Clean Technology Approach For Ciprofloxacin Sequestration Using Modified Banana Stalk

Toyin Adedayo OREOFE

Landmark University

Oladipupo Olaosebikan OGUNLEYE

Ladoke Akintola University of Technology

Olugbenga Solomon Bello (✉ osbello06@gmail.com)

Ladoke Akintola University of Technology <https://orcid.org/0000-0001-8732-1816>

Research

Keywords: Ciprofloxacin, Banana stalk, Acid activation, Activated carbon, Desorption studies

Posted Date: October 23rd, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-92704/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

The adsorption mechanisms and capacity of adsorbent derived from banana stalks in removing ciprofloxacin (CIP) from aqueous solutions were investigated in this study. The Banana Stalk Activated Carbon (BSAC) was prepared through acid activation and were characterised via SEM, FTIR and pH_{pzc} . The SEM micrograph of BSAC revealed prominent well-developed pores which aid the adsorption process. The FTIR spectra shows the presence of various functional groups for efficient CIP adsorption. The effects of temperature (30 – 70 °C), adsorbent dosage (0.01 – 0.05 g/L), pH (2 - 10), initial adsorbate concentration (1 - 5 mg/L) and contact time (10 - 360 min) were evaluated using batch operations. Optimum CIP adsorption was obtained at pH 6. The maximum monolayer adsorptive capacity of the acid-treated banana stalk was 222.22 mg/g at 30 °C. Langmuir isotherm was the most appropriate isotherm model while pseudo second order kinetics best describe the kinetic process. Its thermodynamic studies indicated endothermic and spontaneous process. The cost implication of BSAC preparation (12.35 USD/kg) indicates that it is about 21 times cheaper than Commercial activated carbon (270.8 USD/kg) while the desorption studies reflects the reusability efficiency of the spent adsorbent. BSAC was found to be effective, efficient and economically viable for ciprofloxacin removal from aqueous solution.

1. Introduction

The release of trace level chemicals classified as emerging contaminants into the environment through daily human activity such as domestic, industrial and agricultural activity has become a source of concern [1, 2]. The chemicals persist in the environment thereby pose a public health risk and threatened the availability of potable water [3]. A subset of emerging contaminant known as Endocrine Disruptive Chemicals (EDCs) deters the regular synthesis of the endocrine system, inhibits the metabolism and secretion of natural hormones thereby affecting the reproduction of man, plants and animals [4, 5].

Numerous chemicals are classified as emerging contaminants due to adverse health hazards on the ecosystem through continual direct contact [6]. Some of these chemicals are pharmaceuticals [7], (Li *et al.*, 2020), personal care products [8], pesticides [9] and plastic products [10]. Researchers have used various techniques to remove these trace compounds from water and waste water. Some of these removal techniques include electrochemical treatment [11], biological treatment [12], ozonation [13] and adsorption [14–16].

Ciprofloxacin ($\text{C}_{17}\text{H}_{18}\text{FN}_3\text{O}_3$) a fluoroquinolone antibiotic is an example of pharmaceutical often used to treat broad spectrum bacterial infectious diseases [17]. It is a yellow to light yellow crystalline powder, 331.346 g/mol molecular weight, soluble in 0.1 M hydrochloric acid and water. It is the most prescribed or widely used antibiotics due to its therapeutic purpose. Its concentration in wastewater ranges between

$\frac{\mu\text{g}}{\text{L}}$ to mg/L

and was noticed to increase about 31 mg/L times in the effluents of pharmaceutical plant [18]. Ciprofloxacin is pH-dependent and zwitterionic in nature, at $\text{pH} \leq 4.0$ it exists in cationic (CIP^+)

nature, $4.0 \text{ pH} \leq 8.0$ it exists in zwitterionic ($\text{CIP}^{\pm}$) while $\text{pH} > 8$ it is in anionic (CIP^-) nature [19]. Ciprofloxacin is released into the water environment either by defecation of unmetabolized chemical or direct disposal into the environment [20]. The effect of minimal concentration of CIP in the environment is a prolonged allergic reaction in the ecosystem and antibiotic resistance in bacteria [21–23].

Agricultural residues are ligno-cellulosic materials with different functional groups and high adsorptive capacity. They are generated in high quantity as a result of industrialization and commercialization [24]. Different research work has been carried out using agricultural residues as adsorbent. Some of these includes: eggshell [25], date seeds [26], bean pod [27], Barbara nut chaff [28] amongst others. Banana (*Musa paradisiaca*) is a perennial fruit, one of the most widely grown which originates from Southeastern Asia. It is cultivated in both tropical and sub-tropical regions. It is widely traded fresh fruit as a result of its high nutrient level and sweet taste [29]. In medicine, it is mostly recommended because of its antimicrobial [30] and antioxidant [31] characteristics. Two main residues are derived from banana fruit plantation which is stalks and peel. Improper disposal of these residues constitutes environmental menace hence, the need for alternative usage.

Banana stalks are readily available at little or no cost hence a single step acid activation and carbonization was carried out to produce low cost activated carbon in this study. Five different operational parameters were investigated into namely: solution pH, contact time, initial CIP concentration, temperature and adsorbent dose. Sequel to batch adsorption studies, the data were analyzed using four isotherm models namely: Freundlich[32], Dubinin- Radushkevich[33], Langmuir[34] and Temkin[35]. Also, the process kinetics model was examined by analyzing the data using the pseudo first order, pseudo-second order and intraparticle diffusion model. Also, the cost of commercial activated carbon (CAC) was compared with the cost of preparation of the adsorbent to justify its economic viability. Desorption studies was also investigated into so as to determine the efficiency of reuse of spent adsorbent.

