was contacted with 15 mL of 100 mg/L of 2-Nitrophenol at 25ºC in 100mL conical flask. The experiment was performed at pH 2, 4, 6, 7, 8, and 10. The reaction mixtures were agitated for 2 hours after which they were filtered with Whatman filter paper having a pore size of 9.0cm. The filtrate was analyzed for the residual adsorbate concentration on UV-V spectrophotometer. The experiment was carried out in duplicate using both the magnetic and non-magnetic cowpea husk powder. The pH was studied keeping the solution concentration, adsorbent dose, contact time and temperature constant.

Determination of Equilibrium Time

0.1g of a sample of the CHP and CHPI was weighed into 15 mL of 100 mg/L of 2-NP at 25ºC in 100 mL conical flask. The mixtures were agitated with an orbital shaker at a speed of 100 rpm for 10min for 2 hours after which they were filtered with Whatman filter paper. The mixture was filtered and then analyzed using UV-Visible spectrophotometer. The procedure was repeated by varying the time at 20, 30, 40, 60, 80, 120 and 140 minutes.

Effect of Adsorbent dose

Different grams of a sample of cowpea husk powder (0.05g, 0.1g, 0.2g, 0.4g and 0.6g) was weighed into 15 mL of 100 mg/L of 2-NP at 2ºC in 100 mL conical flask. The sample mixture was adjusted to pH of 10. The reaction mixtures were agitated for 2 hours after which they were filtered with Whatman filter paper. The filtrate was analyzed for the residual adsorbate concentration on UV-V spectrophotometer. The experiment was carried out in duplicate for CHP and CHPI

Optimum Adsorbate Concentration

0.1 g of a sample of the cowpea husk powder was contacted with 15 mL of different concentration (100, 200, 300, 400 and 500 mg/L) of 2-NP at 25ºC in 100 mL conical flask. The sample mixture was adjusted to pH of 10. The reaction mixtures were agitated for 2 hours after which they were filtered with Whatman filter paper with a pore size of 9.0 cm. The filtrate was analyzed for the residual adsorbate concentration on UV-V spectrophotometer. The experiment was carried out in duplicate for CHP and CHPI.

Effect of Temperature

0.1 g of a sample of the cowpea husk powder was contacted with 15 mL of 100 mg/L of Nitrophenol at varying temperature of 25, 30, 35, 40, 45 and 50ºC in 100 mL conical flask. The sample mixture was adjusted to pH of 10. The mixtures were agitated for 2 hours after which they were filtered with Whatman filter paper having a pore size of 9.0 cm. The filtrate was analyzed for the residual adsorbate concentration on UV-V spectrophotometer. The experiment was carried out in duplicate for both CHP AND CHPI

RESULTS AND DISSCUSION

Effect of Different Parameters on Adsorption

pH of Adsorption

Figure 1 shows that there is a gradual increase in the adsorption of 2-nitrophenol as the pH increases and pH 10 correspond the maximum adsorption for both the adsorption carried out by magnetic and the non-magnetic cowpea husk powder. The increase in adsorption capacity at a more basic pH is due to the lower concentration of hydrogen ions in the solution and at the adsorption sites of the cowpea powder.

Comparing the adsorption maxima of the magnetic and the non-magnetic powder, the magnetic powder shows more adsorption capacity compared to the non-magnetic powder at pH 10.

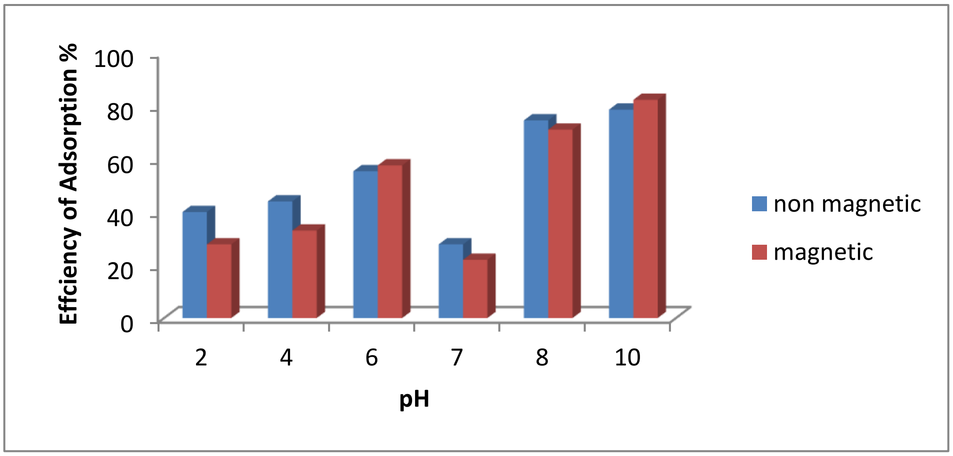

Figure 1: Graph showing the comparison of the effect of pH on 2-nitrophenol adsorption onto magnetic and the non-magnetic cowpea husk powder

