Arabian Journal of Chemical and Environmental Research Vol. 08 Issue 2 (2021) 193–213



Removal of Pentachlorophenol (PCP) from Aqueous Solution using Canna indica L.: Kinetics, Isotherm and Thermodynamic Studies

C.E. Enyoh¹* and B.O. Isiuku¹

¹Department of Chemistry, Faculty of Physical Science. Imo State University, PMB 2000 Owerri, Nigeria.

Received 27 March 2021, Revised 02 June 2021, Accepted 04 June 2021

Abstract

In this study, the efficiency of *Canna indica* L in the removal of pentachlorophenol (PCP) in aqueous solution using a hydroponic set-up was investigated. The evacuation proficiency increased with days and initial concentrations. The ideal removal pH was 4.0. The equilibrium data acquired were evaluated by Langmuir, Freundlich, Temkin, Elovich and Dubinin-Radushkevich isotherm models. The Langmuir model gave the best relationship with monolayer biosorption capacity of 40.89 mg/g. The pseudo-zero-order kinetics was able to describe the biosorption process. The intraparticle diffusion and liquid film diffusion was also used to study the removal process with the former showing the best fit. Thermodynamic modeling using the standard free energy (ΔG_0) indicated that the process was spontaneous with -12589.18 kJ/mol. The PCP residual factors (0.09 to 0.35) were highest in 25th day indicating high efficiency of *C. indica*. *C. indica* used in this study is eco-friendly, widely available and offers greater potential for wastewater treatment for removal of chlorinated pollutant such as PCP from aqueous solutions. The PCP residual factors (0.09 to 0.35) were most noteworthy in 25th day showing high productivity of *C. indica* L. According to this study, *C. indica* L. could prove to be a promising low cost phytoremediator of chorophenols in aqueous solutions.

Keywords: Aquatic phytoremediation, Canna lily, Biosorption, Equilibrium isotherm, Hydroponics, Kinetics, Pentachlorophenol

*Corresponding author.

E-mail address: cenyoh@gmail.com

1. Introduction

Since 1930s, most chlorinated phenol subordinates, for example, pentachlorophenol (PCP), have been normally utilized as pesticides, herbicides, wood additives, and defoliants [1]. Their wide use is because of ideal properties for such purposes. Effluents from numerous enterprises like pesticide, wood, drugs, color fabricating, agribusiness, paper and mash fill in as regular hotspots for chlorophenol contamination of the water, soil and air [2]. For instance, [3] revealed that profluent from wood-treatment plants contain PCP which went from 25 to 150 mg/L. PCP is currently universal in nature and has been recognized in various ecological media, food just as in human milk, fat tissue, and pee [1].

In Nigeria, uses of pesticides in farmland fill in as the primary source of chlorinated contamination of ecosystem. Subsequently, huge rates of populaces are dealing with issues identified with water quality because of substance tainting in both surface and groundwater sources [4-5]. Presently, more than 70 % of surface waters in Nigeria are of poor or low quality [6]. Organochlorine (OC) pesticides buildup were evaluated in water and silt from Ero River in South Western Nigeria and results showed that 100 % of the samples gathered were sullied with the contemplated OC (< 0.02 to 9.10 μg/L) [7]. There are additionally reports of chlorophenol present in ocean food varieties, for example, fishes [8]. Impressive concern exists about unfriendly impacts PCP posture to biological systems and human wellbeing. Unsafe impacts to human over momentary openness to huge fixation incorporate harm to sensory system, liver, blood, lungs, kidneys, insusceptible framework, and gastrointestinal lot [1]. PCP is named plausible human cancer-causing agent thus prolonged exposure may likewise be related with cancer-causing, renal, and neurological impacts [1]. Because of its belongings to biological systems and human wellbeing, it is relevant thusly to eliminate PCP from the environment.

In eliminating chlorophenols from water, numerous treatment strategies have been created and applied. These strategies incorporate organic and physicochemical techniques (photochemical, air stripping and cremation, adsorption innovation including utilization of initiated dirt and carbons produced from plant-based sources [46]. A portion of these techniques have been accounted for to be successful yet they are very hard to plan and described. The utilization of water plants in wastewater treatment is currently an arising technique for contamination remediation. A few examinations, for example, Singh [9], Zhang [10], Tran [11] and Isiuku and Enyoh [5] have now shown the adequacy of utilizing plant for wastewater treatment utilizing a developed wetland, a pilot scale or hydroponic arrangement. These investigations by and large uncovered that the removal proficiency shifted with various plant species and their productivities [5]. Nigeria, as other tropical nations, has discovered numerous plants valuable for the expulsion contaminant from water.

Canna (or canna lily) is a sort of 10 types of blooming plants [12-13]. The nearest living relations to the cannas are the other plant groups of the request Zingiberales, that is the Zingiberaceae (gingers), Musaceae (bananas), Marantaceae, Heliconiaceae, Strelitziaceae, and so forth [13]. Albeit a plant of the jungles, most cultivars have been created in mild environments and are not difficult to fill in many nations of the world as long as they get in any event 6–8 hours normal daylight. The morphology of this specie is the presence of stem, leaves, blossoms and natural product. The expansive, level, substitute leaves that are such an element of this plant outgrow a stem in a long, restricted roll and afterward spread out. The leaves are normally strong green, yet a few cultivars have glaucose, tanish, maroon, or even variegated leaves [12].

Canna indica L. is a prevailing lentic plant in Nigeria water environment [14]. Besides, past reports have shown that the plant is a decent contender for phytoremediation of inorganic and natural pollutants [5,11,15-16], getting by in a territory encountering extraordinary contamination [14]. Literature reviewed [5] uncovered that studies utilizing water plants in hydroponic framework to eliminate organic contaminations is scarce and specifically chlorophenols. Supposedly, this is the principal study assessing the proficiency of *C. indica* L. to eliminate PCP from watery solutions. The overall point of the study was to investigate the remediation capability of *Canna indica* L. for PCP in water. The equilibrium and kinetic data of the removal studies were analyzed to understand the removal kinetics, isotherms, and thermodynamics, as well as the mechanism of PCP removal by the plant.