2. Materials And Techniques

2.1 Chemicals Used

Four main chemicals were used in the adsorption process and these include ciprofloxacin ($\text{C}_{17}\text{H}_{18}\text{FN}_3\text{O}_3$), 0.1 M Hydrochloric acid (HCl), 0.3 M orthophosphoric acid (H_3PO_4) and 0.1 M sodium hydroxide. These chemicals are purely analytical grade and further purification is not necessary.

2.2 Sample Collection and Pretreatment

The banana stalk was collected from a local market in Omu-Aran Kwara State, Nigeria. Specks of dirt and impurities on the stalks were removed by washing with distilled water. The stalks were further reduced in size by cutting with a knife after it was transferred into an oven operated at 105°C until a consistent weight was attained. The dried samples were screened to $106\text{ }\mu\text{m}$ particle size sequel to crushing and subsequently kept in a closely tight container for further experimental use.

2.3 Activated Carbon Preparation

The acid-treated activated carbon was prepared by mixing 600 cm³ of 0.3 M ortho-phosphoric acid (H₃PO₄) with 30 g banana stalk powder in 1000 cm³ graduated beaker. The combination was stirred continuously and heated up on a hot plate until a paste is formed [27]. Four clean crucibles were heated in a furnace at 250 °C for 30 min to remove impurities therein and it was later placed in a desiccator for it to cool. The paste was transferred into the crucibles and heated at 650 °C in a furnace for 35 min and allowed in a desiccator. The pH of the activated carbon was adjusted to neutrality by washing severally with distilled water. After which it was dried to a consistent weight in an oven operated at 105 °C. Subsequently, for further use, BSAC was kept in an air tight container.

2.4 Preparation of adsorbate stock solution

Ciprofloxacin is soluble in acid and partially soluble in water. 0.1 g of the adsorbate was dissolved in 1 L of 0.1 M HCl to prepare a stock solution. The working solutions were obtained through serial dilution of the stock solution to obtain preferred concentration.

2.5 Characteristics of BSAC

2.5.1 Scanning electron microscopy (SEM)

SEM analysis was used to describe the surface topology and composition of BSAC. This electronic microscope works with a unique principle that focused electron beams via scanning and hence produces sample images. The interaction of the electron with domicile sample atoms produces a signal that gives adequate information on the adsorbent [27].

2.5.2 Fourier transform infrared spectroscopy

BSAC characteristic functional group was described by Fourier Transform Infrared Spectroscopy (FTIR) analysis. These functional groups were interpreted by the various bands on the adsorbent surface for efficient adsorption process.

2.5.3 pH point of zero charges (pH_{pzc})

The point on the adsorbent surface with which pH net charge is zero is referred to as the pH point of zero charges. The adsorbent surface is positively charged at pH less than pH_{pzc} and negatively charged at pH greater than pH_{pzc} [25].

2.6 Batch equilibrium studies

The batch adsorption studies of ciprofloxacin over BSAC were investigated by analyzing the effect of initial ciprofloxacin concentration, solution pH, adsorbent dosage, temperature and contact time. For this study, ciprofloxacin concentration was varied between 1–5 mg/L. 100 ml of ciprofloxacin solution was added to 0.01 g BSAC in a 250 cm³ volumetric flask for each concentration. Afterward, the flask was

placed in a water bath shaker set at 26°C and 130 rpm agitation speed. The sample was withdrawn at a different time interval and the supernatant was separated. The absorbance of the supernatant was taken using a single cell holder Jenway UV Visible spectrophotometer operated at 277 nm[36]. The process of sample withdrawal and absorbance was repeated until equilibrium was attained. The percentage removal of ciprofloxacin adsorbed was determined using Eq. 1.

$$\% \text{ Removal} = \frac{(C_i - C_t)}{C_i} \times 100 \quad (1)$$

where C_i and C_t (mg/L) are the concentration of ciprofloxacin in aqueous solution at the initial time and specific time t respectively.

3. Results And Discussion

3.1 Characteristics of the prepared adsorbent

The physicochemical and proximate analysis of BSAC was determined with results obtained presented in Table 1. The bulk density, ash content and moisture content of the adsorbent is very low. The low moisture and ash content obtained from BSAC made banana stalk an appropriate precursor for activated carbon preparation [37]. The high specific surface area of BSAC indicates its good potential for ciprofloxacin adsorption in an aqueous solution. Acid activation and carbonization of the precursor enhanced the development of the pores and subsequently resulted in a high specific area of BSAC [38].

3.1.1 Fourier transform infrared spectroscopy (FTIR)

The specific functional group on banana stalk activated carbon (BSAC) and ciprofloxacin laden banana stalk activated carbon (CLBSAC) as shown by FTIR spectral is depicted in Fig. 1a and b. The hydroxyl stretch of alcohol and phenols (O–H) was observed at a broad absorption band at 3412 cm^{-1} . The alkanes stretch (C–H) was observed at 2806 cm^{-1} , alkyne stretch ($\text{C} \equiv \text{C}$) at 2370 cm^{-1} , ketone stretch ($\text{C} = \text{O}$) at 1707 cm^{-1} , carboxylic acid stretch ($\text{C} = \text{O}$) at 1616 cm^{-1} while alcohols stretch (C–O) at 1236 cm^{-1} for ciprofloxacin adsorption [38]. After ciprofloxacin adsorption, some peaks shifted, new peaks emerged and some disappeared. Table 2 shows an explicit presentation of the various bands' assignment of the spectra.