Equilibrium Time

The removal of 2-nitrophenol increases with increase in the adsorption time for both magnetic and the non-magnetic cowpea husk powder (*figure 2*). The equilibrium time was reached at 120 min for both magnetic and the non-magnetic powder. The magnetic powder shows high adsorption efficiency compared to the non-magnetic powder as the time increases. After the equilibrium time was attained, there was no significant change in adsorption efficiency with increase time.

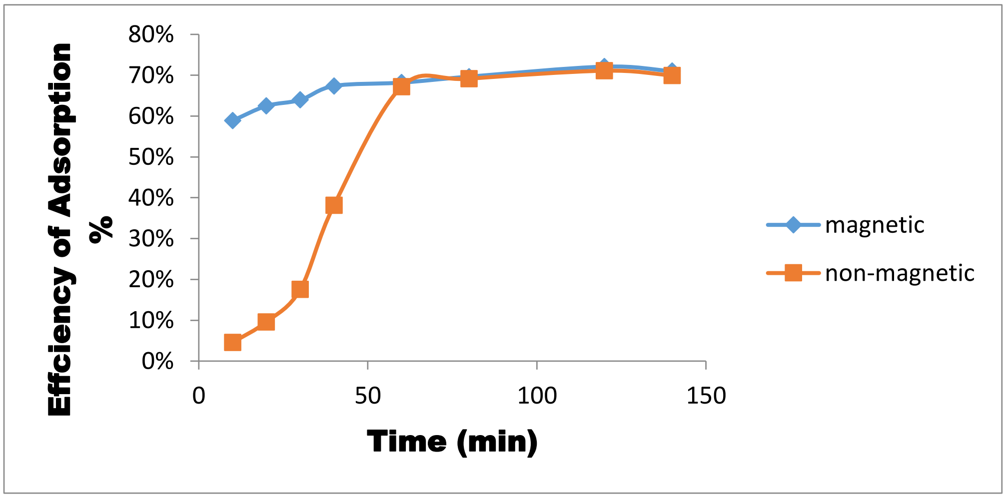

Figure 2: Graph of the effect of equilibrium time on 2-nitrophenol adsorption onto magnetic and the non-magnetic cowpea husk powder.

Initial concentration of Adsorbate

The effect of initial concentration of adsorbate on rate of 2-nitrophenol is shown in *Figure 3*. The figure indicates that the percentage removal decreases with the increase in the initial concentration, the percentage sorption decreased from 80 to 52 % for the magnetic cowpea husk powder and 75 to 57 % for the cowpea husk powder as the initial concentration of Pb (II) ions increased from 100 to 500 mg dm^{-3} showing greater absorption for the magnetic cowpea husk powder. The decreased adsorption with increased concentration shows there were no more adsorption sites on the adsorption surface of the adsorbent material as concentration increases.