2. Materials and methods

Preparation of plant material and pesticide solution

The plant materials were set up from seeds as described in our previous reports [47]. The PCP (99.5 %, analytical grade) was bought from Finlab, Owerri and used minus any additional refining. The attributes of PCP are introduced in Table 1. The solutions in this study were set up by utilizing refined water and ethanol as portrayed recently [17]. The stock and working (50, 100, 150, 200 and 250 mg/L) solutions was prepared as described in our recent study [47]. These working solutions were used to generate the calibration curves when measured using UV-Vis spectrophotometer at 220 nm.

Batch studies

Take-up of PCP by *Canna indica* L in pesticide-sullied water was evaluated in batches utilizing hydroponic, pots with measurements 18 cm long, 37 cm in breadth (outer) and 19 cm depth. The pots were loaded up with 500 mL working solutions (Figure 1).

Table 1: Some physicochemical properties of PCP

Properties	PCP
Molecular structure	CI
	CICI
IUPAC name	2,3,4,5,6-
	Pentachlorophenol
Chemical formula	C ₆ Cl ₅ OH or C ₆ HCl ₅ O
CAS number	87-86-5
Molecular weight (g/mol)	266.34
Water solubility	Slightly

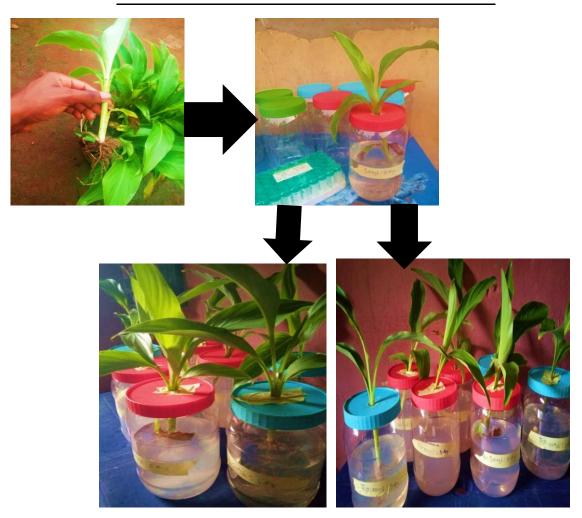


Figure 1. Typical hydroponic set-up used in the study

At that point the plant were brought into the arrangement and permitted to stand. This was accomplished for four different pots, which address other time terms (for example 10 days, 15 days, 20 days and 25 days). Altogether, 5 pots were readied and at every timespan days a plant was eliminated and the solution is analyzed by UV-vis spectrophotometer at 220 nm.

The impact of pH on the PCP removal by *C. indica* L. was resolved in 500 mL of test pots containing 100 mg/L of PCP at various pH (4, 5, 6, 7, 8 and 9). 1 M nitric acid (HNO₃) and 1 M sodium hydroxide (NaOH) were utilized for pH changes. The pH of every arrangement was estimated with a computerized pH meter (Model Jenway 3510). The underlying and last groupings of PCP arrangements were resolved on an UV–visible spectrophotometer (Spectrum Lab 23A) at its greatest absorbance frequency of 220 nm.

All set-ups were done in triplicate and were set haphazardly with position moved once every week. All set-ups were enhanced with N.P.K. composts (1 %) weekly.

Data analysis

Obtained experimental data were analyzed by IBM SPSS Statistics version 20. Mean of triplicate analysis were reported while the Root mean square (RMSE) and chi-squared (\aleph^2), were computed using equations (1) and (2) for error analysis

$$RMSE = \sqrt{\left(q_{cal} - q_{exp}\right)^2} \tag{1}$$

$$\aleph^2 = \sum_{i=1}^N \frac{\left(q_{exp} - q_{cal}\right)^2}{q_{cal}} \tag{2}$$

% R in equation 3 represents removal rate of PCP at a given time t. In equation (4), the q_e amount adsorbed by the C. inidea L. at equilibrium per unit mass while the maximum removal per unit mass is determined by equation (5):

$$\% R = \frac{(C_o - C_t)}{C_o}$$
 (3)

$$q_e = \frac{(C_o - C_e).V}{1000 \, m} \tag{4}$$

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \tag{5}$$

Where C_o and C_t = concentration of PCP at initial and final stages (mg/L), while C_e represents equilibrium concentration (mg/L) in solution, V = solution volume (L) and m = C. indica L. mass (g) from the control set-up.

Data modelling

The data were examined by the most usually utilized kinetics and isotherms model including Pseudo-first order (PFO), Pseudo-second order (PSO), Pseudo-zero order (PZO), intraparticle diffusion, liquid

film dispersion, Langmuir, Freundlich, Dubinin–Radushkevich (D–R), Temkin and Elovich isotherm models. These models were utilized as described in our previous reports on trichlorophenol [47].

Results and discussion

Effect of initial concentration

The impact of initial concentration on the evacuation and greatest biosorption limit of PCP by *C. indica* at 25 °C is displayed in Figures 3 and 4. Fundamentally taking a gander at the entire removal process, there was a fast biosorption of PCP at the underlying phases of contact (from 0-10 days) and afterward there was slow lessening in expulsion (10-20 days), until it arrived at an equilibrium (at twentieth day) where the measure of PCP being eliminated by the plant was estimated to the measure of PCP desorbing from the plant (Figure 3). Comparative perception was made for the most extreme biosorption limit (Figure 4). This finding is in concurrence with investigations of [25] ascribed to the rhizo-degradation capability of plant for organic pollutants. So, at initial contact the rhizosphere of plant is still very active and thus effectively degrading PCP in the solution. Other reason could be due to the availability of a large number of vacant surface sites and vice versa for slower rate at later days due to the reduction or saturation of these vacant [2,26].