3.1.2 pH point of zero charge (pH_{pzc})

The value of pH_{pzc} is at pH 4 and this was determined at the point on the x-axis where the curve cut through the pH_0 axis. The net charge is in the acidic medium with pH_{pzc} at 4. At $\text{pH} < 4$ the adsorbent surface is positively charged and this aids the adsorption of anions. Also, at $\text{pH} > 4$ the adsorbent surface

is negatively charged and this aids the adsorption of cations. This result shows that BSAC has a positive charged surface up till pH 4 [25, 39]. The pH_{pzc} of BSAC as investigated is shown in Fig. 3.

3.1.3 Scanning electron micrograph (SEM)

The surface characteristics of acid-activated BSAC and ciprofloxacin - laden BSAC are shown in Fig. 3a and b. Numerous well-developed pores were shown on the adsorbent surface which can be attributed to the activating agent (H_3PO_4) used for its modification [27]. Rough cavities and openings were also visible on the surface which is a result of lignocellulosic material breakdown coupled with the evaporation of volatile organic compounds at high temperature [40]. From Fig. 3b, the adsorbent surface was completely altered sequel to adsorption of ciprofloxacin. The well-developed pores observed before adsorption were presumed to be filled with ciprofloxacin molecules after adsorption [41].

3.2 Adsorption Studies using batch operations

3.2.1 Effects of contact time and initial ciprofloxacin concentration

The adsorbate-adsorbent interaction as related to varying ciprofloxacin concentration at the initial stage and contact time is shown in Fig. 4. From this figure, the quantity adsorbed at a specific time increases as the initial concentration increased from 1 mg/L to 5 mg/L. For these concentrations, the adsorption process reached an equilibrium between 90 min to 360 min. Rapid adsorption of ciprofloxacin was observed from the figure and consequently, the adsorption became slower until equilibrium was reached. The speedy uptake could be ascribed to numerous widely open active sites on the adsorbent surface. A likely report was given in the study of modified activated carbon as a good adsorbent for quinoline sequestration [42]. Also, it was observed that the quantity of ciprofloxacin adsorbed for the initial concentration considered increased from 61.24 to 170.30 mg/g at equilibrium. Adsorption rate increases as the diffusion process increased at equilibrium [43].

3.2.2 Effects of adsorbent dosage

Figure 5 depicts the percentage removal efficiency of ciprofloxacin with varied adsorbent doses ranging between 0.01 g/L to 0.05 g/L with 0.01 g/L interval. The percentage removal efficiency of ciprofloxacin is directly proportional to the adsorbent dose. That is an increase in one leads to the increase of the other (72.90% – 91.61%). It can be inferred that on the adsorbent surface there are numerous adsorption active sites that aid the high percentage removal efficiency [44].

3.2.3 Effects of solution pH

From Fig. 6, adsorption at pH 6 and pH 2 gave the maximum and minimum percentage removal efficiency of 92.85% and 72.72%. This observation shows the zwitterionic nature of ciprofloxacin that is at different pH values its molecule exists in different forms. Solution $pH < 5.9$ ciprofloxacin molecules exist as cationic form, at solution $pH > 8.89$ it exists in an anionic form while at pH between 6.1 and 8.7 the zwitterionic and neutral form is prevalent [45]. The electrostatic interaction that exists between

ciprofloxacin and BSAC determines the adsorption rate. The lower percentage removal observed at $\text{pH} < 4$ could be as a result of the positively charged surface of the adsorbent and the cationic nature of the molecule. At $\text{pH} 4-5$ a slight increase was observed and this can be described as the effect of reduction in the cationic charge on the adsorbent surface. The maximum adsorption recorded at $\text{pH} 6$ can be presumed to be as a result of the zwitterionic nature of ciprofloxacin and the negative sites of the adsorbent. Researchers have reported related results for oat hull and bamboo-based carbon [20, 44].

3.2.4 Effects of temperature

The quantity of ciprofloxacin adsorbed increased with an increase in temperature, quantity adsorbed increased from 41.08 to 70.54 mg/g from 30°C to 70°C temperature range (Fig. 7). This specifies that the system considered is an endothermic system that can be related to an increase in the adsorptive sites in which ciprofloxacin molecules penetrate [44]. This phenomenon also is presumed the movement of adsorbate molecules is increased with increasing temperature of the solution thereby ciprofloxacin molecule may have generated energy that overcomes the activation barrier [44].

3.3 Kinetic studies

The rate-determining step and adsorption mechanism of this process were determined. This is achievable via the analysis of the process adsorption data using three different kinetic models. These models include pseudo first order, pseudo-second order and intraparticle diffusion model. Considering the values reported in Table 3 pseudo second order best described the kinetics of this process. There is close agreement between $q_{\text{calculated}}$ and $q_{\text{experimental}}$, with low SSE value and correlation coefficient (R^2) close to unity. The intraparticle diffusion model interprets the adsorption mechanism of this process. The q_t value shows a linear correlation with $t_{1/2}$ (Fig. 8 iii), the slope and intercept of the plot are rate constant (K_{diff}) and boundary layer effect (C) respectively. In examining the intraparticle diffusion model in the adsorption process a linear regression plot of q_t against $t^{1/2}$ that passes through the origin shows that the model is the main rate-determining step. Also, there is a boundary layer resistance at the solid-liquid interface of the process if it does not pass through the origin [46]. In this study, the adsorption rate is also controlled by the boundary layer because the plot did not pass through the origin that is the two processes occurred simultaneously[47].

