



Aqueous Phase Sorptive Removal of Tetracycline and Ciprofloxacin: Isotherm Study and Synergistic Effect Consideration

T.T. Weor^{1*}, A.U Itodo², I.S. Eneji², S.T. Iningev¹, G.T. Buluku¹

¹Department of Chemistry, Benue State University, PMB 102119 Makurdi, Nigeria

²Department of Chemistry, Federal University of Agriculture, PMB 2373 Makurdi, Nigeria

*Corresponding Author: timtorwejp@yahoo.com

Abstract The persistence of antibiotic residues in our environment is very threatening and has become a global challenge. The removal of antibiotics' residue from the environment has received global attention due to their potential hazards. The study investigated and compared the adsorption potential of three adsorbents; Pure Chitosan (PChi), Pure Starch (PSt) and Chitosan-Starch Polymeric Blend (CS42) in removing two antibiotics; Tetracycline (TET) and Ciprofloxacin (CIP) from aqueous solution in a batch equilibrium studies. Commercial Activated Carbon (CAC) was used in the study as control adsorbent. The influence of time and initial concentration on the adsorption process was examined. Langmuir, Freundlich and Temkin isotherm models were employed to evaluate the equilibrium experimental data and the regression coefficients obtained depicted good applicability to the tested isotherms of the antibiotics onto PChi, PSt and CS42. Assessment of the removal efficiency (%) of antibiotics adsorbed onto the three adsorbents showed that CIP was better adsorbed than TET. The affinity of the adsorbents for antibiotics via removal efficiency (%) also followed the trend: CS42 (94.6, 99.4) % > PChi (81.0, 85.8) % > PSt (75.1, 83.6) % for TET and CIP respectively, indicating that the combination of PChi and PSt provided a great synergistic effect leading to enhanced removal of the antibiotics from aqueous solutions. The adsorption process was found to be time dependent and the results revealed that the optimum time for adsorption of TET and CIP onto the Chitosan-Starch Polymeric Blend (CS42) occurred at 60 minutes whereas the individual adsorbents (PChi and PSt) reached their equilibrium time at varied times ranging from 90 – 150 minutes. The results also depicted that, commercial activated carbon (CAC) which was used in this study as control adsorbent exhibited lower adsorption efficiency compared to CS42 and PChi but better than PSt.

Keywords Synergistic Effect, Sorption, Antibiotics, Adsorbents

Introduction

Antibiotics are a type of trace organic contaminants that have become increasingly a big problem globally. Antibiotic residues in the environment have become a potential environmental and ecological hazard, affecting the normal activity of microbiological, animal, and plant life, and ultimately human health [1-2]. Antibiotic contamination is a problem that cannot be ignored. Recently, emerging environmental contaminants, including antibiotics and antibiotic resistant genes have been detected in various environments [3-5], and there are many reports concerning the detection of antibiotics in soil, water, and sediment samples [6].



For the removal of antibiotics from wastewater, it is important to have effective and cheap adsorbents available for large-scale treatment applications. In recent years, attempts to remove residual antibiotics from contaminated water have required the consideration of various approaches for the development of cheap, more effective and environmentally benign sorbents containing natural polymers [7]. Polysaccharides like chitosan and starch which are abundant, renewable and biodegradable hold great potential as adsorbent. The easy availability, nontoxic and eco-friendly nature of chitosan and starch has been documented [8-10].

Blending polymers is a promising way to modify, enhance and extend their application [11]. Absorbent polymeric Blends (APBs) are crosslinked hydrophilic polymeric materials with properties to absorb and retain a considerable amount of water or other aqueous fluids in the aqueous environment with swelling of up to a hundred times its original size [4]. Starch and chitosan can be crosslinked and/or modified with great potential for being cheap, readily available and low-cost adsorbents [12].

In this study, four adsorbents, Pure chitosan (PChi), Pure starch (PSt), a combination of both adsorbents (Chitosan-Starch Polymeric blend (CS42)) and commercial activated carbon (CAC) were compared for their efficiency in removing tetracycline (TET) and ciprofloxacin (CIP) from aqueous solutions. The effects of time and concentration were monitored and the sorption mechanisms were tested using two adsorption isotherm models.