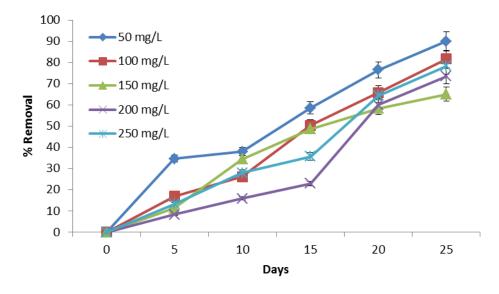


Figure 3: Effect of contact time on removal of PCP from aqueous solution by C. indica

Increase in take-up of PCP with days followed decline in initial PCP concentrations from 250 to 50 mg/L. The pace of removal arrived at the highest (90 %) in 25th day for 50 mg/L while the in same day was 65.07 % for 150 mg/L, which was least (Figure 3). With an increase in starting concentration from 50 to 250 mg/L, the maximum biosorption limit q_t, increased from 1.59 to 10.57 mg/g (Figure 4). Comparable results have been made in related investigations [2,22-23]. As the underlying concentration

is increased, the mass transfer driving force turns out to be high because of the increase in the quantity of particles seeking the accessible binding sites on the plant root, which could be liable for the observation.

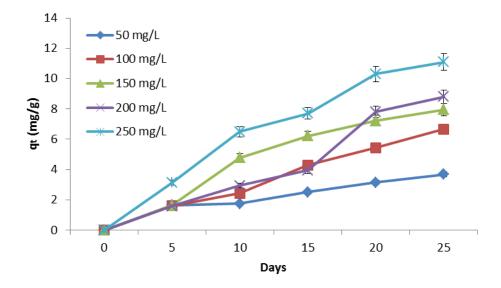


Figure 4: Effect of initial PCP concentration on biosorption capacity of PCP by C. indica

Effect of solution pH

The impact of solution pH on PCP removal was studied by shifting the pH of the solution from 4 to 9 at an initial concentration of 100 mg/L (Figure 5). As can be seen from Figure 5, the rate of removal with time increased and highest when the pH was low (more acidic).

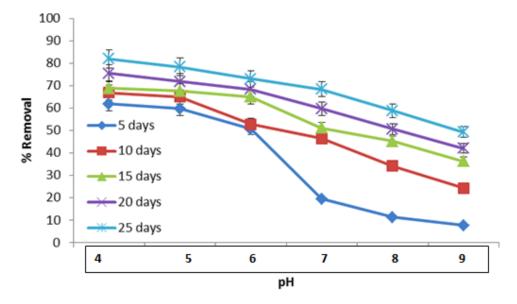


Figure 5. Effect of initial pH on PCP removal by C. indica

However, when the pH of the solution is increased and thus becoming more alkaline, the removal rate

dropped. This is practically identical to the outcomes gotten by Tan [27], Fan [2] and Zazouli [28]. PCP is a feeble corrosive thus, lower pH underneath its pKa (4.98) will result to scattering associations and subsequently expanding the take-up and rhizo-degradation [5]. At the point when the solution pH turns out to be high the compound is ionized in part prompting low take-up. From the results, the ideal pH was taken as 4.0. In other studies, on removal of chlorophenol, ideal pHs of 5 were accounted for by Kumar [29] by Acacia leucocephala bark and Zazouli [28] by Azolla based-activated carbon. Ideal pH of 2.0 was acquired by Sahnoun [30] by modified halloysite samples while ideal pH of 4.0 was gotten by activated carbon gotten from loosestrife [2].

Biosorption kinetics modelling

To portray the biosorption kinetics; the accompanying dynamic models, pseudo-first-, pseudo second-order, zero-order and intraparticle dissemination models were thought of. The summary kinetic parameters for PCP sorption by C.indica at 25 ± 2 °C are presented in Table 2.

Table 2: Kinetic parameters for PCP sorption by *C.indica* at 25±2 °C

Model	Parameter	Initial PCP concentrations (mg/L)				
		50	100	150	200	250
Experimental	$q_{e exp} (mg/g)$	3.1600	5.4200	7.2200	10.0000	13.300
Pseudo first order	$q_{e\;cal}(mg/g)$	1.5000	5.1800	6.1700	17.5500	23.900
(PFO)	K_1 (1/hr)	0.0232	0.0756	0.0866	0.1242	0.1312
	\mathbb{R}^2	0.2874	0.8321	0.7817	0.9216	0.8605
	Error (RMS)	1.6600	0.2400	0.0500	7.5500	10.600
	Error (\varkappa^2)	1.1100	0.0100	0.1800	3.2500	4.7000
Pseudo second	$q_{e cal} (mg/g)$	3.9700	8.8300	11.6100	11.730	12.990
order (PSO)	K_2 (g/ mg-hr)	0.0018	0.0003	0.00016	0.00018	0.00040
	\mathbb{R}^2	0.8070	0.4866	0.4721	0.3385	0.7557
	Error (RMS)	0.8100	3.4100	4.3900	1.7300	0.3100
	Error (\varkappa^2)	0.1700	1.3200	0.1800	0.1500	0.0200
Pseudo zero order	Vm (mg/L-hr)	0.0713	0.1379	0.1716	0.2533	0.3292
(PZO)	\mathbb{R}^2	0.9668	0.9916	0.9675	0.9065	0.9757
	C	46.546	101.23	147.03	215.54	257.24
Intraparticle	$K_{ip} \ (mg/g.hr^{1/2})$	0.1449	0.2695	0.3485	0.3278	0.4531
diffusion	Intercept (C)	0.0870	0.0720	0.0690	0.0640	0.0621
	\mathbb{R}^2	0.9689	0.9155	0.9423	0.8596	0.9717
Liquid film	$K_{fd} \; (mg/g.hr^{1/2})$	0.0003	3E-05	3E-05	0.0028	0.0027
diffusion	Intercept (C)	0.6267	0.4262	0.5400	0.1767	0.0200
	\mathbb{R}^2	0.0131	9E-05	9E-05	0.9049	0.9874

Pseudo first order (PFO)

