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BIOSORBABILITY OF COCONUT HUSK CHAR IN POLYATOMIC IONS SEQUESTRATION FROM CONTAMINATED SURFACE WATER

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ABSTRACT

Agricultural waste has increased colossally with development in agricultural production causing environmental nuisance and degradation. Utilization of coconut husks, one of such type of waste, as a biosorbent for polluted surface water treatment, was considered in this study. Polluted surface water was gently passed through two similar columns loaded with 100 and 200 g of coconut husk char respectively. The treated water samples collected after 30, 60, 90, 120 and 150 mins were examined for SO_4^{2-}, NO_3^- and PO_4^{3-} ions concentration. Removal efficiency for SO_4^{2-}, NO_3^- and PO_4^{3-} ions on 100 g coconut husk char after 150 mins detention time were 70, 78 and 91% respectively. Freundlich isotherm model gave a better description of the data ($R^2 > 0.96$). Sorption data was well described by second order pseudo kinetics ($R^2 > 0.85$). An amount of 100 g of the biosorbent has a strong affinity for these types of ion removal in contaminated water. Coconut husk char as a biosorbent is a panacea to significant concentrations of polyatomic ions in polluted surface water.

Keywords: Agricultural waste; Coconut husk char; Isotherm model; Polyatomic ions; Pseudo kinetic model

1. INTRODUCTION

Agricultural wastes are gradually becoming a nuisance due to increased competition to meet the escalated fruit demand. Fruit consumption has grown in the last five years from 2005 to 2011 especially among the children's age bracket. The demand is equally projected to increase by 4% in the next 5 years based on population growth (PBHF, 2015). This sporadic growth and projection have influenced the matching of agricultural waste with other waste sources in terms of management consciousness and environmental concerns. Coconut is one of the most extensively consumed tropical fruit crop in the world, due to its nutritional and health benefit (Prades et al., 2003). From 2012 to 2013, the fruit had an annual production capacity of 21.89 billion nuts with solid waste generation (husk, shell and frond) from the nuts representing over 60% of the quantity produced (Shinde & Datar, 2015). Recently, Cimons (2014) documented the annual global quantity of the fruit at about 50 billion nuts, with most of the waste dumped in the environment. Though the waste has little environmental effect with respect to odour, poor management could reduce building and environmental aesthetics. It could as well become a

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harbour for destructive rats, rodents and dangerous reptiles. Hence, reusability and recyclability of biowaste should be considered in order to address the growing interest to explore mass and environmental impacts. Adsorption of contaminants using biological materials has been investigated by considering some mass and environmental impacts. Aside from the application of the available and cheap materials, such as fermentable sugar (Ding et al., 2012), particle board (Greer, 2008), energy source (Vaithanomsat et al., 2011) and compost (Tripetchkul, 2012), the treatability of fouled surface water with biowaste will be an area of interest to explore. Adsorption of contaminants using biological materials has been investigated by some researchers with predictable outcomes. The treatment method examines the property of a material to adhere to a contaminant such that the latter forms part of the molecular structure of the adsorbent. Advantages of the method include the simplicity, effectiveness and affordability (Mahajan & Sud, 2011; Habuda-Stanić et al., 2014). Biosorbents studied recently were sourced from locust beans husk (Ajayi-Banji et al., 2015), banana peel (Muhammad et al., 2011), palm kernel shell (Oluyemi et al., 2012), water hyacinth (Mahamadi, 2011) and yeast (Moyo et al., 2012). Results from the utilization of biosorbents show high treatability for contaminants, such as heavy metals, coliform count and phenol. Isotherm and pseudo-kinetic descriptive models were employed in most adsorption studies to further assess biosorbents (V´azquez et al., 2007; Tu et al., 2012; Sangodoyin & Ajayi-Banji, 2014). Other contaminants worthy of note are phosphate, nitrate and sulphate ions. This biosorption study seeks to explore sorption potential and applicability of coconut husk char in the process of phosphate, nitrate and sulphate ions removal from polluted surface water used for irrigation.

2. MATERIALS AND METHOD

Four thousand grammes of coconut husks were sourced from local farmers in Ilorin, a metropolis located in Nigeria. The precursors (husks) were carefully collected and transported to the desired location to avoid secondary contamination. Noticeable foreign materials were manually removed during cleaning. The cleaned husk was carbonized in batches under hermetic conditions at 350^{o}C for 30 mins using a Model SXL muffle furnace. Char generated (adsorbent) was washed in distilled water to remove dirt, subsequently oven dried at 105^{o}C for 6 hrs and crushed to 1400 µm particle size before storage (Figures 1 and 2). Adsorbent physical and chemical properties were investigated. The column adsorption set up for the experiment includes 3400 cm^3 volumetric capacity temporary storage tank, two 1300 cm^3 cylindrical bioreactors, 750 cm^3 plastic containers and a 2 cm diameter hose used as connector. Gravity flow arrangement was employed for the set–up. Surface water collected from the Pipeline road in Ilorin, Kwara State of Nigeria, was stored in the storage tank and then channelled through the connector to the bioreactors. The bioreactors were underlaid with cotton wool (50 grammes), prior to the introduction of 100 and 200 grammes of granulated coconut husk char and then overlaid with a similar quantity of the absorbent (cotton wool). This was to minimize any biosorbent that might escape from the bioreactors. Stored surface water was gradually introduced from the temporary storage tank into the bioreactors at a flow rate of 14 cm^3/min. Treated surface water from the bioreactors was discharged into the collectors (plastic containers) after 30, 60, 90, 120 and 150 mins. Sulphate, phosphate and nitrate ions concentrations in water samples were investigated before and after treatment. Analyses were replicated with mean values used for further investigation of removal efficiency, isotherm model and pseudo-kinetic descriptive models.