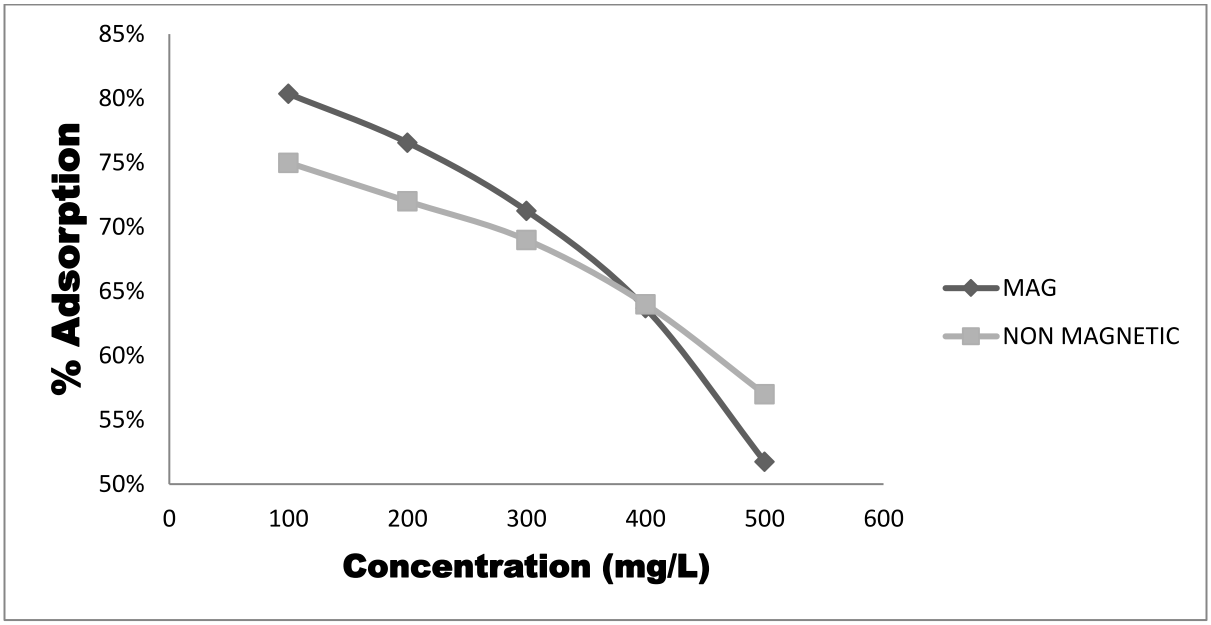

Figure 3: Adsorption capacity comparison between CHPI and CHP at different initial concentration of adsorbate.

Effect of Temperature on Adsorption Capacity

Temperature dependence of 2-NP adsorption onto CHP and CHPI was carried out within the temperature range of 25ºC to 50ºC as shown in Figure 4. The experiment was carried out at equilibrium time and equilibrium pH. The concentration of adsorbate and weight of adsorbent was kept constant. A gradual increase in the efficiency of adsorption was observed. Increased sorption with temperature increase may be due to increase in the number of active surface sites available for sorption on the adsorbent as temperature increases due to bond rupture and it signifies endothermic nature of the adsorption process.

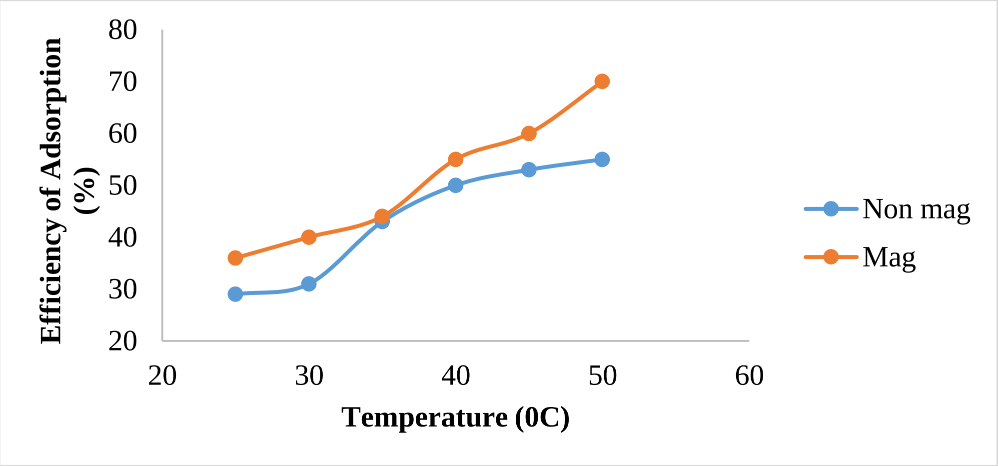

Figure 4: Effect of Temperature on the Adsorption of 2-nitrophenol using magnetic and non-magnetic cowpea husk powder

Thermodynamic Studies

The thermodynamics of the system considered under this study is shown in *Figure 5*. The enthalpy change, entropy change, and the Gibbs free energy change is related by the equation below:

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

The study of temperature dependence of adsorption gives valuable information about the enthalpy and entropy changes during adsorption. The negative value of ΔG (*Table 1*) indicates that the adsorption process is spontaneous for the temperature range evaluated which is usually the case for many adsorption systems in solution. The positive value of ΔH shows that the adsorption is endothermic, so raising the temperature leads to a higher adsorption.