In Table 2, for the first order kinetic model, the obtained R^2 , $q_{e \text{ (cal)}}$ and removal constant (K_1) values as well as the error (root mean square and chi-squared) are presented. The PFO didn't completely fit well especially for initial concentration of 50 mg/L to 150 mg/L while for 200 mg/L and 250 mg/L, the R² values were significant (0.9216 and 0.8605 respectively). Therefore the PCP removal process by C. indica could not be identified by PFO. In other studies [2,28,30] on chlorophenols removal using activated carbon, higher R² values were obtained and the model was able to describe the removal process. Studies using hydroponic to study chlorophenol removal from aqueous solution is lacking. difference in the obtained results by the listed authors could due to the different in biosorbent (here, C. indica were grown in the simulated water and not an activated carbon) and the experimental set-up. Therefore, the sorption rate of the biosorbent is very much different. In generally, as pointed by Bekins [20] the PFO model in certain conditions is a poor representation of biodegradation process of pollutants in aquifers and in this case. For the PFO, the qe (cal) were much lower than the experimental qe(exp) at initial concentrations of 50 mg/L. At 100 and 150 mg/L, the qe (cal) were much closer to the experimental values while for initial PCP concentration of 200 and 250 mg/L, the calculated q_{e (cal)} were much higher than the experimental $q_{e(exp)}$ with values of 17.55 mg/g and 23.90 mg/g respectively. The root mean square error ranged from 0.05 to 10.60 while the chi-squared error ranged from 0.01 to 4.70.

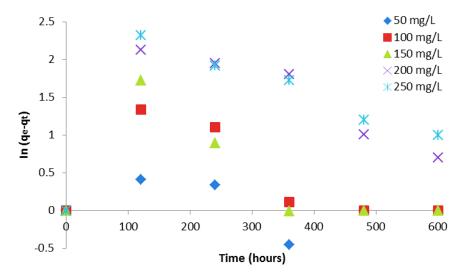


Figure 6: PFO kinetic plots for the removal of PCP from aqueous solution by Canna indica

The rate of pollutants degradation in a treatment system by plant is normally represented by the PFO removal rate constants (k_1) [11]. The k_1 value for the PFO is presented in Table 2. A linear plot of the removal rate constants at different days with the removal rate is shown in Figure 7. For the PCP removal, the relationships showed significant relationship coefficient values (R^2) except on the 25th day (R^2)

0.5). The positive and significant relationship is indicative that the removal rate increased slightly as the initial concentration increased from 50 to 250 mg/L from the 5th day to 20th day where equilibrium was reached.

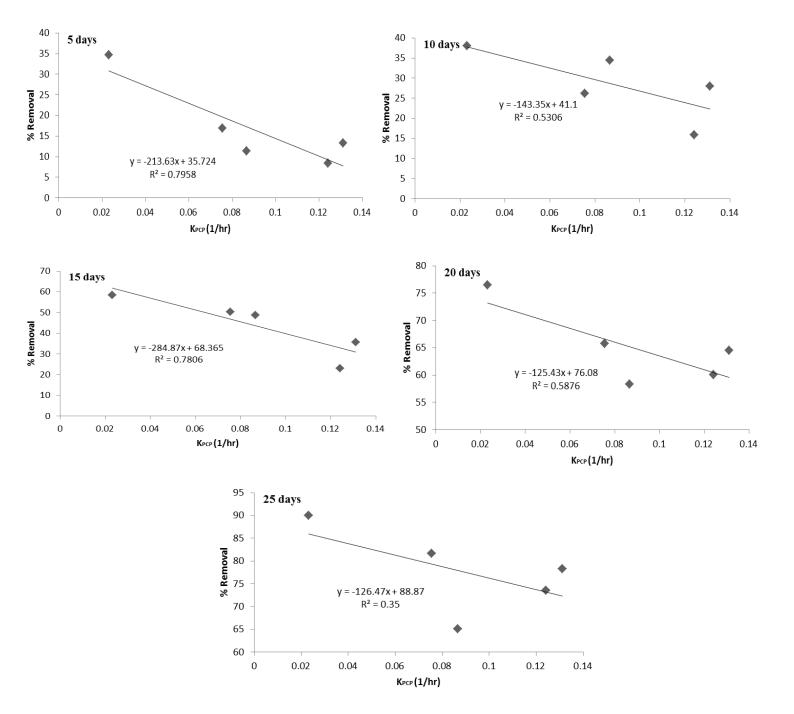


Figure 7. Correlation between PCP removal efficiency and PFO removal rate constant "k₁" for PCP Studies are generally lacking for comparison. However, [11] using the same plant (*Canna indica*) made

similar observation for organic pollutants viz NH₄-N and PO₄-P removed from wastewater using hybrid constructed wetlands system. In the same study, biological oxygen demand (BOD₅) had low correlations

with the first order removal rate constants. Other authors [31-33] using different aquatic plants and constructed wetlands have obtained similar but stronger correlations for BOD₅. The set-up for the study as well as the tested chemical could play a part in the removal of the pollutant. In this study, we used a hydroponic system and we obtained positive and significant correlations. The stabilization of hydroponic system played an important role in this removal compared to the constructed wetlands. Nevertheless, the high values of k for the PCP removal (k_{PCP}) do not necessarily indicate high removal efficiency when relating the value of k_{PCP} and removal efficiency (% removal) (Figure 7). At higher K_{PCP} values the removal rate dropped slightly.

Pseudo second order (PSO)

From Table 2, the estimation of the relationship coefficient for the second-order kinetic model was discovered to be in the range 0.3385 to 0.8070, demonstrating poor materialness of the pseudo-second-order kinetic model to depict the sorption cycle of PCP on C. indica L. The q_e values from the experiment were close at initial concentrations (50 mg/L to 250 mg/L) to the computed data (Table 2).

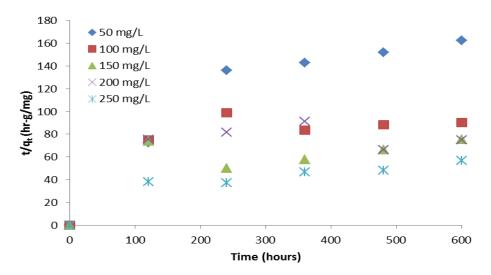


Figure 8: PSO kinetic for the removal of PCP from aqueous solution by Canna indica

Pseudo-Zero order (PZO)

The PZO were computed as the PFO and PSO were unable to describe the removal process of PCP in aqueous solution by *C. indica*. The computed PZO is presented in Figure 10 while the summary of obtained results is presented in Table 2. The R² values for the PZO were very significant (> 0.9) for all initial concentrations, therefore indicating that the PZO best fitted and described the removal process for PCP using *C. indica* in hydroponic set-up. By interpretation, the biodegradation rate of PCP by *C. indica* is apparently independent of the reactant concentration. Similarly, [20] also obtained that the PZO best fitted the removal process of phenol in aqueous solution.

