SciencePG
Science Publishing Group

Removal of Ciprofloxacin Hydrochloride from Aqueous Solution by Pomegranate Peel Grown in Alziedab Agricultural Scheme - River Nile State, Sudan

Mutasim Elhag Elhussien[1, *], Maathir Ahmed Abde lraheem[2], Rashida Mohammed Hussein[3], Mawia Hassan Elsaim[4]

[1]Department of Chemistry, Faculty of Education, Nile Valley University, Atbara, Sudan

[2]Chemical Laboratories, Ministry of Health & Population, Atbara, Sudan

[3]Department of Chemistry, Inaya Medical College, Riyadh, Kingdom of Saudi Arabia

[4]Department of Chemistry, Faculty of Science and Technology, Abdulatif Alhamed University of Technology, Merowe, Sudan

Email address:
mutasim1966@yahoo.com (M. E. Elhussien)
[*]Corresponding author

Abstract: Removal of Ciprofloxacin (CIP) antibiotic from aqueous solution onto Activated carbon derived from pomegranate peel wastes collected from Alziedab Agricultural Scheme at River Nile state, Sudan as a novel precursorby chemical activation with Potassium Hydroxide (KOH), at specific condition of carbonization temperature at 500°C and 1 hour as a holding time and detonated as (AC(PPZS)KOH). The obtained material was submitted to measurements of active surface area, Fourier Transform Infrared Spectroscopy (FTIR) analysis and scanning electron microscope (SEM). Batch-adsorption studied had been carried out to examine the adsorption capacity of the AC(PPZS)KOH for the removal of Ciprofloxacin from aqueous solution. The effect of various process parameters like pH, initial antibiotic concentration, adsorbent dose, and contact time, on the efficiency of Ciprofloxacin removal was investigated. Maximum adsorption of Ciprofloxacin on AC(PPZS)KOH, $(86.4 \pm 5.7\%)$ was observed at pH 8. The optimum adsorbent dose was determined as 0.05 g at 25°C. Initial Ciprofloxacin concentrations has important effect on AC(PPZS)KOH in the studied range (50–300 mg/L) where the removal percentage increases as the antibiotic concentration decrease. The adsorption equilibrium data was well explained by Freundlich isotherm. The results reveal the Langmuir model is not able to describe the experimental data properly, poor less of fitting on AC(PPZS)KOH. The Freundlich isotherm experimental data obtained showed (Correlation Coefficient, $R^2 = 0.991$) higher than Langmuir isotherm, $R^2 = 0.919$). The porous characteristics and adsorption efficiencies of prepared AC(PPZS)KOH were also investigated.

Keywords: Adsorption Isotherms, Activated Carbon, Pomegranate Peel, Ciprofloxacin, SEM, FTIR

1. Introduction

The removal of conventional pollutants, such as persistent organic pollutants was in focus for the last decades and so their behavior is well understood [1]. On the other side very little is known about the behavior of trace pollutants yet, which are present in the environment in extremely low concentrations. Pharmaceuticals are an example for the variety of man-made trace pollutants that are introduced in surface or subsurface water bodies [2]. Pharmaceuticals have been identified in the environment, including antibiotics, analgesics, psychiatric drugs, and natural and synthetic hormones [3]. Unused human pharmaceuticals may also enter the environment through

landfill leachate [4, 5].

Adsorbents such as charcoal [6], polymers [7] and bentonite [8-12] in adsorption of drug, are recognized in clinical practice and environmental treatment. The safety, high adsorptive capacity, and high specific surface, have been accepted for a long time.

Pharmaceuticals poisoning also has been defined as a condition produced by any substance which when swallowed, inhaled, injected or absorbed precutaneously is capable of causing death, injury, toxic or untoward reactions [13].

Ciprofloxacin hydrochloride (CIP) is a synthetic chemotherapeutic antibiotic (1-cyclopropyl-6-fluoro-1, 4-dihydro-4- oxo-7-(1-piperazinyl)-3-quinoline carboxylic acid), Its empirical formula is $C_{17}H_{18}FN_3O_3$ and its molecular weight is 331.4 g/mol. The broad spectrum antibiotic Ciprofloxacin (CIP) is used in human and veterinary medicine that is readily transported into the environment via domestic wastewaters and through direct runoff. (CIP) is a member of the Fluroquinolones antibiotics which is frequently used to the treatment of infections caused by bacteria aerobic like Klebsiella, Shigella which result in inflammation of the respiratory tract, inflammation of the ear, sinus, urinary tract, gonorrhea, inflammation of the skin and tissue infections and bone. In the event of over dose will cause poisoning and kidney pains and muscle acheate [14].

In the literature, several studies related to the adsorption of CIP to natural materials or components of natural materials have been published (activated carbon [15], activated charcoal and talc [16], date palm leaflets [17], montmorillonite [18], soil [19, 20, 21], dioctahedral clay minerals [22]; kaolinite [23]; modified coal fly ash [24]; aerobically digested biosolid [25], sawdust[26], birnessite, a layered manganese oxide [27], (Fe_3O_4/C) a new magnetic mesoporous carbon composite [28], Chitosan-Zn (II), Chitosan-Fe (III), Chitosan-Fe(II) microparticles [29], aluminum and hydrous oxides [30], andnano-sized magnetite [31]).