Table 1: Thermodynamic parameters of adsorption of 2-nitrophenol using magnetic and non-magnetic cowpea husk powder

	ΔH	**ΔS**	**R^2**	**ΔG**					
				298K	303K	308K	313K	318K	323K
Cowpea husk	16.951	0.0698	0.9785	-3.789	-4.183	-4.621	-5.076	-5.193	-5.536
Magnetic cowpea husk	22.105	0.0916	0.9323	-5.314	-5.690	-6.088	-6.293	-6.782	-7.823

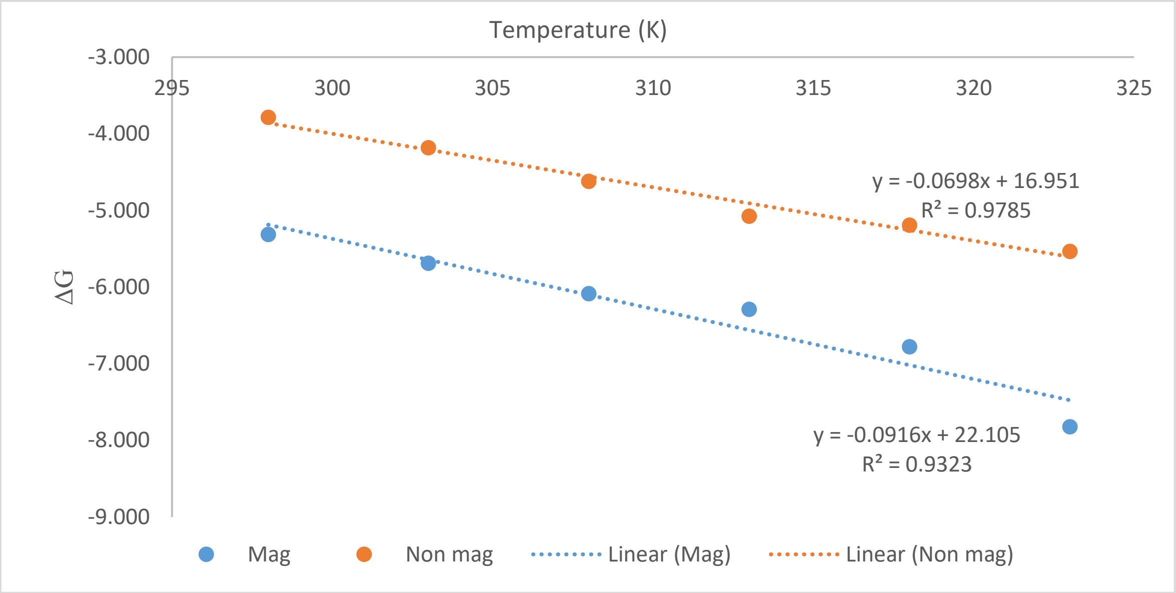

Figure 5: Thermodynamic Plot of the Adsorption process

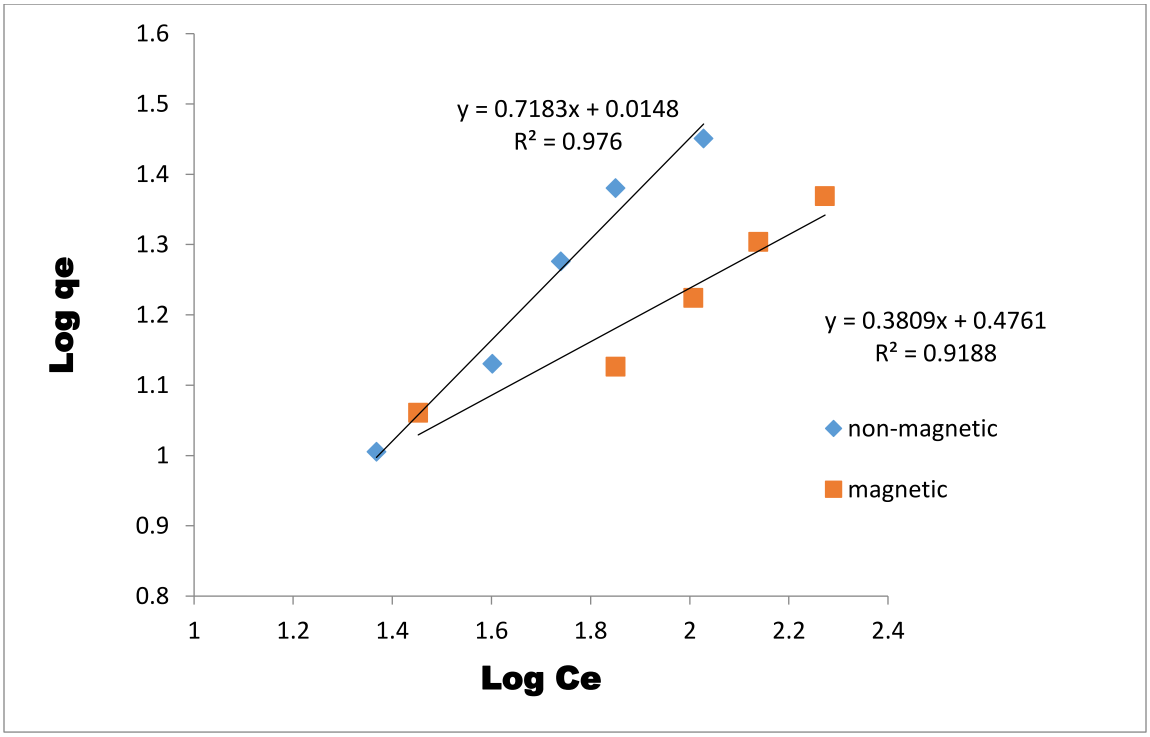

Figure 6: Graph showing Linearized Freundlich adsorption isotherm

Adsorption Isotherm

According to the *Figure 6*, the experimental data fitted into Freundlich isotherm equation perfectly, indicating monolayer adsorption of the adsorbate on the surface of the adsorbate on the surface of the adsorbent. The high value of the correlation coefficient R^2 (0.9188), the straight-line graph.