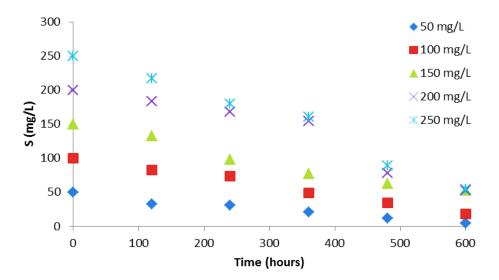


Figure 9: PZO kinetic for the removal of PCP from aqueous solution by Canna indica

The maximum removal velocity (V_m) values for the different initial concentrations are presented in Table 2. The values increased with increasing initial concentrations from 0.0713 to 0.3292 mg/L-hr, indicating that the removal rate velocity increase with time as the initial concentrations increased.

Intraparticle diffusion

The diffusion mechanism and rate limiting step of PCP removal measure by C. indica couldn't be recognized by PFO and PSO model, the intraparticle model was tried as depicted [47]. Assuming the adsorption interaction follows the intraparticle model, qt versus $t^{1/2}$ will be straight and in the event that the plot goes through the inception, intraparticle diffusion is the sole rate-limiting step. Otherwise, some other component alongside intraparticle dispersion is additionally included.

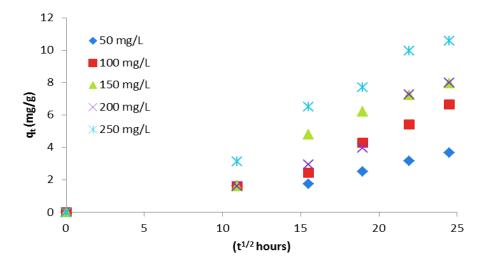


Figure 10: Intraparticle diffusion kinetic for the removal of PCP from aqueous solution by *Canna indica*

The plot for the model is presented in Figure 10 while the model parameters are summed up in Table 2. The relapse was not totally direct and the lines didn't go through the origin (Figure 10), proposing that more than one method of sorption alongside intraparticle diffusion is associated with the PCP removal process [34-35]. As the initial concentrations increased, the K_{ip} values increased (Table 2). This suggests that the driving force was greater with the increasing concentrations. Comparable outcomes were accounted for by [2] for trichlorophenol removal and [35] for Pb(II), Zn(II), and Cu(II) adsorption on submerged aquatic plant (*Ceratophyllum demersum*).

External film diffusion

The liquid film diffusion model can be applied when the outer diffusion of the biosorbate from the fluid stage to the solid stage is the rate determining step [20]. The qualities for the model introduced in Table 2 showed that liquid film assumes little part during the interaction since capture values are farther to 0 than in the event of intraparticle diffusion model (Table 2).

Biosorption isotherm modeling

To depict the adsorption isotherm the accompanying isotherm models, Langmuir, Freundlich, Temkin, Elovich and Dubinin-Radushkevich were thought of. These models help to clarify how adsorption particles disperse between the fluid stage and the solid stage in the entire biosorption process, and give an exhaustive comprehension of the adsorption nature.

Langmuir

In the utilization of Langmuir isotherm, it is accepted that the pollutant take-up happens at explicit homogeneous sites inside the rhizosphere of the plant and once a PCP particle possesses a site, no further adsorption happens at that site.

Freundlich isotherm

The Freundlich isotherm is an exact condition expecting that the adsorption cycle happens on a heterogeneous surface through a multi-facet adsorption system, stronger sites are involved first and that the strength for binding is identified with the concentration of PCP at equillibrium [17].

Temkin isotherm

The Temkin isotherm considers the impacts of circuitous adsorbate—adsorbate collaborations on adsorption, and proposes that the heat of adsorption of the relative multitude of particles in the layer would diminish directly with inclusion because of these cooperations [23].

Elovich isotherm

Elovich isotherm model accepts that the adsorption sites increment dramatically with adsorption, which suggests a multi-facet adsorption.

Dubinin-Radushkevich (D-R) isotherm

The presumption on which the D-Rmodel is based is that the pore filling component followed for the biosorption cycle has a multi-facet character [36-37].

Table 3: Isotherm parameter for PCP sorption by *C. indica* at 25±2 °C

Model	Parameter	Value
Langmuir	q _m (mg/g)	40.49
	$K_L (L/mg)$	2.89
	\mathbb{R}^2	0.9695
	Error (RMS)	1.19
	Error (\varkappa^2)	0.05
Freundlich	1/n	1.4431
	n	0.69
	$K_F [mg/g (L/mg)^{-1/n}]$	2.70
	\mathbb{R}^2	0.9312
	Error (RMS)	3.70
	Error (\varkappa^2)	1.37
Temkin	B (J/mol)	0.1867
	$b_T (J/mol/K)$	13270.34
	A (L/mg)	271736.20
	R^2	0.7869
	Error (RMS)	_
	Error (\varkappa^2)	_
Elovich	q _m (mg/g)	20.24
	K _E (L/mg)	0.012
	R^2	0.3785
	Error (RMS)	20.19
	Error (\varkappa^2)	0.99
Dubinin-Radushkevich	q _m (mg/g)	10.10
	$B_D (\text{mol}^2/\text{kJ}^2)$	431.02
	E (kJ/mol)	0.03
	\mathbb{R}^2	0.7115
	Error (RMS)	_
	Error (\varkappa^2)	-

The relationship coefficients (R^2) for all isotherm models applied for removal of PCP in aqueous solution by *C. indica* L. at 25±2 °C are summed up in Table 3. The most elevated R^2 value was given by the Langmuir isotherm model (0.97) with the most minimal mistake (root mean square = 1.19 and chi-squared = 0.05) trailed by the Freundlich isotherm model (0.93) while the least was given by the Elovich isotherm model (0.38) (Table 3). The Langmuir isotherm model hence is best in depicting the PCP

removal by C. indica. Comparative outcome was acquired by [28] for TCP removal utilizing activated carbon produced using Azolla (an aquatic plant). The calculated separation factor (R_L) values against the PCP initial concentrations in Figure 11 ranged from 0.00138 to 0.00687, which fell somewhere in the range of 0 and 1, demonstrating that the PCP removal by *C. indica* L. was positive in this examination by Langmuir model. It was also shown in Figure 11 that the R_L dropped as initial concentration increased indicating that the removal was more favorable at higher initial concentration. Comparative outcome was acquired for TCP by [2].