Adsorption of Ciprofloxacin from aqueous solutions by Pomegranate Peel wastes grown in Alziedab Agricultural Scheme (PPZS) has been studied in this work. Batch adsorption experiment were investigated to study the sorption behavior of (PPZS) towards Ciprofloxacin as a function of initial concentration, reaction time, adsorbent dosage and pH. Time dependent showed that the adsorption process reached equilibrium at 30 min. Two adsorption isotherms equations were employed including Freundlich and Langmuir. The equilibrium data could be well described by Freundlich equation for the adsorption on pomegranate peel waste.

2. Materials and Methods

The carbonaceous precursor used for preparation of activated carbon (AC) was Pomegranate Peel, collected from Alziedab Agricultural Scheme (PPZS) at River Nile State,

Sudan. Prior to use, sample was washed gently several times with distilled water to remove impurities present on the surface and then dried for one week. All chemical reagents used in this work were BDH, used without further purification.

2.1. Preparation of Activated Carbon

Pomegranate Peel dried, crushed and grinded in a ball mill. The grinded sample was sieved to obtain particles ofuniform size90 mesh sieves. The precursor obtained was washed to remove surface bounded impurities and dried at 105°C for 24 h. 100g of the precursor was impregnated with potassium hydroxide, KOH for 24 h in ratio of 1: 1.5 at 50°C to achieve well penetration of the chemical into the interior of the precursor.

After impregnation, the sample was dried for 24 h at 105°C. Activation treatment was carried out in a Carbolite™ furnace at 550°C, using 25 g of the impregnated and dried sample. After cooling the solid residue to room temperature, washed with double distilled water followed by 0.1 M hydrochloric acid (HCl) to remove the residual chemical agents until the pH value of the rinsed water was neutral. The adsorbents prepared were denoted as AC(PPZS)KOH, throughout the work.
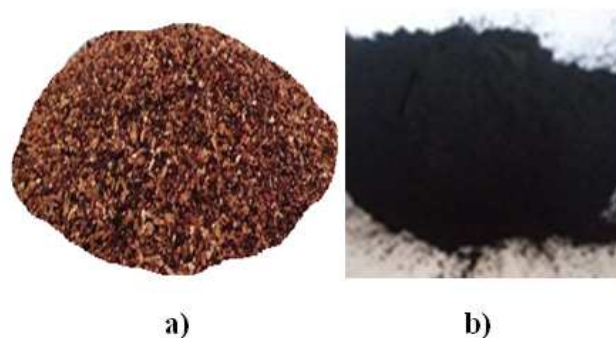

Figure 1. Images of activated carbon obtained from Pomegranate Peel wastes grown in Alziedab Agricultural Scheme a) before and b) after carbonization process.

2.2. Ciprofloxacin Standardization and Wavelength Selection

Ciprofloxacin (CIP) used as adsorbate, obtained from Amipharama Laboratories Ltd, Sudan. A stock solution of 1000 mg/Lwas prepared by dissolving appropriate amount of (CIP) in1000 ml double distilled water in volumetric flask, different concentrations were prepared by diluting the stock solution to the initial concentrations ranging from 50-300 mg/L. Spectra of ciprofloxacin was measured by UV visible Jenway 7305 spectrophotometer, using 200 mg/L solution, scanned in the 200-300 nm UV regions. The maximum wavelength (λ_{max}) was observed at 274 nm which was adopted for absorbance measurement. Measurements of the absorbance of each standard solution (50, 100, 150, 200, 250 and 300 mg/L) in 1cm cuvette at 274 nm, using double distilled water as a blank to verify Beer's – Lambert law were carried out [32].
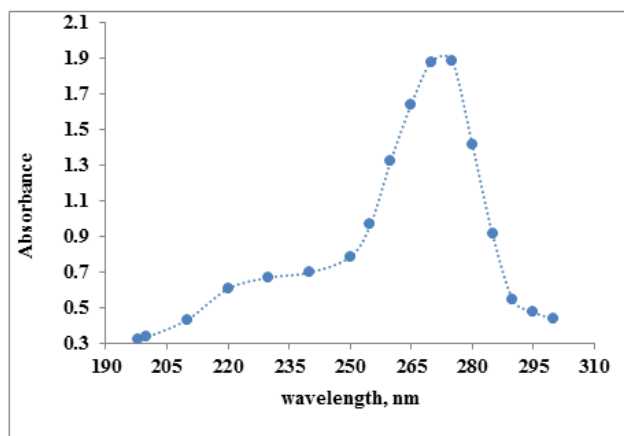
Figure 2. UV- Visible Spectrophotometric Determination of λ_{max} for ciprofloxacin Absorption..

2.3. Evaluation of Activated Carbon

The activated carbon sample was evaluated two ways:

2.3.1. Fourier Transform Infrared Spectroscopy

The surface functional groups of the ACs were estimated by Fourier Transform Infrared (FTIR) spectroscopy (Shimadzu, Japan). FTIR spectra of the prepared AC(PPZS)KOH samples were recorded within 400 – 4000 cm^{-1}. The transmission spectra of the samples were recorded using the KBr pellet. About 1.0 – 2.0% of each sample was mixed with dry KBr and grinded in mortar. Then the samples were transferred to hydraulic press. The pellets which are homogeneous and transparent in appearance were dried overnight at 100°C, and then inserted into the IR sample holder for the analysis.