Materials and Methods

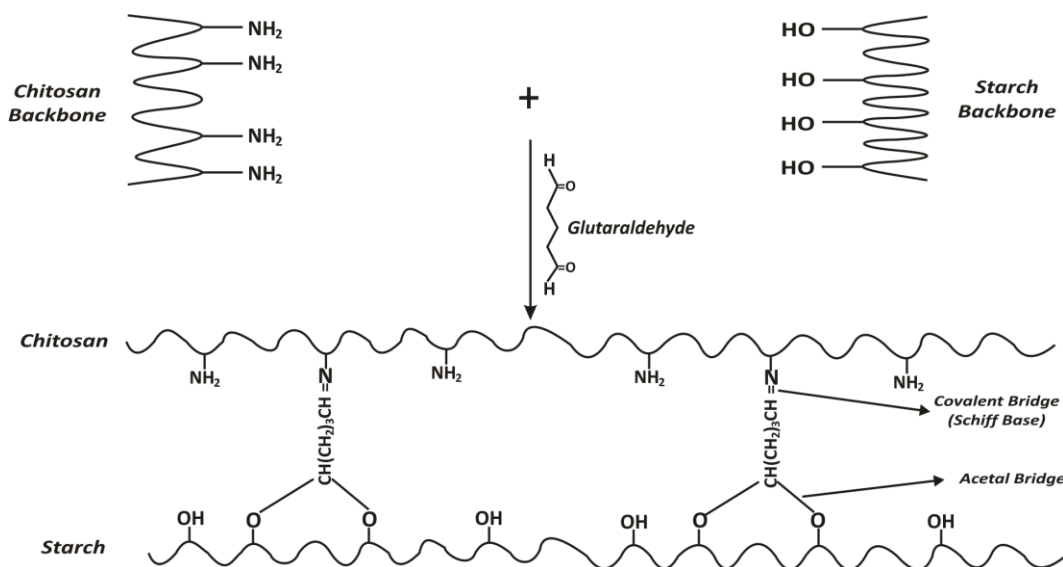
Materials

Sorbent: High molecular weight Chitosan ($C_{12}H_{24}N_2O_9$; viscosity 800 cp) and Glutaraldehyde 25 %wt ($OHC(CH_2)_3CHO$; density of 1.06) were supplied by Sigma-Aldrich, Germany. Soluble Starch powder and glacial acetic acid 99.5 % were supplied by Merck.

Adsorbate: Analytical grade Antibiotics; tetracycline and ciprofloxacin (Sigma Aldrich) were used for determination of Λ_{max} and preparation of standard curves [13].

Methods

Preparation of stock and standard solutions: Standard solutions were prepared following routine laboratory procedures. Reagents prepared include 1 % (v/v) acetic acid solution, 2 % (v/v) glutaraldehyde solution, 2 % (w/v) Chitosan solution, 2 % (w/v) Starch solution and 1000 ppm Antibiotics solution [13].



Scheme 1: Crosslinking reaction of Chitosan –Starch GLA



Formulation of Sorbent: The method adopted was that reported by Fahanwi [14] for Chitosan-Starch Polymeric Blend (CSPB) with slight modifications in mass-volume ratios. The polymeric blends were synthesized via the chemical crosslinking method employing the casting/solvent evaporation technique. The solutions of chitosan:starch were prepared in different ratios (1:5, 2:4, 3:3, 4:2, 5:1), separately. The solutions were mixed using a magnetic stirrer for 30 min at 350 rpm to obtain a homogeneous solution and then 4 mL of 2 % (v/v) glutaraldehyde was gradually added to the solution using a pipette followed by continuous stirring for cross-linking to occur. Crosslinking was made evident by increase in viscosity of the gel upon stirring at 250 rpm. The gel was poured in Petri dishes covered with foil paper and placed at room temperature to set dry, stored and labelled for further investigations. Sorbent formulation codes and descriptions were earlier presented [13].