Kinetic Modeling

The experimental data above were tested using the kinetic models to study the mechanism of the adsorption of 2-nitrophenol onto the magnetic and the non-magnetic powder and potential rate determining step. Using the Lagergren pseudo-first order kinetic model (*equation 2*) for the adsorption of 2-nitrophenol by the magnetically coated powder (*Figure 7*) and the non-magnetic powder, the linearization of the graph gives a vivid explanation to the kinetic of the adsorption of 2-nitrophenol on the magnetic cowpea husk powder at high and low adsorption rate.

$$In(q_e - q_t) = Inq_e - k_1 \qquad (2)$$

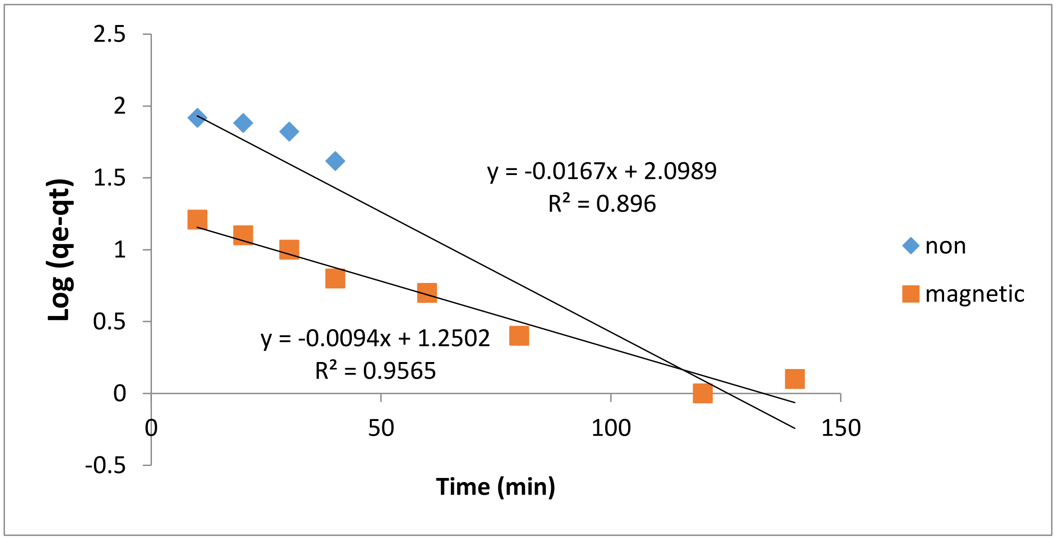

Figure 7: Graph of Lagergren-pseudo first order model for the adsorption of 2-nitrophenol onto magnetic and non-magnetic cowpea husk powder.