2.3.2. Scanning Electron Microscopy (SEM)

SEM analysis of samples was performed by using (JSM-6380LA) scanning electron microscope. The SEM instrument was operated at 5 kV/SE (Accelerating Voltage Machine), and 50°C inclination. Before analysis, all samples were ground and coated in a sputter coating unit (Edwards Vacuum Components Ltd., Sussex, England) to reduce charging and improve the secondary electron signals for imaging. The micrographs were recorded using photographic techniques.

2.4. Effect of Process Parameters

Batch adsorption experiments for adsorption of CIP on AC(PPZS)KOH were conducted using aqueous solutions of CIP. A stock solution of 1000 mg/L was prepared by dissolving appropriate weight of CIP from Amipharama Laboratories Ltd, Sudan. The stock solution was diluted as required to obtain different concentrations of antibiotic solutions. For each run, a definite amount of AC(PPZS)KOH was added to 25 ml of CIP solution taken in 100 ml Erlenmeyer flasks. All the adsorption experiments were carried out at constant temperature of 25°C.

2.4.1. Effect of pH

Effect of pH on antibiotic adsorption was monitored over a

pH range of 2 to 12, using electronic pH - Meter (3510). In this study, 25 ml of separate solutions 50 mg/L (CIP) was transferred into100 ml conical flasks shaking well for 30 min with 0.1g AC(PPZS)KOH at 25°C. The mixture was filtered and the filtrate analyzed for residual CIP using UV visible Spectrophotometer (Jenway 7305).

2.4.2. Effect of Contact Time

In order to study the effect of contact time on the percent removal of (CIP) from aqueous solution, experiments were carried out at initial concentration of 50 mg/L using (0.1g)AC(PPZS)KOH dose and different contact times from 15 to 150 minutes The mixtures were filtered and residual of (CIP) in filtrate analyzed spectrophotometrically.

2.4.3. Effect of Adsorbent Dosage

To determine the optimum adsorbent dosage, experiments were carried out by adding different weights of AC(PPZS)KOH ranging from (0.025 to 0.2 g) to 20 ml of desired concentration of (CIP) in 50 ml conical flask at pH 8, temperature 25°C and shaken for 30min. Aliquots concentration was analyzed to determine the extent of adsorption of (CIP) at equilibrium.

2.4.4. Effect of Initial Drug Concentration

20 ml solutions of CIP drug with different initial concentrations (50-300 mg/L) were contacted with optimized adsorbent dosage 0.1 g and pH 8. The mixtures were shaken well for 30min at 25°C. The mixtures were filtered and filtrate analyzed for residual drug concentrations.

2.5. Equilibrium Adsorption Studies

Batch adsorption experiments were studied by adding 0.1 g of AC(PPZS)KOH in to 100 ml conical flask filled with 20 ml of CIP solution of known initial concentration ranging from 50 to 300 mgl^{-1} at pH 8. The conical flasks were sealed and shaken well at 25°C for 30 min; the samples were then withdrawn and filtered. The residual CIP concentration at equilibrium was estimated spectrophotometrically and the amount adsorbed, q_e (mg/g) was calculated using the following expressions [33, 34]:

$$q_e = (V/w) (C_o - C_e) \qquad (1)$$

$$\% \text{ Removal} = 100 (C_o - C_e)/C_o \qquad (2)$$

Where q_e is the amount of the (CIP) adsorbed by the AC(PPZS)KOH sample in (mg/g), C_o and C_e are the initial and equilibrium concentrations of (CIP) respectively in (mg/L), V is the volume of the solution treated in (L) and w is the adsorbent mass of AC(PPZS)KOH in (g).

From the Beer's- Lambert's plot for the Ciprofloxacin Hydrochloride drug previously made, the amount of free drug in solution was determined. From the results, the time to attain equilibrium for adsorbent was determined.

The equilibrium data were recorded for investigations using Freundlich and Langmuir isotherms models [35, 36].

3. Results and Discussion

3.1. Evaluation of the Prepared Activated Carbon Sample

The obtained results from Fourier Transform Infrared Spectrum(IR) and Scanning Electron Microscopy (SEM) were used to evaluate the prepared activated carbon sample as follow:

3.1.1. Fourier Transform Infrared Spectroscopy (FTIR)

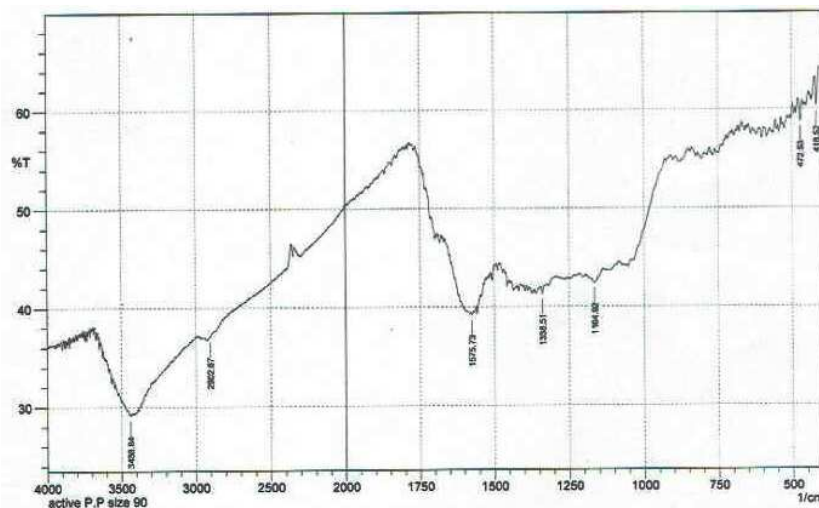The FTIR analysis of prepared AC(PPZS)KOH reveals a simple spectrum, shown on figure 3. The spectrum showed the absorption bands at these regions (2900-3650cm^{-1}), (1520-1650 cm^{-1}), (1000-1260cm^{-1}) and (472-419cm^{-1}) The broad peak at around 3438 cm^{-1} is assigned to presence of OH groups (adsorbed moisture) on surface. The sample showed a broad band with a maxima at 2900cm^{-1} which is attributed to C-H interaction with the surface of the carbon. The presence of amine groups are confirmed by the peaks observed at 1612 and 1575 cm^{-1} while the band at 1158 cm^{-1} is due to the C – N stretching. The sharp absorption band at 1125 cm^{-1} is ascribed for C-O stretching in alcohol, ether or hydroxyl groups.

Figure 3. *FTIR spectrum of prepared AC(PPZS)KOH.*

3.1.2. Scanning Electron Microscope (SEM)

The prepared activated carbon AC(PTLS)ZnCl$_2$ was examined by Scanning Electron Microscope (SEM) to analyze the surface of the adsorbents. SEM micrograph of the chemically activated carbon by KOH, was presented in Figure 4. Well-developed porous surface was observed at higher magnification. The pores observed from SEM imageis having diameter in micrometer (μm) range. These pores are considered as channels to the microporous network. From the figure, it can be observed that, the adsorbent have rough texture with heterogeneous surface and a variety of randomly distributed pore size.
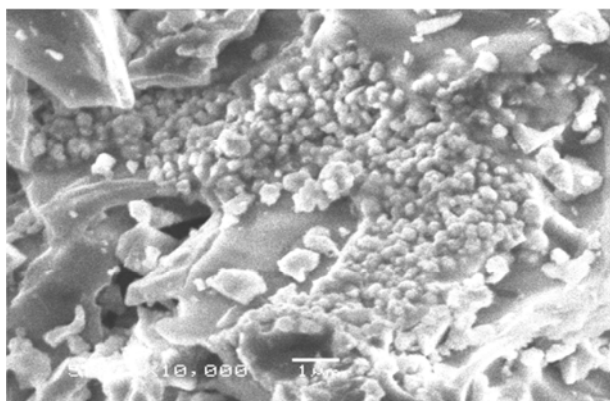

Figure 4. *SEM image of the prepared AC(PPZS)KOH, Magnification X10000.*

3.2. Effect of Process Parameters

3.2.1. Effect of pH

Solution pH is one of the important process parameters that significantly influences the adsorption of CIP on adsorbent [33, 34]. The adsorption of CIP from 50 mg/L concentration on given AC(PPZS)KOH was studied at pH ranging (2-12). The result in Figure 5, shows that the adsorption of CIP increased from the initial pH to 8and then decreased over the pH rang of 9-12. Therefore, in this study we found that pH 8 as the optimum pH. At low pH region the surface of the adsorbent will be largely protonated. The positive ions (H$^+$) provide an electrostatic attraction between the AC(PPZS)KOH surface and the drug molecules leading to maximum adsorption, 86.4% ± 5.7. On the other hand, at pH above 8 the degree of protonation of the surface of the AC(PPZS)KOH will be less, which result in the decrease in diffusion and adsorption, thereby due to electrostatic repulsion. Furthermore, lower adsorption of the Drug molecules in alkaline medium can be attributed to the competition from excess Hydroxide ions (OH$^-$) with the drug molecules for the adsorption sites.
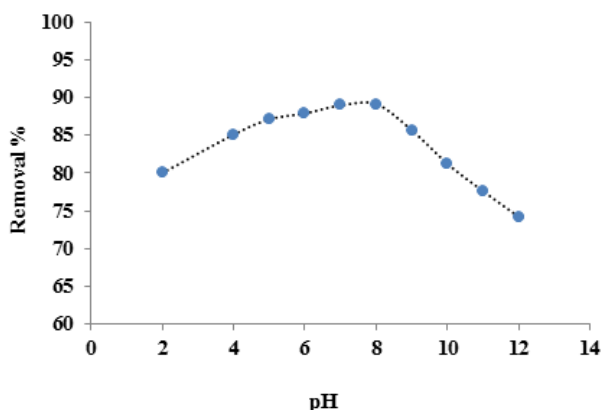
Figure 5. Effect of pH on CIP removal by AC(PPZS)KOH (Initial concentration –50 mg/L, adsorbent dose – 0.050g, Agitation speed – 100 rpm, contact time – 30 min, and temperature –25°C).