Batch Sorption Experiment

The antibiotic sorption experiments were performed by the batch method and the effect of contact time and concentration were studied. The sorption experiments were performed in 250 mL flask placed on a mechanical stirrer containing synthetic adsorbate solution with required sorbent dose (0.5) g and sorbate concentration (20 – 100) ppm at room temperature and shaken at a constant rate, allowing sufficient time for sorption equilibrium. The sorption measurements were performed at the constant agitation speed of 350 rpm for 150 min. Filtrate was analyzed using UV-vis spectrophotometer.

The removal efficiency, E (%) of sorbent on adsorbate was calculated using equation 1 [15].

$$E (\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

Results and Discussion

Effect of Contact time

Table 1 indicates that antibiotics (TET and CIP) removal increases with an increase in contact time before equilibration. From the result, CS42 gave the highest percentage removal of 94.6 % at 60 minutes for TET. The highest percentage TET removal for PChi (81.0 %) > PSt (75.1 %) < CAC (80.6 %) was achieved at 150, 120 and 120 min respectively. This implies that removal of TET from aqueous solution is controlled by the rate of transport of the adsorbate species [16]. The sorption efficiency of CIP for all the sorbents was rapid at the beginning. This may be linked to available larger surface area of the sorbent at the initial, an indication of well-exposed sorption sites [17]. CS42 (99.4 %) had the highest removal efficiency. A time-dependent sorption was generally observed for CIP.

Table 1: Effect of Contact Time on Sorption Efficiency for Tetracycline and Ciprofloxacin uptake on CS42, PChi, PSt and CAC

Exp.	Time (min)	C _o (ppm)	Tetracycline	Ciprofloxacin
			RE (%)	RE (%)
CS42	30	50	77.3	83.2
	60		94.6	99.4
	90		91.6	96.4
	120		93.6	97.3
	150		94.2	98.0
PChi	30	50	73.2	80.2
	60		78.3	85.4
	90		80.5	85.8
	120		80.4	84.5
	150		81.0	85.4
PSt	30	50	69.4	78.4
	60		69.7	81.5
	90		73.1	83.5
	120		75.1	83.6



	150		74.4	82.3
CAC	30	50	71.1	79.4
	60		74.3	82.7
	90		78.8	83.8
	120		81.6	85.6
	150		80.7	85.3

Effect of initial concentration: Higher initial adsorbate concentration provides significant driving force to overcome the mass transfer resistances of the adsorbate between the aqueous and solid phases, therefore increasing sorption. Results shows that percentage removal decreased as initial antibiotics concentration increased. The sorbent with highest removal efficiency at 100 ppm concentration for both antibiotics (TET and CIP) was CS42. The poorer uptake at higher antibiotics concentration could be linked to occupation or saturation of available vacant sites [18-20].

Table 2: Effect of Concentration on Sorption Efficiency for Tetracycline and Ciprofloxacin uptake on CS42, PChi, PSt and CAC

Exp.	Time (min)	C _o (ppm)	Tetracycline	Ciprofloxacin
			RE (%)	RE (%)
CS42	150	20	95.1	99.5
		40	96.4	99.0
		60	93.1	98.3
		80	80.5	97.6
		100	76.2	91.4
PChi	150	20	71.0	82.2
		40	65.3	80.8
		60	61.2	80.6
		80	59.4	76.9
		100	59.1	73.6
PSt	150	20	60.3	74.9
		40	54.7	71.6
		60	54.2	71.1
		80	51.8	69.9
		100	49.2	69.6
CAC	150	20	68.0	81.8
		40	62.8	79.9
		60	59.8	75.7
		80	59.2	75.3
		100	54.9	73.9

Adsorption Isotherms

It is essential to know them so-as-to compare the effectiveness of different adsorbent materials under different operational conditions and also to design and optimize an adsorption system. The isotherms signify the relation between adsorption capacity and concentration at equilibrium and can portray the sorption mechanism. Adsorption isotherm is established when the concentration of an adsorbate (antibiotics) in a bulk solution (C_e) is in dynamic balance with that at the interface. The antibiotics uptake capacities in the present study was evaluated using the Langmuir, Freundlich and Temkin isotherm models

Langmuir Isotherm Model

The Langmuir isotherm represents the equilibrium distribution of antibiotics between the solid and liquid phases. The isotherm is mainly based on the monolayer adsorption on the active sites of the adsorbent and is generally expressed as Chengwen [21].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

Where K_L (L/mg) and q_m are Langmuir isotherm constants [22].