3.4 Adsorption isotherm studies

From Figure 8 (i), a linear graph with 0.9774 correlation coefficient R^2 value was obtained from evaluating the data using the Langmuir model. The dimensionless parameter R_L determines the favourability of the process. A process is favourable if $0 < R_L < 1$, it is an irreversible process when $R_L = 1$ and unfavourable when $R_L > 1$ [48]. However, in this study the adsorption process is favourable. The monolayer adsorption

capacity at the maximum level (q_m) was experimentally determined to be 222.22 mg/g. Further analysis of the data obtained for the Freundlich model with adsorption capacity (n) greater than 1 point to the favourability of the process [48]. Although monolayer adsorption is prevalent in the ciprofloxacin uptake onto BSAC, the Freundlich isotherm model has moderately high R^2 value which indicated some degree of multilayer adsorption in the system. The positive value of heat of adsorption obtained in the Temkin model analysis indicates an endothermic process. Also, the process mechanism is physisorption with E less than 8 kJ/mol. With reference to correlation coefficient R^2 the efficiency of the isotherms can be described thus: Langmuir ($R^2 = 0.9774$) > Freundlich ($R^2 = 0.9671$) > Temkin ($R^2 = 0.8995$) > Dubinin-Radushkevich ($R^2 = 0.8383$). This result shows that Langmuir isotherm best fits the adsorption of ciprofloxacin onto BSAC. Similar trends of the efficacy of Langmuir model were reported using date pal leaflets [49], bamboo [44], different biomass wastes [50], *Enteromorpha prolifera* [45] and bean husk [27] as adsorbent.

Adsorption thermodynamics studies

The interaction of the solid-liquid interface, spontaneity and feasibility of the process was investigated by examining relevant thermodynamic parameters. The Gibbs free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) are the parameters considered. Vant Hoff's plot of ciprofloxacin uptake onto BSAC is shown in Fig. 9 and the parameters were calculated. A positive enthalpy value (ΔH°) obtained suggests an endothermic process. Value of ΔS° is positive and this explains an increase in randomness at the system's boundary layer. The negative values obtained for Gibbs free energy (ΔG°) indicates a spontaneous system [38].

3.5 Cost Analysis

The summary of the cost of production of BSAC and the purchase of commercial activated carbon (CAC) is as presented in Table 7. The major significant cost in the production of BSAC includes the cost of energy, transportation, ortho-phosphoric acid and deionized water. The total cost of preparation and production of BSAC is 12.35 USD/kg (12,350 USD /ton). This amount is economically friendly compared with the cost of commercially activated carbon (270.8 USD/kg; 270,800 USD/ton). From this analysis, one kg of BSAC is about twenty-one (21) times cheaper than CAC. Hence, BSAC can be a good substitute for the commercial activated carbon.

3.6 Desorption and regeneration studies

Sequel to adsorption process the regeneration of exhausted adsorbent is very important in the water treatment process. The possibility of reuse of the adsorbent heightens the economic viability of the process [51, 52]. For this study, five different eluents were used for the evaluation of desorption efficiency which includes acetic acid (CH_3COOH), water (H_2O), potassium hydroxide (KOH), hydrochloric acid (HCl) and sodium hydroxide (NaOH). The percentage desorption efficiency was evaluated to be less than 10%

with all the eluents. Acetic acid and water have the highest desorption efficiency (Table 6) whereas HCl desorbed 3.2%, NaOH desorbed 1.6% and KOH has the least desorption efficiency of 1.3%. The desorption efficiency follows the order $\text{CH}_3\text{COOH} = \text{H}_2\text{O} > \text{HCl} > \text{NaOH} > \text{KOH}$. Numerous active sites on the adsorbent surface aid large adsorption energy and this can be related to the low desorption efficiency. This in turn makes it difficult for the adsorbed molecule to be released from the surface and hence low desorption efficiency [53]. Also, complexes might have been formed via interaction of the active sites and the functional groups of the adsorbates. This suggests that some amount of the adsorbates might have been chemisorbed onto the surface of the adsorbents [54].

4. Conclusions

This study considered the efficiency of the adsorptive capacity of the banana stalk in sequestering ciprofloxacin in aqueous solutions. The feature of BSAC was investigated using SEM, FTIR, and pH_{pzc} . Considering the four isotherm models, the adsorption process was best described by the Langmuir model with a maximum monolayer adsorption capacity of 222 mg/g. Likewise in the kinetic study, the process was best interpreted by pseudo second order kinetics. The results obtained from the thermodynamic studies revealed that the adsorption process was endothermic, spontaneous and high randomness rate at the solid-liquid interphase. The cost analysis of the preparation and production of BSAC revealed that the adsorbent is about 21 times cheaper than CAC which makes it economically viable. Acid treated banana stalk is economically viable, efficient and effective for sequestering ciprofloxacin from aqueous solutions.