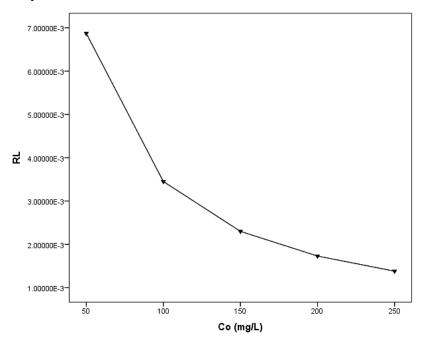


Figure 11: Separation factor R_L of PCP removal by *C. indica*

The slope 1/n and n gotten from the Freundlich model showed estimations of 1.44 and 0.69 demonstrating that the expulsion isn't great with Freundlich model not fitting admirably and Langmuir model is most appropriate [38]. Comparable outcome was gotten for TCP eliminated in liquid solution by modified halloysite clay [30]. Be that as it may, interestingly, lower 1/n values (< 1) and higher n values (> 1) were acquired for TCP and toluene blue dye removal from aqueous solution using aquatic plants by [2] and [22] respectively. However, it not viable with past work on the adsorption of chlorophenols including the utilization of various activated carbons [39-40].

The maximum monolayer adsorption limit, q_m , which has been broadly used to look at the effectiveness of an absorbent, can likewise be gotten from Table 3. Writing information is by and large missing concerning the utilization of aquatic plants in hydroponics to contemplate pesticides removal, so data obtained in this study was compared with certain phenols adsorped onto activated carbons (Table 4). The plant utilized in this study had a moderately low PCP adsorption limit of 40.89 mg/g, when

contrasted for certain past investigations announced in the writing including the utilization of activated carbon however higher than some other studies (Table 4). Activated carbons generally have huge surface region compared with the plant and accordingly could be justification of its enormous adsorption limit.

Table 4: Comparison of maximum monolayer adsorption capacity of *C. indica* with various chlorophenols on various activated carbons

Adsorbent	Adsorbate	Maximum monolayer	References
		adsorption capacity (mg/g)	
C. indica	Pentachlorophenol	40.89	This study
Fiber-based activated Carbon	Pentachlorophenol	320.00	[41]
Loosestrife-based activated	2,4,6-trichlorophenol	367.65	[2]
carbon			
Paper mill sludge	2,4- dichlorophenol	4.89	[42]
Commercial grade coconut shell-	2,4,6-trichlorophenol	112.35	[43]
based activated carbon			
Rattan sawdust activated carbon	4-chlorophenol	188.68	[44]
Azolla-based activated carbon	2,4,6-trichlorophenol	5.90	[28]
Untreated Agro-Waste Pine	2,4,6-trichlorophenol	243.90	[17]
Cone			

Biosorption thermodynamics

Free energy change is the main thrust of adsorption measures. In this manner changes in standard free energy (ΔG^o) were acquired to decide the thermodynamics of the entire adsorption measure. The gotten standard free energy was - 12589.18 kJ/mol. This shows that the cycle is highly spontaneous and may continue chiefly by chemisorption measure [30,45]. Conversely, [2] recorded a non-spontaneous response with standard free energy which went from 4.23 to 5.89 for TCP onto activated carbon from an aquatic plant. [23] revealed standard free energy for metanil yellow removal onto egg shell film to be - 5.009 kJ/mol, likewise demonstrate an spontaneous and chemisorption measure.

Estimated PCP residual factor (eRF)

The estimated residual factor (eRF) for PCP by *C. indica* was calculated according to equation (21) as the ratio of PCP residue concentration in the water to the initial PCP concentrations:

$$eRF = \frac{PCP_{Residue\ Concentration}}{PCP_{Initial\ Concentration}} \tag{21}$$

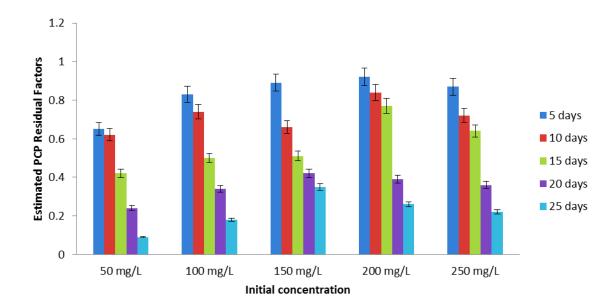


Figure 12. Estimated PCP residual factors

Residual factors are interpreted to represent the strength of the *C. indica* in removing PCP from the solution. When the estimated residual factors (eRF) range from 0 to 0.3, the efficiency of the plant is considered "high"; when ranging from > 0.3 to 0.5, the efficiency of the plant is considered "moderate"; when ranging from > 0.5 to 0.7, the efficiency of the plant is considered "low" while from > 0.7 to 1, the efficiency of the plant is considered "poor". The residual factors for the PCP removal at initial concentrations of 50 to 250 mg/L with days are presented in Figure 11. In generally, the efficiency of the *C. indica* increased with days in all initial concentrations studied as the residual factors decreased. With days, there was no definite trend for residual factors except for the 5th day which increased with increasing initial concentrations (Figure 12). At later days, residual factors increased with initial concentrations of 50 mg/L to 150 mg/L, after which it decreased with initial concentrations of 200 mg/L to 250 mg/L.