The above equation can be rewritten as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \quad (3)$$

Where C_e is the equilibrium concentration of adsorbate in the solution (mg/L), q_e is the equilibrium adsorbate concentration (mg/g) on the adsorbent.

The linear plots of $\frac{1}{q_e} V_S \frac{1}{q_m}$ (not presented) showed that the adsorption study followed the Langmuir adsorption isotherm model. The adsorption of the antibiotics onto CAC was best described by the Langmuir model indicating that the adsorption process may have proceeded through a monolayer coverage. The Langmuir constants, q_m and R_L for the three adsorbents (PChi, PSt and CS42) alongside with the control adsorbent (CAC) were evaluated from the slope and intercept of the linear Langmuir plots and are presented in Table 3. The q_m values are used to compare the efficiencies of the adsorbents in this study (PChi, PSt and CS42) with CAC, which have been applied for the removal of the same antibiotics from aqueous solutions. The q_m values obtained from this study indicate better removal for CIP than TET and that the Chitosan-Starch Polymeric Blend (CS42) displayed higher removal efficiency for the antibiotics as compared to the PChi and PSt and even the control adsorbent (CAC) as shown in table 3. This result shows that the combination of the two adsorbents (PChi and PSt) may have produced a strong synergistic effect leading to enhanced uptake of the antibiotics from aqueous solutions. Also, the values of the linear regression coefficient (R^2) displayed in Table 3 are all close to 1, suggesting a good fitting of the experimental data into the Langmuir isotherm equation.

The essential characteristics of the Langmuir isotherm is expressed in terms of a dimensionless constant termed separation factor or equilibrium parameter, R_L , which is used to predict whether an adsorption system is “favorable” or “unfavorable”. The separation factor, R_L is defined as Anusiem, *et al.*, [23].

$$R_L = \frac{1}{(1+K_L C_m)} \quad (4)$$

The isotherm is described as: unfavorable when $R_L > 1$, linear when $R_L = 1$, favorable when $0 < R_L < 1$ and irreversible when $R_L = 0$. The R_L values obtained from the present study were all less than 1 ($0 < R_L < 1$), showing that the sorption process was favourable under the conditions of this study and also indicated that the adsorbents could be good substrates for the removal of the antibiotics from aqueous solutions.

Freundlich Isotherm

The linearized form of Freundlich adsorption isotherm is represented as;

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

Where K_F and n are Freundlich constants describing both capacity and the intensity of the adsorption process respectively. Linear plots of $\log q_e$ vs $\log C_e$ according to Freundlich isotherm equation are not presented). The constants K_F and n were calculated from the intercept and slope of the linear Freundlich plots and are presented in Table 3. Assessment of the R^2 values for the three adsorbents (PChi, PSt and CS42) along with CAC shows that the adsorption of the antibiotics onto PSt was best described by the Freundlich model. The correlation coefficients (R^2) were generally high for all the adsorbents, indicating the fit of the experimental data into the isotherm. K_F is an approximate indicator of adsorption capacity while n indicates favourability and intensity of the adsorbate/adsorbent systems. If $n = 1$ then the partition between the two phases are independent of the concentration. If the value of n is below 1, it indicates a normal adsorption but when greater than 1, indicates cooperative adsorption [24], and n values between 1 and 10 represent favourable adsorption conditions [25]. In all cases reported here, the range of the values of n was within the range of 1.174 to 2.793 for the adsorption process indicating beneficial adsorption for the system under study. The high R^2 values suggest an excellent fitting of experimental data into the Freundlich model.