Declarations

AVAILABILITY OF DATA AND MATERIALS

All data generated or analysed during this study are included in this published article

COMPETING INTERESTS

The authors declare that they have no competing interests

FUNDING

All sources of funding for the research has been reported (purchase of research equipments only)

AUTHORS' CONTRIBUTIONS

1. Conceptualization, Methodology, Software

Oladipupo Olaosebikan OGUNLEYE, Olugbenga Solomon BELLO

2. Data curation, Writing- Original draft preparation: Visualization, Investigation.

Toyin Adedayo OREOFE, Oladipupo Olaosebikan OGUNLEYE, Olugbenga Solomon BELLO

3. Supervision.

Oladipupo Olaosebikan OGUNLEYE, **Olugbenga Solomon BELLO**

4. Software, Validation

Oladipupo Olaosebikan OGUNLEYE, Olugbenga Solomon BELLO

5. Writing- Reviewing and Editing:

Toyin Adedayo OREOFE, Oladipupo Olaosebikan OGUNLEYE, Olugbenga Solomon BELLO

ACKNOWLEDGEMENTS

The authors acknowledge Landmark University, Omu-aran, Nigeria for the support in making some laboratory facilities available.

AUTHORS' INFORMATION

Oladipupo Olaosebikan OGUNLEYE: Professor of Chemical Engineering. Lecturing and Research

Olugbenga Solomon BELLO: Professor of Physical Chemistry. Lecturing and Research.

References

[1] Sophia, C., Lima, E.C. 2018. Removal of emerging contaminants from the environment

by adsorption. *Ecotoxicology and Environmental Safety*, 150: 1-17.

[2] El Bastawesy, M., Adel, S., Mohamed, I.N.L. 2018. Management of waste water discharge within the Nile Valley of Egypt: The collapse of Al Ballanah waste water's lake in Aswan in September 2013. *The Egyptian Journal of Remote Sensing and Space Sciences*, 21: 149-158.

[3] Botero-Coy, A.M., Martínez-Pachón, D., Boix C., Rincón R.J.,Castillo N., Arias-Marin L.P., Manrique-Losada, L., Torres-Palma R., Moncayo-Lasso, A., Hernández F. 2018. 'An investigation into the occurrence and removal of pharmaceuticals in Colombian wastewater'. *Science of the Total Environment*, 642: 842-853.

[4] Al-Jandal, N., Saeed, T., Azad, I., Al-Subiai, S., Al-Zekri, W., Hussain, S., Al-Hasan, E. 2018. Impact of endocrine disrupting compounds in sewage impacted coastal area on seabream. *Ecotoxicology and Environmental Safety*, 150: 280-288.

- [5] Lu, J., Wu, J., Zhang C., Zhang, Y. 2020. Possible effect of submarine groundwater discharge on the pollution of coastal water: Occurrence, source, and risks of endocrine disrupting chemicals in coastal groundwater and adjacent seawater influenced by reclaimed water irrigation. *Chemosphere*, 250:126323.
- [6] Locatelli M., Sciascia F., Cifelli R., Malatesta L., Bruni, P., Croce F. 2016. Analytical methods for the endocrine disruptor compounds determination in environmental water samples. *Journal of chromatography A*, 1434: 1-18.
- [7] Li Z., Liu Y., Zou S., Lu C., Bai H., Mu H., Duan J. 2020. Removal and adsorption mechanism of tetracycline and cefotaxime contaminants in water by NiFe_2O_4 -COF-chitosan-terephthalaldehyde nanocomposites film. *Chemical Engineering Journal*, 382: 123008.
- [8] Hsieh, C-J., Chang, Y-H., H,u A., Chen, M-L., Sun, C-W., Situmorang, R.F., Wu, M-T., Wang, S-L., TMICS study group. 2019. Personal care products use and phthalate exposure levels among pregnant women. *Science of the Total Environment*, 648: 135-143.
- [9] Combarous, Y. 2017. Endocrine Disruptor Compounds (EDCs) and agriculture: The case of pesticides. *Comptes Rendus Biologies*, 340: 406-409.
- [10] Jung, J-W., Kang J-S., Choi, J., Park, J-W. 2020. Chronic toxicity of endocrine disrupting chemicals used in plastic products in Korean resident species: Implications for aquatic ecological risk assessment. *Ecotoxicology and Environmental Safety*, 192: 110309.
- [11] Ahmadzadeh, S., Dolatabadi M. 2018. Electrochemical treatment of pharmaceutical wastewater through electrosynthesis of iron hydroxides for practical removal of metronidazole. *Chemosphere*, 212: 533-539.
- [12] Ooi, G.T.H., Tang, K., Chhetri, R.K., Kaarsholm, K.M.S., Sundmark, K., Kragelund, C., Litty, K., Christensen, A., Lindholst, S., Sund, C., Christensson, M., Bester, K., Andersen H.R. 2018. Biological removal of pharmaceuticals from hospital wastewater in a pilot-scale staged moving bed biofilm reactor (MBBR) utilising nitrifying and denitrifying processes. *Bioresource Technology*, 267: 677-687.
- [13] Yanyan, L.,Kurniawan, T.A., Zhu, M., Ouyang, T., Avtar, R., Othman, M.H.D., Mohammad, B.T., Albadarin, A.B. 2018. Removal of acetaminophen from synthetic wastewater in a fixed-bed column adsorption using low-cost coconut shell waste pretreated with NaOH, HNO_3 , ozone, and/or chitosan. *Journal of Environmental Management*, 226: 365-376.
- [14] Sharma, V., Kumar R.V., Pakshirajan, K., Pugazhenth, G. 2017. Integrated adsorption-membrane filtration process for antibiotic removal from aqueous solution. *Powder Technology*, 321: 259-269.
- [15] Karri, R.R., Sahu, J.N., Jayakumar, N.S. 2017. Optimal isotherm parameters for phenol adsorption from aqueous solutions onto coconut shell based activated carbon: Error analysis of linear and non-linear methods. *Journal of the Taiwan Institute of Chemical Engineers*, 80: 472-487.