3.2.2. Effect of Adsorbent Dose

The effect of adsorbent dose on removal percentage of CIP using AC(PPZS)KOH was illustrated in Figure 6. Different doses of adsorbents ranging from 0.025 – 0.200 g were considered and other process parameters were maintained constant (pH – 8, CIP concentration – 50.0 mg/L, Agitation speed – 100 rpm, contact time – 30 min, and temperature – 25°C).

An increase in adsorption capacity with increasing adsorbent dose up to a maximum of 0.05g giving the corresponding optimum removal percentage of89.68%. On the other hand, it is found that any further addition over the above mentioned weight (0.05g) will not make any enhancement in the adsorption process, where almost negligible increase of removal efficiency over the specific adsorbent dose. The initial increase in adsorption capacity with increasing adsorbent mass is explained by the increase in the number of exchangeable sites for CIP adsorption, after which equilibration was attained [16-19, 32, 34].
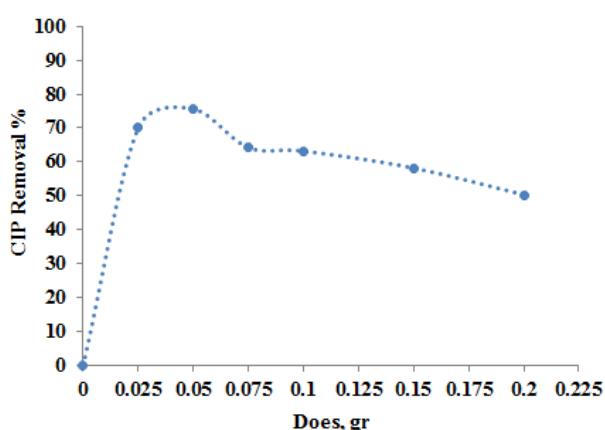

Figure 6. Effect of adsorbent dose on CIP removal by AC(PPZS)KOH ((pH–8, Initial concentration – 50 mg/L, Agitation speed – 100 rpm, contact time – 30 min, and temperature –25°C).

3.2.3. Effect of Contact Time

The effect of contact time on the removal of CIP is shown in Figure 7. The amount of the adsorbed drug increases with increasing time until it levels off after some 30 min. A

constant adsorption is indicative of equilibration due to saturation of adsorption sites. Rapid adsorption of CIP drug during the initial stages was due to the large initial concentration gradient between the adsorbate in solution and the number of available vacant sites on AC(PPZS)KOH adsorbent surface [16-22, 32, 34].
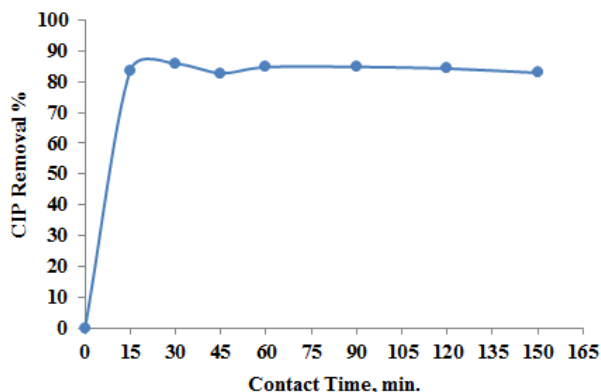

Figure 7. Effect of contact time on CIP removal by AC(PPZS)KOH (pH–8, Initial concentration – 50 mg/L, adsorbent dose – 0.050 g, Agitation speed – 100 rpm, and temperature –25°C).

3.2.4. Effect of Initial Ciprofloxacin Concentration

The initial concentration of CIP in the solution is an important parameter since its concentration change over a broad range in effluents applications.

The batch adsorption experiments were carried out with different initial concentrations (C_i) (50, 100,150, 200, 250 and 300 mg/L). The variation of percentage removal the drug with different initial concentration for the prepared activated carbon AC(PPZS)KOH was clarified in Figure 8. The figure shows a excellent performance of the prepared activated carbon at equilibrium state and clarify the optimum drug initial concentration used at confined experimental conditions.

It is also evidently observed that the percentage removal of the CIP drug is sufficiently high, (86.4% ± 4.73) at low concentration (50 mg/L) and no significant further increase as the concentration increases [15-25, 34].
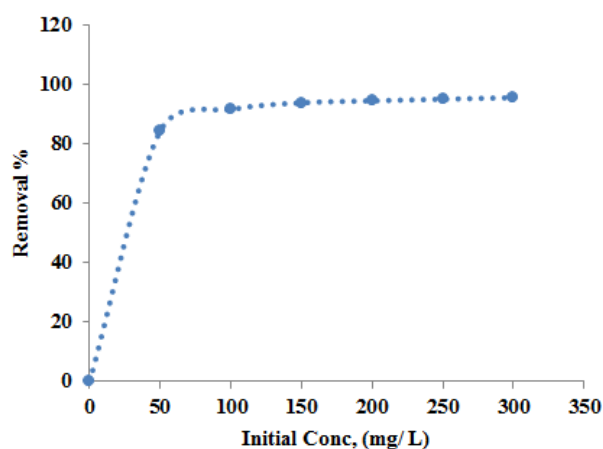

Figure 8. Effect of CIP initial concentration on its removal by AC(PPZS)KOH, (pH–8, contact time – 30 min, adsorbent dose – 0.050 g, Agitation speed – 100 rpm, and temperature –25°C).