Temkin Isotherm



Coefficient of regression (R^2) recorded for all the adsorbates by the adsorbents in question were all close to 1. It can be deduced that all the adsorbents had good applicability (Table 3). Allen *et al.* [26] reported that b_T is a constant related to the heat of adsorption, where a high value indicate strong interaction between adsorbate and the adsorbent. From the result, the constant b_T was observed to be high for all the adsorbents in regards to TET (>1000 KJ/mol) and CIP (>800 KJ/mol) adsorbates. The high values of b_T in this study indicates a very strong interaction between adsorbates and the adsorbents. Temkin isotherm assumes that the heat of adsorption of the molecules increases linearly with coverage [27].

Table 3: Isotherm Experimental Constants for TET and CIP Sorption on PSt, PChi, CS42 and CAC

Isotherms	Constants	PSt		PChi		CS42		CAC	
		TET	CIP	TET	CIP	TET	CIP	TET	CIP
Langmuir									
	R^2	0.994	0.996	0.992	0.998	0.985	0.984	0.996	0.998
	R_L	0.053	0.017	0.059	0.027	0.059	0.088	0.055	0.034
	q_m (mg/g)	4.340	5.569	4.983	5.826	6.176	7.056	4.784	5.834
Freundlich									
	R^2	0.997	0.999	0.998	0.982	0.965	0.924	0.997	0.996
	n	1.292	1.174	1.395	1.319	2.577	2.793	1.368	1.326
	K_F (L/mg)	0.241	0.373	0.398	0.670	2.421	5.152	0.351	0.631
Temkin									
	R^2	0.962	0.941	0.936	0.988	0.942	0.968	0.963	0.954
	b_T KJ/mol)	1233	842	1133	855	1499	1434	1159	879
	K_T (L/mg)	0.200	0.284	0.282	0.454	4.201	29.55	0.258	0.431

Synergistic Study

The synergistic study investigated the adsorption potential of three adsorbents; Pure Chitosan (PChi), pure Starch (PSt) and the derived adsorbent (CS42) in removing two antibiotics (TET and CIP) from aqueous solution. A control adsorbent, Commercial Activated Carbon (CAC) was assessed alongside PChi, PSt and CS42. The influence of time and initial concentration were used for the investigation. Figures 1 – 4 compares the percentage removal (% RE) of PChi, PSt, CS42 and CAC. From the results, the assessment of adsorbents synergy via RE (%) of antibiotics onto the adsorbents followed the trend: CS42 (94.6, 99.4) % > PChi (81.0, 85.8) % > PSt (75.1, 83.6) % for TET and CIP respectively. It was also observed that, the derived adsorbent (CS42) had the best RE (%) and this fate was achieved at an optimum time of 60 min whereas, PChi and PSt reached their equilibrium time at varied times ranging from 90 – 150 minutes. It can be inferred that CS24 may have provided a great synergistic effect that led to enhanced removal of the antibiotics compared to PChi and PSt. The results also depicts that the control adsorbent (CAC) exhibited lower adsorption efficiency compared to CS42 and PChi but better than PSt.



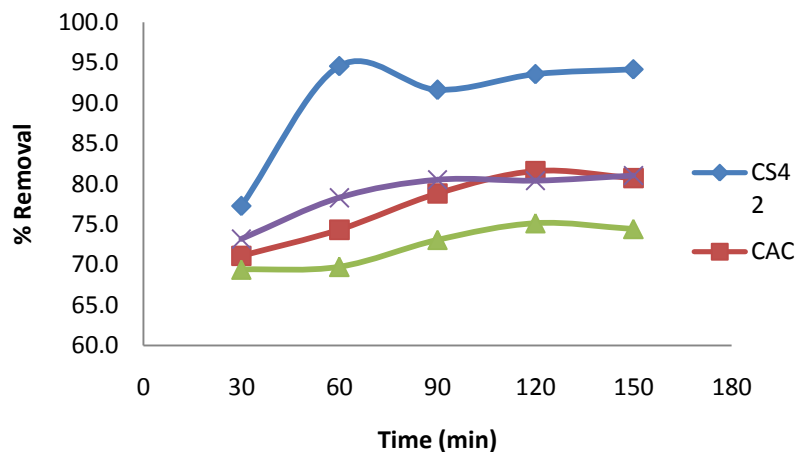


Figure 1: Plot of percentage removal vs Time for adsorption of TET onto PChi, PSt, CS42 and CAC