The low correlation coefficient of non-magnetic powder, R^2 value of (0.896) indicate that Lagergren model does not work well for it unlike adsorption carried out with magnetic cowpea husk having a high correlation coefficient, R^2 value of (0.9566). The rate constant for the adsorption was evaluated to be $9.4x10^3$ $g{\cdot}mg^{-1}{\cdot}min^{-1}$ for the magnetic cowpea husk powder and $1.67x10^2$ $g{\cdot}mg^{-1}{\cdot}min^{-1}$ for the cowpea husk powder showing that the magnetic cowpea husk powder is a better adsorbent.

CONCLUSION

The mechanism of the adsorption 2-Nitrophenol on cowpea husk powder tethered on iron oxide (CHPI) and pristine cowpea husk powder (CHP) aqueous medium was investigated using kinetic and equilibrium studies. The equilibrium time was found to be 120 min for min for both magnetic and the non-magnetic powder. Maximum adsorption for 2-NP was found to occur at pH 10. Kinetic evaluation of the adsorbent using Lagergren pseudo-first-order model shows that the iron tethered cowpea husk powder as a better adsorbent. The rate constant increased with initial adsorbate concentration and evaluated to be $9.4x10^{-3}$ $g·mg^{-1}·min^{-1}$ for CHPI and $1.67x10^{-2}$ $g·mg^{-1}·min^{-1}$ for CHP respectively.

Adsorption isotherm reveals that the experimental data fitted into Freundlich isotherm equation. This shows a monolayer adsorption of the adsorbate on the surface of the adsorbent. T Enthalpy, entropy and free energy changes shows a spontaneous and endothermic adsorption processes. Although both CHPI and CHP shows favorable results, the former has the advantage of convenient adsorbent separation.

REFERENCES

1. Saleh TA, Adio SO, Asif M, Dafalla H. (2018) Statistical analysis of phenols adsorption on diethylenetriamine-modified activated carbon. J. Clean. 182:960-968.

2. Stelmaszewski A (2012). Application of fluorescence in studies of marine petroleum pollutants, Scientific Journal of Gdynia Maritime University, No. 76, pp. 74-83, 2012

3. Vermerris W., and Nicholson R. (2008) Phenolic Compounds and their Effects on Human Health. In: Phenolic Compound Biochemistry. Springer, Dordrecht. https://doi.org/10.1007/978-1-4020-5164-7

4. Afilah AG, Mohd YS, Khalilah AK, Farrah AD, Ariff K, and Siti AA. (2014) Phenol and Phenolic Compounds Toxicity. Journal of Environmental Microbiology and Toxicology, 2(1):11-23.

5. Dutta NN, Borthakur S, and Baruah R. (1998). A novel process for recovery of phenol from alkaline wastewater: laboratory study and predesign cost estimate. Journal of water environment research 1:4-9.

6. Mu’azu, ND, Nabeel J, Mukarram Z, and Omar Alagha. (2017). "Removal of Phenolic Compounds from Water Using Sewage Sludge-Based Activated Carbon Adsorption: A Review" International Journal of Environmental Research and Public Health 14, no. 10: 1094. https://doi.org/10.3390/ijerph14101094

7. Hind Y, Zuo S, Mustapha M, Mina G, and Said S. (2015). Adsorption isotherm, kinetic and mechanism studies of 2-nitrophenol on sedimentary phosphate. Mediterranean Journal of Chemistry, 4(4):289-296

8. Alinnor IJ, and Nwachukwu M. (2011). A study on removal characteristics of para-nitrophenol from aqueous solution by fly ash. Journal of Environmental Chemistry and Ecotoxicology 3(2): 32-36

9. Busca G, Berardinelli S, Resini C, and Arrighi L. (2008). Technologies for the removal of phenol from fluid streams: a short review of recent developments. J Hazard Mater, 160(2-3):265-88. doi: 10.1016/j.jhazmat.2008.03.045.

10. Kazemi P, Mohammad P, Alireza B, Toraj M, and Omid B. (2014). Stability and extraction study of phenolic wastewater treatment by supported liquid membrane using tributyl phosphate and sesame oil as liquid membrane. Chemical engineering research and design 92(2): 375-383.

11. Sharma S, and Bhattacharya A. (2017) Drinking water contamination and treatment techniques. Applied Water Science 7(3): 1043-1067.