3.3. Adsorption Isotherms

The successful representation of the dynamic adsorptive separation of solute from solution by an adsorbent depends upon a good description of the equilibrium between the two phases. Adsorption equilibrium is established when the amount of solute being adsorbed onto the adsorbent is equal to the amount being desorbed [15-27]. The equilibrium adsorption isotherms were depicted by plotting solid phase concentration (q_e) against liquid phase concentration (C_e) of solute.

Adsorption isotherm explains the interaction between adsorbate and adsorbent and is critical for design of adsorption process. The Freundlich and Langmuir isotherms are the most frequently used models to describe the experimental data of adsorption. In the present work these two isotherms were applied to investigate the adsorption process of CIP on prepared AC(PPZ)KOH at different conditions of process parameters.

3.3.1. Freundlich Isotherm Model

Freundlich isotherm is derived to a model of the multilayer adsorption and for the adsorption on heterogeneous surfaces, the linearized form of Freundlich equation is given by (15-18, 35, 36):

$$\ln q_e = \ln k_F + (1/n)\ln C_e \qquad (3)$$

where k_F and n are Freundlich constants, q_e is the extent of CIP adsorbed per unit mass of adsorbent (mg/g) and C_e is the equilibrium concentration of CIP (mg/L). A plot of log q_e against log C_e would give the values of n and k_F from the slope and it ercept respectively. The slope of $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero, while k_F represents the quantity of adsorbate on to the adsorbent. The values of Freundlich constants with the correlation coefficients are shown in Table 1 and Figure 9. The results show a better fit of experimental data of CIP uptake by AC(PPZS)KOH waste, high agreement with Freundlich, and poor less fitting with Langmuir.
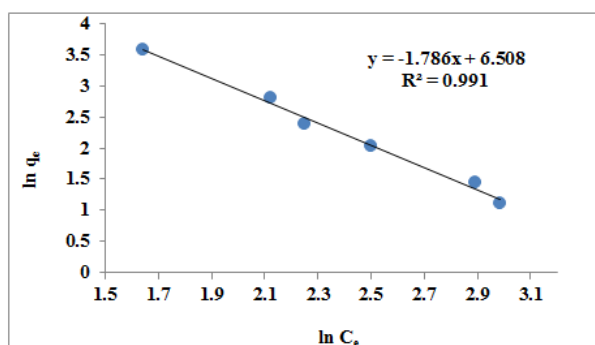
Figure 9. Freundlich isotherms of AC(PPZS)KOH for CIP removal at 25°C.

3.3.2. Langmuir Isotherm Model

To understand the adsorption isotherm, the Langmuir equation is perhaps the most widely used model due to its simplicity and Strong theoretical reasoning behind. This model suggests monolayer sorption on a homogeneous surface without interaction between sorbed molecules. In addition the model assumes uniform energies of sorption on to the surface and no transmigration of the sorbate. The linearized form of the Langmuir isotherm equation is represented as [15- 28, 35]:

$$C_e/q_e = 1/K_L\,q_m + C_e/q_m \qquad (4)$$

Where q_e (mg/g) is the amount adsorbed per unit mass of adsorbent corresponding to complete coverage of sites, C_e (mg/L) is the equilibrium concentration of CIP in solution, q_m(mg/g) is the monolayer adsorption capacity of the adsorbent and K_L(L/mg) is the adsorption energy. The related parameters are summarized in Table 1, and the linearized Langmuir equation is shown in Figure 10. The results reveal the Langmuir model is not able to describe the experimental data properly, poorless fitting on AC(PPZS)KOH.
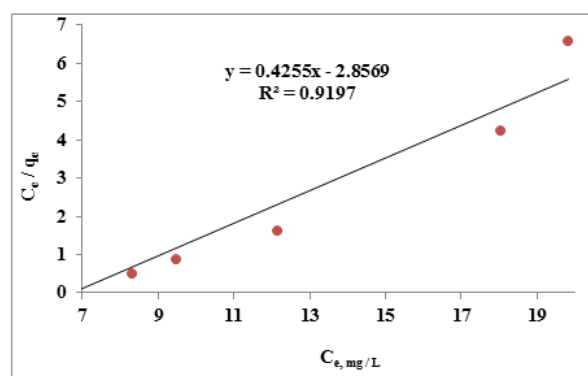
Figure 10. Langmuir isotherms of AC(PPZS)KOH for CIP removal at 25°C.

Table 1. Langmuir, Freundlich, isotherm constants for the CIP removal on the prepared AC(PPZS)KOH at 25°C.