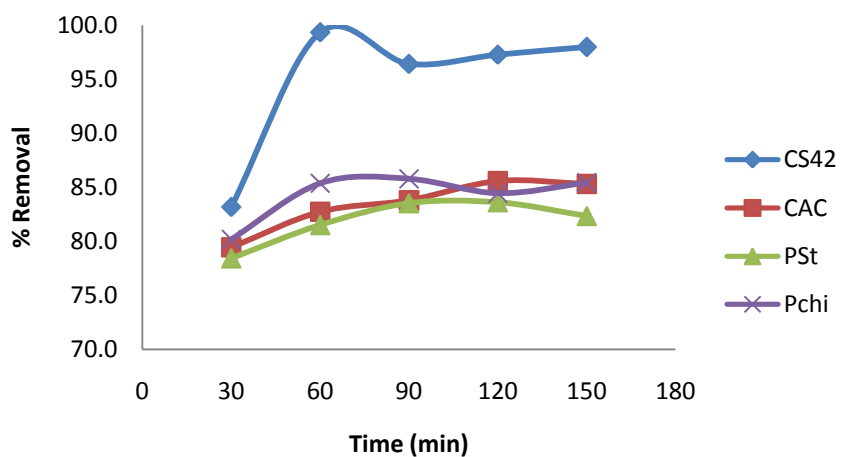


Figure 2: Plot of percentage removal vs Time for adsorption of CIP onto PChi, PSt, CS42 and CAC

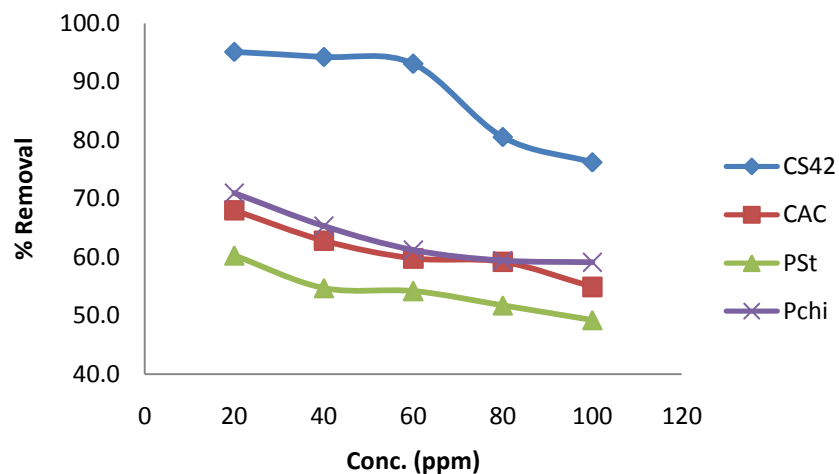


Figure 3: Plot of percentage removal vs Conc. for adsorption of TET onto PChi, PSt, CS42 and CAC



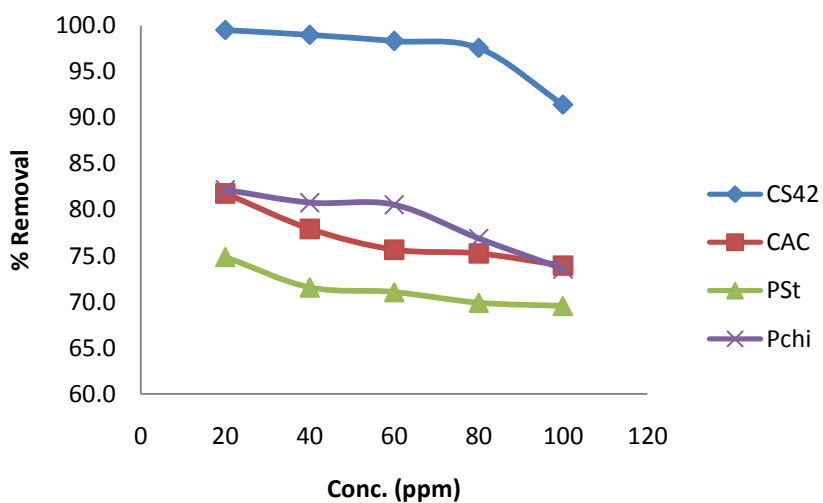


Figure 4: Plot of percentage removal vs Conc. for adsorption of CIP onto PChi, PSt, CS42 and CAC