- [16] Benally, C., Messele, S.A., Gamal El-Din, M. 2019. Adsorption of organic matter in oil sands process water (OSPW) by carbon xerogel. *Water Research*, 154: 402-411.
- [17] Ao, X., Liu, W., Sun, W., Cai, M., Ye, Z., Yang, C., Lu, Z., Li, C. 2018. Medium pressure UV-activated peroxymonosulfate for ciprofloxacin degradation: Kinetics, mechanism, and genotoxicity. *Chemical Engineering Journal*, 345: 87-97.
- [18] Zhang, B., Han, X., Gu, P., Fang, S., Bai, J. 2017. Response surface methodology approach for optimization of ciprofloxacin adsorption using activated carbon derived from the residue of desilicated rice husk. *Journal of Molecular Liquids*, 238: 316-325.
- [19] Duan, W., Wang, N., Xiao, W., Zhao, Y., Zheng Y. 2018. Ciprofloxacin adsorption onto different micro-structured tourmaline, halloysite and biotite. *Journal of Molecular Liquids*, 269: 874-881.
- [20] Movasaghi, Z., Yan, B., Niu, C. 2019. Adsorption of ciprofloxacin from water by pretreated oat hulls: Equilibrium, kinetic, and thermodynamic studies. *Industrial Crops & Products*, 127: 237-250.
- [21] Chen, H., Gao, B., Li, H. 2015. Removal of sulfamethoxazole and ciprofloxacin from aqueous solutions by graphene oxide. *Journal of Hazardous Materials*, 282: 201-207.
- [22] Mao, H., Wang, S., Lin, J-Y., Wang, Z., Ren, J. 2016. Modification of a magnetic carbon composite for ciprofloxacin adsorption. *Journal of Environmental Sciences*, 49: 179-188.
- [23] Afzal, M.Z., Sun, X-F., Liu J., Song, C., Wang, S.G., Jave, A. 2018. Enhancement of ciprofloxacin sorption on chitosan/biochar hydrogel beads. *Science of the Total Environment*, 639: 560-569.
- [24] Kadhon, M., Albayati, N., Alalwan, H., Al-Furaiji, M. 2020. Removal of dyes by agricultural waste. *Sustainable Chemistry and Pharmacy*, 16: 100259
- [25] Eletta, O.A.A., Ajayi, O.A., Ogunleye, O.O., and Akpan, I.C. 2016. Adsorption of cyanide from aqueous solution using eggshell: Equilibrium and optimisation studies. *Journal of Environmental Chemical Engineering*, 4(1): 1367-1375.
- [26] Ogungbenro, A.E., Quang, D.V., Al-Ali, K.A., Vega, L.F., Abu-Zahra, M.R.M. 2018. Physical synthesis and characterization of activated carbon from date seeds for CO₂ capture. *Journal of Environmental Chemical Engineering* 6:4245-4252
- [27] Bello, O.S., Alao, O.C., Alagbada, T.C., Olatunde, A.M. 2019. Biosorption of ibuprofen using functionalized bean husks. *Sustainable Chemistry and Pharmacy* 13 (2019) 100151, 13: 100151.
- [28] Inyinbor, A.A., Adekola, F.A., Olatunji, G.A. 2019. Low cost adsorbent prepared from Vigna subterranean waste: Physicochemical, morphological and surface chemistry data set. *Chemical Data Collections* 24: 100294