12. Stephen JA, Bogdana K, Kircheva Z, and Nenkova S. (2005). Adsorption of 2-Nitrophenol by Technical Hydrolysis Lignin: Kinetics, Mass Transfer, and Equilibrium Studies Industrial & Engineering Chemistry Research 44 (7), 2281-2287 DOI: 10.1021/ie049455d

13. Edris B, Ferdos KM, and Hossein JM. (2013). Phenolic Compounds: Health effects and its removal from aqueous environments by low-cost adsorbents. Health scope, 2(2): 65-66

14. Lee CG, Hong SH, Hong SG, Choi JW, and Park SJ. (2019) Production of biochar from food waste and its application for phenol removal from aqueous solution. Water Air Soil Pollut.. 230:70.

15. Cheng S, Zhang L, Xia H, and Peng J. (2017). Characterization and adsorption properties of La and Fe modified activated carbon

for dye wastewater treatment. Green Process Synth., 6:487-498

16. Tan Y, Sun Z, Meng H, et al. (2019). A new MOFs/polymer hybrid membrane: MIL-68(Al)/PVDF, fabrication and T application in high-efficient removal of p-nitrophenol and methylene blue. Sep. Purif. Technol., 215:217-226.

17. Tian H, Hu Y, Xu X, et al. (2019). Enhanced wastewater treatment with high o-aminophenol concentration by two-stage MABR and its biodegradation mechanism. Bioresour. Technol., 289:121649.

18. Khan A, Chen Z, Zhao S, et al. (2019). Micro-aeration in anode chamber promotes p-nitrophenol degradation and electricity generation in microbial fuel cell, Bioresour. Technol., 285:121291.

19. Massa A, Hernándeza S, Ansaloni S, Castellino M, Russo N, and Fino D. (2018). Enhanced electrochemical oxidation of phenol over manganese oxides under mild wet air oxidation conditions. Electrochim. Acta., 273:53-62.

20. Víctor-Ortega MD, Ochando-Pulido JM, Martínez-Férez A. (2016). Phenols removal from industrial effluents through novel polymeric resins: Kinetics and equilibrium studies. Sep. Purif. Technol. 160:136-144.

21. Villegas LGC, Mashhadi N, Chen M, Mukherjee D, Taylor KE, and Biswas N. (2016). A short review of techniques for phenol removal from wastewater. Curr. Pollut. Rep., 2:157-167

22. Flox C, Garrido J, Rodriquez R, Centellas F, Cabot P-L, Arias C. And Brillas, E. (2013). Degradation of 4.6-dinitroo-cresol from water by anodic oxidation with a boro-doped diamond electrode. Electrochim. Acta. 50: 3685.

23. Chern JM, and Chien YW. (2002). Adsorption of nitrophenol onto activated carbon: isotherms and breakthrough curves. Water Res**.**, 36, 647.

24. Juang R, Tseng R, and Wu F. (**2001**). Role of microporosity of activated carbons on their adsorption abilities for phenols and dyes. Adsorption 7, 65.

25. Rajagopal C, and Kapoor J. (**2001**). Development of adsorptive removal process for treatment of explosives contaminated wastewater using activated carbon. J. Hazard. Mater., 87, 21

26. Nidhi Y, Dhruv M, Shalu R, and Jiwan S. (2020). Adsorption and equilibrium studies of phenol and para-nitrophenol by magnetic activated carbon synthesized from cauliflower waste. Environ. Eng. Res. 2020; 25(5): 742-752. https://doi.org/10.4491/eer.2019.238

27. Hor KY, Mun J, Chee C, et al. (2016). Evaluation of physicochemical methods in enhancing the adsorption performance of natural zeolite as low-cost adsorbent of methylene blue dye from wastewater., 118:197-209

28. Dehghani MH, Sanaei D, Ali I, and Bhatnagar A. (2016). Removal of chromium (VI) from aqueous solution using treated waste newspaper as a low-cost adsorbent: Kinetic modeling and isotherm studies. J. Mol. Liq., 215:671-679

29. Abdelkreem M. (2013). Adsorption of phenol from industrial wastewater using olive mill waste. APCBEE Procedia, 5:349-357.

30. Hameed, B., Tan, I. and Ahmad, A. (2008). Adsorption isotherm, kinetic modeling and mechanism of 2, 4, 6-trichlorophenol on coconut husk-based activated carbon, Chemical Engineering Journal, 144 (2): 235-244