Conclusion

Antibiotics contamination pose a great risk to human and animal husbandry as resistance genes have been detected in various environments. For the removal of antibiotics from wastewater, it is important to have effective and cheap adsorbents available for large-scale treatment applications. This study investigated the potential of three adsorbents; chitosan, starch, a combination of both (chitosan-starch) and a control adsorbent (commercial activated carbon) in removing two antibiotics: Tetracycline and Ciprofloxacin from aqueous solution. The influence of time and concentration on the sorption process was examined. The equilibrium experimental data were tested with three isotherm models - the Langmuir, Freundlich and Temkin isotherms. Assessment of the antibiotics adsorbed onto the adsorbents showed that the derived adsorbent CS42 had better sorption efficiency compared to PChi, PSt and even the control adsorbent; CAC. The affinity of adsorbents for the antibiotics also follows the trend: CS42 > PChi > CAC > PSt indicating that the derived adsorbent (CS42) may have provided a great synergistic effect that lead to enhanced removal of the antibiotics by the adsorbent.

References

- [1]. Liu F., Ying G.G., Tao R., Zhao J.L., Yang J.F. and Zhao L.F. (2009). Effects of six selected antibiotics on plants growth and soil microbial and enzymatic activities. *Environmental Pollution*, 157, 1636–1642.
- [2]. Underwood J.C., Harvey R.W., Metge D.W., Repert D.A., Baumgartner L.K., Smith R.L., Ronane T.M. and Barber L.B. (2011). Effect of antimicrobial sulfamethoxazole on groundwater bacterial enrichment. *Environmental Science and Technology*, 45, 3096–3101.
- [3]. Cheng W., Chen H., Su C. and Yan S. (2013). *Environment International*, 61, 1–7.
- [4]. Wanga W. and Wang A. (2010). Synthesis and swelling properties of pH-sensitive semi-IPN superabsorbent hydrogels based on sodium alginate-g-poly (sodium acrylate) and polyvinylpyrrolidone, *Carbohydrate Polymers*. 80: 1028–1036.
- [5]. Frey S.K., Topp E., Khan I.U.H., Ball B.R., Edwards M., Gottschall N., Sunohara M. and Lapen, D.R. (2015). *Science of Total Environment*, 532, 138–153.
- [6]. Shi Y., Gao L., Li W., Liu J. and Cai Y. (2012). Bulletin of Environmental Contamination and Toxicology., 89, 857–861.
- [7]. Sim W.J., Lee J.W., Lee E.S., Shinb S.K. and Hwang S.R (2011). Occurrence and distribution of pharmaceuticals in wastewater from households, livestock farms, hospitals and pharmaceutical manufactures. *Chemosphere*, 82:179–86.
- [8]. Bhatnagar A. and Sillanpää M. (2009). Applications of chitin- and chitosan-derivatives for the detoxification of water and wastewater: A short review, *Advances in Colloid and Interface Science*. 152:26–38.
- [9]. Pareta R. and Edirisinghe M.J. (2006). A novel method for the preparation of starch films and coatings. *Carbohydrate Polymer*. 63: 425–431.
- [10]. Zhang J.F. and Sun X.Z. (2004). Mechanical properties of PLA/starch composites compatibilized by maleic anhydride. *Biomacromolecules*. 5: 1446–1451.
- [11]. Choi E.J., Kim C.H and Park J.K. (1999). Synthesis and characterization of starch-g-polycaprolactone copolymer. *Macromolecules*. 32: 7402–7408.
- [12]. Bolto B.A. (1995). Soluble polymers in water purification. *Progressive Polymer Science*. 20:987– 1041.
- [13]. Itodo A.U., Eneji I.S. and Weor T.T. (2018). Chitosan-Starch Polymeric Blend Hydrogels as Scavengers of Antibiotics from Simulated Effluent: Sorbent Characterization and Sorption Kinetic Studies. *J. Chem Soc. Nigeria*, Vol. 43, No. 4, pp 667 -677.
- [14]. Fahanwi A.N. (2014). Synthesis, Characterization of superabsorbent Chitosan- Starch Hydrogel and its Application for Removal of Direct Red 80 Dye. A thesis submitted to the Institute of Graduate Studies and research, Eastern Mediterranean University, North Cyprus. P. 49-50.