- [29] Luo, L-N., Cui-Ling, L., Wu, F., Li, S-P., Han, S-Q., Li, M-F. 2018. Desuckering effect of KH_2PO_4 mixed with paclobutrazol and its influence on banana (*Musa paradisiaca* AA) mother plant growth. *Scientia Horticulturae*, 240: 484-491.
- [30] Correa, M., Mesomo, M.C., Pianoski, K.E., Torres, Y.R., Corazza, M.L. 2016. Extraction of inflorescences of *Musa paradisiaca* L. using supercritical CO_2 and compressed propane. *Journal of Supercritical Fluids*, 113: 128-135.
- [31] Krishnan, S.S.C., Subramanian, I.P., Subramanian, S.P. 2014. Isolation, characterization of syringin, phenylpropanoid glycoside from *Musa paradisiaca* tepal extract and evaluation of its antidiabetic effect in streptozotocin-induced diabetic rats. *Biomedicine & Preventive Nutrition*, 4: 105-111.
- [32] Freundlich, H. 1906. Over the adsorption in solution. *Journal of physical chemistry*, 57: 385-470.
- [33] Dubinin, M. 1960. The potential theory of adsorption of gases for adsorbents with energetically non uniform surface. *Chemical Reviews*, 60: 235-266.
- [34] Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of American Chemical Society*, 40: 1361-1403.
- [35] Temkin, M., and Pyzhev, V. 1940.. Kinetics of ammonia synthesis on promoted iron catalysts, *Acta physiochimica* 12(3): 217-222.
- [36] Gulen, B. and Demircivi, P. 2020. Adsorption properties of fluoroquinolone type antibiotic ciprofloxacin into 2:1 dioctahedral clay structure: Box-Behnken experimental design. *Journal of Molecular Structure* 1206 (2020) 127659, 1206: 127659.
- [37] Nasrullah, A., Saad, B., Bhat, A.H., Khan, A.S., Danish, M., Isa, M.H., and Naeem, A. 2019. Mangosteen peel waste as a sustainable precursor for high surface area mesoporous activated carbon: Characterization and application for methylene blue removal. *Journal of Cleaner Production*, 211: 1190-1200.
- [38] Ogunleye, O.O., Adio, O., Salawudeen, T.O. 2014. Removal of lead (II) from aqueous solution using Banana (*Musa Paradisiaca*) stalk-Based activated carbon. *Chemical and Process Research*, 28: 2224-7467.
- [39] Norouzi, S., Heidari, M., Alipour, V., Rahmanian, O., Fazlzadeh, M., Mohammadi-Moghadam, F., Nourmoradi, H., Goudarzi, B., Dindarloo, K. 2018. Preparation, characterization and Cr (VI) adsorption evaluation of NaOH activated carbon produced from Date press Cake an agro-industrial waste. *Bioresource Technology*, 256: 48-56.
- [40] Mohammed A.A, Chen C, Zhu Z. 2019. Low-cost, high performance-supercapacitor based on activated carbon electrode materials derived from baobab fruit shells. *Journal of colloid and interface*

- [41] Inyinbor, A.A., Adekola, F.A., Olatunji, G.A. 2015. EDTA Modified Irvingia gabonensis: An Efficient Bioresource Material for the Removal of Rhodamine B. *Pakistan Journal of Environmental Analytical Chemistry*, 16(2): 38-47.
- [42] de Oliveira Ferreira, M.E., Va,z B.G., Borba, C.E., Alonso, C.G., Ostroski, I.C. 2019. Modified activated carbon as a promising adsorbent for quinoline removal. *Microporous and Mesoporous Materials*, 277; 208-216.
- [43] Ojedokun, A.T., Bello, O.S. 2015. Kinetic modeling of liquid-phase adsorption of Congo red dye using guava leaf-based activated carbon. *Applied Water Science*, DOI 10.1007/s13201-015-0375-y.
- [44] Peng, X., Hu, F., Dai, H., Xiong, Q., Xu, C. 2016. Study of the adsorption mechanisms of ciprofloxacin antibiotics onto graphitic ordered mesoporous carbons. *Journal of the Taiwan Institute of Chemical Engineers*, 65: 472-481.
- [45] Wang, M., Li, G., Huang, L., Xue, J., Liu,Q., Bao, N., Huang, J. 2017. Study of Ciprofloxacin adsorption and regeneration of activated carbon from Entermorpha prolifera impregnated with H₃PO₄ and sodium benzenesulfonate. *Ecotoxicology and Environmental Safety*, 139: 36-42.
- [46] Olakunle, M.O., Inyinbor, A.A., Dada, A.O., Bello, O.S. 2017. Combating dye pollution using cocoa pod husks: a sustainable approach. *International Journal of Sustainable Engineering*, <https://doi.org/10.1080/19397038.2017.1393023>.
- [47] Bello, O.S., and Ahmad, M.A. (2012). Coconut (cocos nucifera) Shell Based Activated Carbon for the Removal of Malachite Green Dye from Aqueous solutions. *Separation Science and Technology*, 47:6, 903-912.
- [48] Bello, O.S., Ahmad, M.A., and Ahmad, N. (2012). Adsorptive features of banana (Musa paradisiaca) stalk-based activated carbon for malachite green dye removal. *Chemistry and Ecology*, 28(2):153-167.
- [49] El-Shafey, E.I., Al-Lawati, H., Al-Sumri, A.S. 2012. Ciprofloxacin adsorption from aqueous solution onto chemically prepared carbon from date leaflets. *Journal of Environmental Sciences*, 24(9): 1579-1586.
- [50] Sun, Y., Li, H., Gao, B., Yue, Q., Li, X. 2016. Characterization and ciprofloxacin adsorption properties of activated carbons prepared from biomass wastes by H₃PO₄ activation. *Bioresource Technology*, 217: 239-244.
- [51] Staudt J., Scheufele F.B., Ribeiro C., Sato, T.Y., Canevesi R., Borba C.E. 2020. Ciprofloxacin desorption from gel type ion exchange resin: Desorption modeling in batch system and fixed bed column. *Separation and Purification Technology*, 230: 115857.

[52] Momina, Mohammad, S., Isamil S. 2020. Study of the adsorption/desorption of MB dye solution using bentonite adsorbent coating. *Journal of Water Process Engineering*, 34: 101155.

[53] Fernandez, M.E., Nunell, G.V., Bonelli, P.R.,Cukierman, A.L. 2010. Effectiveness of Cupressus sempervirens cones as biosorbent for the removal of basic dyes from aqueous solutions in batch and dynamic modes. *Bioresource Technology*, 101: 9500-9507.

[54] Ma, X., Yang, C., Jiang, Y., Zhang, X., Wang, Q., Dang, Z. 2019. Desorption of heavy metals and tetracycline from goethite-coated sands: The role of complexation. *Colloids and Surfaces A*, 573: 88-94.