Langmuir			Frenudlich		
K_L(L/m)	q_m(mg/g)	R^2	K_F,[(mg/g) $(L/mg)^{1/n}$]	n	R^2
0.824	2.353	0.919	1.873	0.560	0.991

4. Conclusion

The adsorption of Ciprofloxacin hydrochloride (CIP) onto Activated Carbon derived from Pomegranate Peel wastes collected from Alziedab Agricultural Scheme at River Nile state, Sudan has been studied. Adsorption experiments were tested at various parameters such as sorbent dosage, contact time, pH, and CIP concentration. The equilibrium data were analyzed using Freundlich and Langmuir, isotherm models and the results are well fitted to Freundlich equations. It was found that the equilibrium was reached within 30 min; also it was found that the optimum pH value of the CIP adsorption was 8. The present work concludes that AC(PPZS)KOH agricultural wastes is effective adsorbent in removing CIP from aqueous solutions. The optimum conditions which have been obtained in adsorption process for treating the aqueous phase were 50 mg/L for initial CIP concentration, 8 pH for

solution alkalinity, and 2.50g/L for mass of adsorbent. The equilibrium data obtained for the prepared activated carbon, AC(PPZS)KOH, is fitted to the Freundlich model more than the Langmuir. It was observed that the Freundlich adsorption isotherm conforms to the adsorption of CIP from aqueous solutions using AC(PPZS)KOH, the level of conformity is to a high extent compared to the Langmuir adsorption isotherms as indicated by higher correlation coefficient values of 0.991.

Acknowledgements

References

[1] Caliman, F. A., & Gavrilescu, M. "Pharmaceuticals, Personal Care Products and Endocrine Disrupting Agents in the Environment"- A Review. CLEAN –Soil, A ir, Water, pp 277-303, 2009.

[2] Fick, J., Söderström, H., Linderberg, R. H., Phan, C., Tysklind, M., & Joakim Larsson, D, "Contamination of Surface, Ground, and Drinking Water from Pharmaceutical Production", Environmental Toxicology and Chemistry, pp 2522-2527, 2009.

[3] Giger, W., Alder, A. C., Golet, E. M., Kohler, H.-P. E., Mc Ardell, C. S., Molnar, E., "Occurence and Fate of Antibiotics as Trace Contaminants in Wastewaters, Sewage Sludges, and Surface Waters", Chimia 57, pp 485-491, 2003.

[4] Dror Avisar, Orna Primor, Igal Gozlan and Hadas Mamane, "Sorption of Sulfonamide Tetracyclines to Montmorillonite Clay", Water Air Soil Pollut., 209, 1-4, pp 439-450, 2010.

[5] Kolpin, D. W.; Furlong, E. T.; Meyer, M. T.; Thurman, E. M.; Zaugg, S. D.; Barber, L. B.; Buxton, H. T, "Pharmaceuticals, hormones, and other organic waste water contaminants in U.S. streams, 1999-2000:

[6] Glen D. Park, Pharm D; Reynold Spector, MD; Mark J. Goldberg, MD and George F. Johnson, "Expanded Role of Charcoal Therapy in the Poisoned and Overdosed Patient", Arch Intern. Med. 146(5), pp. 969-973, 1986.

[7] Cassidy S. L., Hale A., Buss D. C. and Routledge P. A., "Invitro drug adsorption to charcoal, silicats, acry late copolymer and silicon oil with charcoal and with acrylate copolymer", Hum. Exp. Toxicol., 16 (1), pp 25-27, 1997.

[8] Reem Adham AL-Bayati," Adsorption– Desorption Isotherm of One of Antidibetic Drug from Aqueous Solutions on Some Pharmaceutical Adsorbents", European Journal of Scientific Research, 40,. 4, pp.580-588, 2010.

[9] Figueroa, R. A., Leonard, A., & Mackay, A. A, "Modeling tetracycline antibioticsorption in clays", Environmental Science & Technology, 38, pp 476–483, 2004.

[10] Ter Laak, T. L., Gebbink, W., & Tolls, J., "The effect of pH and ionic strength on the sorption of sulfachloropyridazine, tylosin, and oxytetracycline to soil", Environmental Toxicology & Chemistry, 25(4), pp 904–911, 2006.

[11] Omar S. Alkhazrajy, Maha A. Al-Abayaji and Mohammed H. Abdul Latif, "Adsorption of Metoclopromide Hydrochloride onto burned initiated Iraqibentonite", journal of Alnahrain University, 15(2), pp 35-46, 2012.

[12] Isa. S. A., Jasim S. M., and Hussein H. K., "Investigation of bentonite clay surface asaphysical antidote of Amitriptyline HCl, chlorpromazine HCl and Chlordizepoxide HCl from solution", J. Iraqi Pharm. 8 (2), pp 62-68, 2002.

[13] Al-Tamimi. R. J.," Study of the ability of selected surface in adsorption of somdrugs from solution", Msc. Thesis, college of Science, University of Baghdad, 2002.

[14] Rossi S, "Australian Medicines Handbook" (2nd ed). Adelaide, 2006.

[15] Carabineiro, S. A. C., Thavorn-amornsri, T., Pereira, M. F. R., Serp, P., Figueiredo, J. L.: Comparison between activated carbon, carbon xerogel and carbon nanotubes for the adsorption of the antibiotic ciprofloxacin. Catalysis Today, 186, 29 -34 (2012).

[16] Ibezim, E. C., Ofoefule, S. I., Ejeahalaka, C. N. E., Orisakwe, O. E.: In vitro adsorption of ciprofloxacin on activated charcoal and talc. American Journal of Terapeutics, 6(4), 199-201 (1999).

[17] El-Shafey, E. S. I., Al-Lawati, H., Al-Sumri, A.S.: Ciprofloxacin adsorption from aqueous solution onto chemically prepared carbon from date palm leaflets. Journal of Environmental Sciences, 24(9), 1579-1586 (2012).