- [15]. Aderonke A.O., Abimbola B.A., Omotayo S.A. and Ifeanyi E.O. (2016). Chitosan-Grafted Carbon for the Sequestration of Heavy Metals in Aqueous Solution. *American Chemical Science Journal*. 11(3): 1-14
- [16]. Veena D.B., Jahagirdar A.A. and Zulfiqar A.M.N., (2012). Adsorption of Chromium on Activated Carbon Prepared from Coconut Shell. *International Journal of Engineering Research and Applications*. 2(5): 364-370.
- [17]. Orumwense F.F.O. (1996). Removal of lead from water by adsorption on a kaolinitic clay. *Journal of Chemical Technology and Biotechnology*. 65 (1996): 363–369
- [18]. Balarak D. and Mostafapour F.K. (2016). Canola residual as a biosorbent for antibiotic metronidazole removal. *Pharmaceutical and Chemical Journal*. 3(2):12-17.
- [19]. Balarak D., Joghatae A., Azadi N.A. and Sadeghi S. (2016). Biosorption of Acid Blue 225 from Aqueous Solution by *Azolla filiculoides*: Kinetic and equilibrium studies. *American Chemical Science Journal*. 12(2):1-10.
- [20]. Balarak D., Mostafapour F.K., Joghatae A and Akbari H. (2017). Adsorption of Amoxicillin Antibiotic from Pharmaceutical Wastewater by Activated Carbon Prepared from *Azolla filiculoides*. *Journal of Pharmaceutical Research International*. 18(3): 1-13.
- [21]. Chengwen S, Shuaihua W, Murong C, Ping T, Mihua S and Guangrui G. (2014). Adsorption Studies of Coconut Shell Carbons Prepared by KOH Activation for Removal of Lead (II) from Aqueous Solutions. *Sustainability*.; 6: 86-98.
- [22]. Karadag D., Yunus K., Mustapha T. and Mustapha O. (2007). A comparative study of linear and non-linear regression analysis for ammonium exchange by Clinoptilolite Zeolite. *Journal of Hazardous Materials*. 144: 432–437.
- [23]. Anusiem A.C.I, Onwu FK and Ogah S.PI (2010). Adsorption Isotherms Studies of Ni (II), Cd (II) and Pb (II) ions from Aqueous Solutions by African White Star Apple (*Chrysophyllum albidum*) Shell. *Int. Journ. Chem.*; 20(4): 265-274.
- [24]. Mohan S and Karthikeyan J., (1997). Removal of lignin and tannin color from aqueous solution by adsorption on to activated carbon solution by adsorption on to activated charcoal *Environ. Pollut.*; 97: 183-187.
- [25]. Dada AO, Olalekan AP, Olatunya AM and Dada O. (2012). Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn^{2+} Unto Phosphoric Acid Modified Rice Husk. *IOSR Journal of Applied Chemistry*.; 3(1): 38-45.
- [26]. Allen, S.J., McKay G. and Porter J.F. (2004). Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems. *Journal of Colloid Interface Science*. 280: 322–333.
- [27]. Srivastava V.C., Mall I.D., Prasad B. and Mishra I. M. (2007). Adsorptive Removal of Phenol by Bagasse fly ash and Activated Carbon: Equilibrium, Kinetics and Thermodynamics. *Colloids and Surfaces. A Physicochemical Engineering Aspects*, 272: 89-104.