Tables

Table 1
Characteristics of BSAC

Parameters	Values
Pore diameter (nm)	6.20
Ash (%)	4.00
BET surface area (m ² /g)	1068.30
Bulk Density (g/cm ³)	0.28
Moisture (%)	3.50
Pore size (nm)	2.24

Table 2
FTIR characteristics of banana stalk adsorbent

IR spectra wavelength number (cm ⁻¹)			
Peak assignment	BSAC	CLBSAC	Variance
O-H alcohols and phenolsstretch	3412	3419	-7
C-H alkanesstretch	2806	2933	-27
C ≡ C alkynesstretch	2370	2081	-11
C = O ketonesstretch	1707	1706	+ 1
C = O carboxylic acidsstretch	1616	1622	-6
C = C aromaticsstretch	1458	1456	+ 2
C-O alcoholsstretch	1236	1230	+ 6

Table 3
Kinetic model parameters for ciprofloxacin adsorption at 303 K using BSAC

Model	Parameters	Ciprofloxacin Concentration (mg/L)				
		1	2	3	4	5
	q_e experimental (mg/g)	61.24	100.03	118.18	137.12	163.3
Pseudo first order	q_e calculated (mg/g)	45.39	72.22	87.09	93.31	95.29
	$K_1 \times 10^{-3}$ (min^{-1})	18.5	15.2	15.9	19.2	14.5
	R^2	0.9604	0.967	0.9529	0.9945	0.9954
	SSE %	1.98	3.47	3.88	5.47	8.50
Pseudo second order	q_e calculated (mg/g)	67.11	108.69	126.58	144.9	172.4
	$K_2 \times 10^{-3}$ (min^{-1})	0.691	0.34	0.35	0.41	0.33
	R^2	0.9937	0.9906	0.9908	0.9969	0.9956
	SSE %	0.48	0.72	0.70	0.64	0.75
Intra particle	R^2	0.8984	0.9035	0.8983	0.8409	0.9216
	$C \times 10^2$ (mg g^{-1})	0.23	0.29	0.42	0.59	0.74
	K_{diff} ($\text{mg g}^{-1} \text{min}^{1/2}$)	1.59	2.11	2.20	2.26	2.38

Table 4
Ciprofloxacin isotherm adsorption parameter using
BSAC at 303K

Isotherm Model	Parameters	
Langmuir	q_m (mg/g)	222.22
	R^2	0.9774
	R_L	0.496
	K_L (L/mg)	0.316
Temkin	K_T (L/g)	12.81
	B	32.73
	b (J/mol)	75.95
	R^2	0.8995
Freundlich	R^2	0.9671
	N	2.31
	K_F	75.5
Dubinin-Radushkevich	β (mol ² /kJ ²)	3E-7
	q_m (mg/g)	159.25
	R^2	0.8383
	E (KJ/mol)	1.29

Table 5
Adsorption thermodynamic parameters of ciprofloxacin uptake onto BSAC

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol/K)
303	-7.94	23.82	104.22
313	-8.74		
323	-9.86		

Table 6
Comparison of maximum adsorption capacity of ciprofloxacin using various adsorbents

Adsorbents	Temperature (K)	q_m (mg/g)	References
Date palm leaflets	298	116.3	El-Shafey et al., 2011
Modified coal fly ash	313	1.547	C.-L. Zhang et al., 2011
Chitosan	303	78.79	Afzal et al., 2018
Oat hulls	318	83	Z. Movasaghi et al., 2019
<i>BSAC</i>	<i>303</i>	<i>222.22</i>	<i>This study</i>

Table 7
Comparison of cost analysis of BSAC and CAC

S/No	Cost of material	Price (USD)	
		BSAC (1Kg)	CAC (1Kg)
1	H ₃ PO ₄	8.45	-
2	Deionized water	0.56	-
3	Energy	2.78	-
4	Transportation	0.56	11.3
5	Market cost		259.5
	Grand Total	12.35	270.8

Table 8
Desorption Efficiency of different eluents for BSAC regeneration

Adsorbate	Desorption Efficiency				
	0.1 M Eluents				
Ciprofloxacin	CH ₃ COOH	H ₂ O	HCL	NaOH	KOH
	3.4	3.4	3.2	1.6	1.3

Figures

Figure 1

FTIR spectral of (a) BSAC (b) CLBSAC

Figure 2

Plot of pH_{pzc} of acid activated BSAC.

Figure 3

Scanning electron micrograph of (a) BSAC (b) CLBSAC

Figure 4

Effect of contact time and initial ciprofloxacin concentration

Figure 5

Effect of adsorbent dosage on ciprofloxacin adsorption

Figure 6

Effects of solution pH

Figure 7

Effects of temperature on ciprofloxacin adsorption

Figure 8

Ciprofloxacin adsorption kinetics plot of (i) pseudo first order (ii) pseudo second order (iii) intra particle diffusion model at 303K using BSAC

(i)

(ii)

(iii)

(iv)

Figure 9

Ciprofloxacin adsorption isotherms plots of (i); Langmuir (ii); Freundlich (iii), Temkin (iv) Dubinin-Radushkevich at 303 K using BSAC

Figure 10

Vant Hoff plot of ciprofloxacin adsorption onto BSAC

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [GRAPHICALABSTRACT.doc](#)