[18] Wu, Q., Li, Z., Hong, H.: Influence of types and charges of exchan geable cations on ciprofloxacin sorption by montmorillonite. Journal of Wuhan University of Technology-Materials Science, 27(3), 516-522 (2012).

[19] Carrasquillo, A. J., Bruland, G. L., Mackay, A. A., Vasudevan, D.: Sorption of ciprofloxacin and oxytetracycline zwitterions to soils and soil materials: influence of compound structure. Environmental Science and Technology, 42, 7634-7642 (2008).

[20] Vasudevan, D., Bruland, G. L., Torrance, B. S., Upchurch, V. G., Mac Kay, A. A.: pH-dependent ciprofloxacin sorption to soil: Interaction mechanisms and soil factors influencing sorption. Geoderma, 151, 68-76 (2009).

[21] Conkle, J. L., Lattao, C., White, J. R., Cook, R. L.: Competitive sorption and desorption behavior for three fluoroquinolone antibiotics in a waste water treatment wetland soil. Chemosphere, 80(11), 1353-1359 (2010).

[22] Wang, C. J., Li, Z., Jiang, W. T.: Adsorption of ciprofloxacin on 2:1 dioctahedral clay minerals. Applied Clay Science, 53,723-728 (2011).

[23] Li, Z., Hong, H., Liao, L., Ackley, C. J., Schulz, L. A., MacDonald, R. A., Mihelich, A. L., Emard, S. M.: A mechanistic study of ciprofloxacin removal by kaolinite. Colloids and Surfaces B: Biointerfaces, 88, 339-344 (2011).

[24] Zhang, C. L., Qiao, G. L., Zhao, F., Wang, Y.: Thermodynamic and kinetic parameters of ciprofloxacin adsorption onto modified coal fly ash from aqueous solution. Journal of Molecular Liquids, 163, 53-56 (2011).

[25] Wu, C., Spongberg, A. L., Witter, J. D.: Sorption and biodegradation of selected antibiotics in biosolids. Journal of Environmental Science and Health Part A, 44: 454-461 (2009).

[26] Bajpai, S. K., Bajpai, M., Rai, N.: Sorptive removal of ciprofloxacin hydrochloride from simulated wastewater using sawdust: Kinetic study and effect of pH. Water SA, 38(5), 673-682 (2012).

[27] Jiang, W. T., Chang, P. H., Wang, Y. S., Tsai, Y., Jean, J. S., Li, Z., Krukowski, K.: Removal of ciprofloxacin from water by birnessite. Journal of Hazardous Materials, 250-251, 362-369 (2013).

[28] Shi, S., Fan, Y. W., Huang, Y. M.: Facile low temperature hydrothermal synthesis of magnetic mesoporous carbon nanocomposite for adsorption removal of ciprofloxacin antibiotics. Industrial & Engineering Chemistry Research, 52(7), 2604-2612 (2013).

[29] Reynaud, F., Tsapis, N., Deyme, M., Vasconcelos, T. G., Gueutin, C., Guterres, S. S., Pohlmann, AR, Fattal, E.: Spray-dried chitosan-metal microparticles for ciprofloxacin adsorption: Kinetic and equilibrium studies. Soft Matter, 7(16), 7304-7312 (2011).

[30] Gu, C., Karthikeyan, K. G.: Sorption of the antimicrobial ciprofloxacin to aluminum and iron hydrous oxides. Environmental Science and Technology, 39, 9166-9173 (2005).

[31] Rakshit, S., Sarkar, D., Elzinga, E. J., Punamiya, P, Datta, R.: Mechanisms of ciprofloxacin removal by nano -sized magnetite. Journal of Hazardous Materials, 246-247, 221-226 (2013).

[32] Edith Cristina Laignier Caze dey, Hérida Regina Nunes Salgado., Spectrophotometric Determination of Ciprofloxacin Hydrochloride in Ophthalmic Solution., Advances in Analytical Chemistry 2012, 2(6): 74-79.

[33] Affo, W., Mensah-Brown, H., Awuku, J. F., Markwo, A. Quantitative Analysis of Ciprofloxacin Sodium Chloride Pharmaceutical Infusions Using Ultraviolet-visible Spectroscopy., ARPN Journal of Science and Technology., Vol. 3, NO. 3, March 2013.

[34] Dhafir T. Ajeel Al-Heetimi, Muna Abdul Rasool Kadhum and Omar S. Alkhazrajy., Adsorption of Ciprofloxacin Hydrochloride from Aqueous Solutionby Iraqi Porcelinaite Adsorbent., Journal of Al-Nahrain University Vol. 17 (1), March, 2014, pp.41-49.

[35] Choy, K. K. H., Porter, J. F., McKay, G. Langmuir isotherm models applied to the multi component sorption of acid dyes from effluent onto activated carbon, *Chemical Engineering Journal*, 45, 2000, 575-584.

[36] Mutasim H. Elhussien, Yusuf M Isa., 2015— Langmuir, Freundlich Adsorption Isotherms and Kinetics for the Removal of Methylene Blue Dye from Aqueous Solution using Activated Carbon Derived from Pods of Acacia nilotica var astringens (Sunt tree) by Chemical Activation with $ZnCl_2$, *Chemical Process and Engineering Research,* vol. (38): 25-34.