Conclusion

In this examination, we have considered pentachlorophenol removal from aqueous solution utilizing C. $indica\ L$ and results for the most part showed it is promising and efficient phytoremediator for the compound. Biosorption of PCP increased with days and initial PCP concentration at a specific cutoff. The ideal pH was demonstrated to be 4 with rate of removal of 82 %. At alkaline pH (> 7-9) with increased contact time C. $indica\ L$. can in any case eliminate PCP up to 68.41 %. The equilibrium data were best portrayed by the Langmuir isotherm model and the adsorption kinetics by pseudo zero order. Langmuir model additionally predicted the maximum take-up biosorption limit of $40.89\ mg/g$ at 25 ± 2 °C. The consequences of the intraparticle diffusion model propose that intraparticle diffusion was by all

account not the only yet the significant rate controlling steps. Based on the residual factors, the efficiency of C. indica in PCP removal is high at with increased time. C. indica utilized in this investigation is ecofriendly, generally accessible and offers more prominent potential for wastewater treatment for removal of chlorinated contamination like PCP from water.

Conflict of interest

The authors declare no conflict of interest regarding the publication of this manuscript.

References

- [1] USEPA, Consumer Factsheet on: Pentachlorophenol. *United States Environmental Protection Agency*. https://www.epa.gov/safewater/contaminants/dw_contamfs/pentachl.html Accessed 06/11/19. (2006).
- [2] J. Fan, J. Zhang, C. Zhang, L. Ren, Q. Shi, Adsorption of 2,4,6-trichlorophenol from aqueous solution onto activated carbon derived from loosestrife. *Desalination*. 267:139–146. (2011)
- [3] D. G. Crosby, Environmental Chemistry of Pentachlorophenol. *Pure Appl. Chem.* 53, 1051-1080 (1981).
- [4] A. W. Verla, E. N. Verla, C. E. Amaobi, C. E. Enyoh, Water Pollution Scenario at River Uramurukwa Flowing Through Owerri Metropolis, Imo State, Nigeria. *International Journal of Applied Scientific Research*, 3, (3):40-46 (2018).
- [5] B.O. Isiuku, C.E. Enyoh, Water pollution by heavy metal and organic pollutants: Brief review of sources, effects and progress on remediation with aquatic plants. *Analytical Methods in Environmental Chemistry Journal*. 2(3):5-38 (2019).
- [6] A.W. Verla, C.E. Enyoh, E.N. Verla, P.N. Okeke, S.S. Pingale, Chemometric Assessment of Orashi River after Confluence with Oguta Lake. *Indonesian Journal of Fundamental and Applied Chemistry*, 4(3):91-103 (2019).
- [7] A.I. Olayinka, F. A. Ademola, I. A. Emmanuel, O. A. Albert, D. A. Rex, Assessment of Organochlorine and Organophosphorus Pesticides Residue in Water and Sediments from Ero River in South Western Nigeria. *Journal of Chemical, Biological and Physical Sciences JCBPS;* Section D, 5(4): 4679-4690 (2015).
- [8] J.E. Ejiako, Assessement Of Polycyclicaromatic Hydrocarbons, Polychlorinated Biphenyls, Organochlorine Pesticides And Heavy Metals In Fish Species From Oguta Lake. *Unpublished M.Sc. Thesis. Submitted to the Department of Chemistry, Imo State University, Nigeria* (2019).
- [9] S. Singh, R. Haberl, O. Moog, R.R. Shrestha, P. Shrestha, R. Shrestha, Performance of an anaerobic baffled reactor and hybrid constructed wetland treating high-strength wastewater in Nepal-a model

- for DEWATs. Ecol. Eng. 35: 654-660 (2009).
- [10] D.Q. Zhang, K. Jinadasa, R. M. Gersberg, Y. Liu, W. J. Ng, S.K. Tan, Application of constructed wetlands for wastewater treatment in developing countries: A review of recent developments (2000-2013). J. Environ. Manage. 141: 116-131 (2014).
- [11] D.H. Tran, T.M.H. Vi, T.T.H. Dang, R. Narbaitz, Pollutant removal by Canna Generalis in tropical constructed wetlands for domestic wastewater treatment. *Global J. Environ. Sci. Manage.*, 5(3): 331-344 (2019).
- [12] I. Cooke, The Gardener's Guide to Growing Canna. Timber Press. (2001).
- [13] M. J. M. Christenhusz, J. W. Byng, The number of known plants species in the world and its annual increase. *Phytotaxa*. 261 (3): 201–217 (2016). doi:10.11646/phytotaxa.261.3.1
- [14] C.E. Enyoh, B.O. Isiuku, Characterisation of some soils from flood basin in Amakohia, Owerri, Nigeria, *International Journal of Environmental Analytical Chemistry*. (2020). https://doi.org/10.1080/03067319.2020.1773455
- [15] C. Nevena, D. Vilotic, M. Nesic, M. Veselinovic, D. Drazic, S. Mitrovic, Phytoremediation potential of Canna indica L. In water contaminated with lead. *Fresenius Environmental Bulletin*. 25 (9):3728-3733 (2016).
- [16] M.H.J.P. Gunarathna, A.I. Ranasingha, S.C. Rathnayake, T.K. De Costa, Can Canna Indica Use as a Phytoremediation Agent in Mitigating High Pollution Concentrations in Reverse Osmosis Concentrate? *Int'l Journal of Advances in Agricultural & Environmental Engg.* 3 (1):52-56 (2016). http://dx.doi.org/10.15242/IJAAEE.ER0116025.
- [17] S.K. Nadavala, M. Asif, A. M. Poulose, M. Suguna, M.I. Al-Hazza, Equilibrium and Kinetic Studies of Biosorptive Removal of 2,4,6-Trichlorophenol from Aqueous Solutions Using Untreated Agro-Waste Pine Cone Biomass. *Processes*. 7(757): 1-17 (2019). http://10.3390/pr7100757
- [18] S. Lagergren, About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar*. 24 (4):1–39 (1898).
- [19] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes. *Proc Biochem*. 34(5):451–65 (1999).
- [20] B.A. Bekins, E. Warren, E.M. Godsy, A comparison of zero-order, first-order and monod biotransformation models. *Ground water*. 36(2)261-268 (1998).
- [21] W.J. Weber, R.R. Rumer, Intraparticle transport of sulphonated alkylbenzenes in a porous solid: diffusion and non-linear adsorption. *Water Resour Res.* 1(3):361–5 (1965).
- [22] E. Neag, D. Malschi, A. Măicăneanu, Isotherm and kinetic modelling of Toluidine Blue (TB)

- removal from aqueous solution using Lemna minor. *International Journal of Phytoremediation*, 20:10, 1049-1054 (2018).
- [23] B.O. Isiuku, F.C. Ibe, Removal of metanil yellow by batch biosorption from aqueous phase on egg membrane: Equilibrium and isotherm studies. *Analytical Methods in Environmental Chemistry Journal*. 2:15-26 (2019).
- [24] O. Hamdaouia, E. Naffrechoux, Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon Part I. Two parameter models and equations allowing determination of thermodynamic parameters. *J Hazard Mater.* 147(1–2):381–94 (2007).
- [25] K. Bhaskara, V. Nadaraja, S. Tumbath, B. Shah, G. P. Veetil, Phytoremediation of perchlorate by free floating macrophytes. *Journal of Hazardous Materials*. 260:901–906 (2013).
- [26] S.G. Poulopoulos, M. Nikolaki, D. Karampetsos, C.J. Philippopoulos, Photochemical treatment of 2-chlorophenol aqueous solutions using ultraviolet radiation, hydrogen peroxide and photo-Fenton reaction. *J. Hazard. Mater.* 153: 582–587 (2008).
- [27] I.A. Tan, A.L. Ahmad, B.H. Hameed, Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. *J Hazard Mater*. 164(2-3):473-482 (2009).
- [28] M.A. Zazouli, D. Balarak, Y. Mahdavi, Application of Azolla for 2, 4, 6-Trichlorophenol (TCP) removal from aqueous solutions. *Arch Hyg Sci*.2(4):143-9 (2013).
- [29] N.S. Kumar, H.S. Woo, K. Min, Equilibrium and kinetic studies on biosorption of 2,4,6-trichlorophenol from aqueous solutions by Acacia leucocephala bark. *Colloids Surf. B Biointerfaces*. 94:125–132 (2012).
- [30] S. Sousna, M. Boutahala, H. Zaghouane-Boudiaf, L. Zerroual, Trichlorophenol removal from aqueous solutions by modified halloysite: kinetic and equilibrium studies. *Desalination and Water Treatment*. 57(34): 15941-15951 (2015). https://doi.org/10.1080/19443994.2015.1075159
- [31] R.H. Kadlec, Comparison of free water and horizontal subsurface treatment wetlands, *Ecol. Eng.* 35: 159–174 (2009).
- [32] T.D.T. Ngo, D. Konnerup, H.H. Schierup, H.C. Nguyen, A.T. Le, H. Brix, Kinetics of pollutant removal from domestic wastewater in a tropical horizontal subsurface flow constructed wetland system: Effects of hydraulic loading rate. *Ecol. Eng.* 36: 527–535 (2010).
- [33] J. Vymazal, The use constructed wetlands with the horizontal sub-surface flow for various types of wastewater. *Ecol. Eng.* 35 (1): 1–17 (2009).
- [34] F. Deniz, S. Karaman, Removal of Basic Red 46 dye from aqueous solution by pine tree leaves. *Chem Eng J.* 170:67–74 (2011).

- [35] O. Keskinkan, M.Z.L. Goksu, M. Basibuyuk, C.F. Forster, Heavy metal adsorption properties of a submerged aquatic plant (Ceratophyllum demersum). *Bioresour Technol.* 92(2):197–200 (2004).
- [36] M.M. Dubinin, The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface. *Chem Rev.* 60 (2):235–41 (1960). doi: 10.1021/cr60204a006.
- [37] B. Nagy, A. Maicaneanu, C. Indolean, S. Burca, L. Silaghi-Dumitrescu, C. Majdik, Cadmium (II) ions removal from aqueous solutions using romanian untreated fir tree sawdust—a green biosorbent. *Acta Chim Slov.* 60(2):263–73 (2013).
- [38] A.N.A. El-henday, Surface and adsorptive properties of carbons prepared from biomass. Appl. Surf. Sci. 252:287-295 (2005).
- [39] I.A. Tan, A.L. Ahmad, B.H. Hameed, Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. *J Hazard Mater*. 164(2-3):473-482 (2009).
- [40] B.H. Hameed, I.A.W. Tan, A.L. Ahmad, Adsorption isotherm, kinetic modeling and mechanism of 2,4,6-trichlorophenol on coconut husk-based activated carbon, *Chem. Eng. J.* 144: 235 (2008).
- [41] P.E. Diaz-Flores, R. Leyva-Ramos, R.M. Guerrero-Coronado, J. Mendoza-Barron, Adsorption of Pentachlorophenol from Aqueous Solution onto Activated Carbon Fiber. *Ind. Eng. Chem. Res.* 45:330-336 (2006).
- [42] A. Kuleyin, Removal of phenol and 4-chlorophenol by surfactant-modified natural zeolite. *J Hazard Mater.* 1,144(1-2):307-15 (2007).
- [43] M. Radhika, K. Palanivelu, Adsorptive removal of chlorophenols from aqueous solution by low cost adsorbent--Kinetics and isotherm analysis. *J Hazard Mater.* 2;138(1):116-24 (2006).
- [44] N. Calace, E. Nardi, B.M. Petronio, M. Pietroletti, Adsorption of phenols by papermill sludges. *Environ Pollut.* 118(3):315-9 (2002).
- [45] M.J. Jaycock, G.D. Parfitt, Chemistry of interfaces. J. Coll. I. Sc. 12-13 (1981).
- [46] M. Uddin, M. Islam, M. Abedin, Adsorption of phenol from aqueous solution by water hyacinth. *ARPN Journal of Engineering and Applied Sciences*, 2: 11-16 (2007).
- [47] C.E. Enyoh, B.O. Isiuku, 2,4,6-Trichlorophenol (TCP) Removal from Aqueous Solution using Canna indica L: Kinetic Isotherm and Thermodynamic Studies. *Chemistry and Ecology* (2020). https://doi.org/10.1080/02757540.2020.1821673

(2021); www.mocedes.org/ajcer