3. EXPERIMENTAL CALCULATION

Removal efficiency, Freundlich and Langmuir models in linear representation and pseudo- first and second-order kinetic models after integration with boundary conditions are expressed by

Equations 1–6. Equations 3 and 4 convey Freundlich and Langmuir expressions, while Equations 5 and 6 express first and second pseudo-kinetic models respectively.

$$Removal\ efficiency = (C_o - C_t)C_o \times 100 \quad (1)$$

$$Q_t = (C_o - C_t)V_t/W_b \quad (2)$$

$$LogQ_t = Log\,K + (1/n)LogC_t \quad (3)$$

$$C_t/Q_t = -1/(Q_m.K_L) + C_t/Q_m \quad (4)$$

$$Log(Q_e - Q_t) = LogQ_e - (K_Q/2.3038)t \quad (5)$$

$$t/Q_t = 1/(K_p Q_e^2) + {}^{t}/_{Q_e} \quad (6)$$

C_o represents the initial concentration of polyatomic ions in water sample before treatment (mg/l); C_t represents the concentration of polyatomic ions in effluent after treatment for a specific contact time (mg/l); Q_t represents the quantity of polyatomic ions adsorbed per adsorbent unit weight at a given retention time (mg/g); Q_e represents the quantity of polyatomic ions adsorbed per adsorbent unit weight equilibrium (mg/g); V_t represents the volume of water in adsorption column at a definite retention time (l); W_b is the mass of biosorbent (g); t represents detention time in hrs; Q_m represents the maximum adsorptive capacity of polyatomic ions (mg/g); K is the Freundlich constant related to the extent of adsorption (mg/g); n is related to the adsorption intensity and K_L is the Langmuir parameter related to the energy of adsorption (l/mg). Values of K and n are constants deduced from the intercept and slope of plot of $Log\ Q_t$ against $Log\ C_t$. K_L and Q_m are obtained from the intercept and slope of plot of C_t/Q_t against C_t. Constants K_Q(l/min) and K_p (g/mg/min) are first and second-order pseudo-kinetic rates.

Figure 1 Coconut husk

Figure 2 Coconut husk char

4. RESULTS AND DISCUSSION

Physical and chemical properties of coconut husk char are documented in Table 1. Calcium to phosphorus ratio of coconut husk char was less than values documented by Lurtwitayapont and Srisatit (2010) in a study on cooked swine bone powder, char and activated char (Table 1). Total carbon was higher than the one reported in a study on ions removal from wastewater using cow bone charcoal (Moreno et al., 2010). Though lower than the value documented by

Nwabanne and Igbokwe (2012) in a research on utilization of activated char from oil palm fibre in lead (II) removal. The disparities observed might be as a result of difference in precursors and variation in the carbonization parameters. Biosorbent dosage of 100 g was more effective in the ions removal than the 200 g sample for most of the contaminant inspected with respect to retention time (Table 2). Similar trend was observed for iron, manganese and copper in a study on locust beans husk char (Ajayi-Banji et al., 2015). This indicates that factors other than adsorbent dosage influence the ions removal. Other factors that could influence such results are influent flow rate and column depth (Ma et al., 2008).

Table 1 Physical and chemical properties of coconut husk char

Properties	Coconut husk char
Ca/P	1.4
Colour	brown black
Loosed Bulk Density (g/cm^3)	0.30
Packed Bulk Density (g/cm^3)	0.52
Total Carbon (%)	53.4
Calcium (mg/100g)	86.7
pH	8.7
Porosity	0.33

Table 2 Average concentration of ions in treated and untreated surface water

	Untreated Surface Water (mg/L)	Treated Surface Water (mg/L)				
		30mins	60mins	90mins	120mins	150mins
100 g						
SO_4	21.50	11.33	8.500	8.167	7.167	6.333
NO_3	15.50	11.53	6.567	4.767	3.633	3.267
PO_4	18.50	8.233	5.467	5.467	4.567	1.567
200 g						
SO_4	21.50	19.00	16.67	14.83	13.17	7.900
NO_3	15.50	12.30	11.33	10.43	8.233	5.133
PO_4	18.50	15.00	14.23	12.33	7.233	6.467

4.1. Removal Efficiency

Increase in removal efficiency was observed with increased retention time for all the contaminants. Though, 100 g coconut husk char had better removal efficiency than the 200 g sample. Phosphate ion has the highest removal efficiency at 150 mins contact time. This is an indication that 100 g coconut husk char has better treatability for phosphate ions in mildly polluted surface water than nitrate and sulphate ions (Table 3). Increase in service time as suggested by Lurtwitayapont and Srisatit (2010) could increase removal efficiency. Rapid initial sorption rate was observed for sulphate and phosphate ions at 30 mins contact time for 100 g adsorbent dosage. This is obviously beyond the contaminants exhibiting strong affinity for coconut husk char at this contact time, as similar trend was not observed for 200 g adsorbent dose. Increase in adsorbent dosage does not result in increased contaminant uptake. This result is not in tandem with Mehrasbi et al., (2008) observation; the possible reason for this contradiction is the difference in the biosorbent and precursor pretreatment process.

Table 3 Removal efficiency for the biosorbent

Removal efficiency (%)	30mins	60mins	90mins	120mins	150mins
100 g					
SO_4	47.29	60.47	62.02	66.67	70.54
NO_3	25.59	57.63	69.25	76.56	78.93
PO_4	55.50	69.73	70.45	75.32	91.53
200 g					
SO_4	11.63	22.50	31.01	38.76	63.26
NO_3	20.65	26.90	32.69	46.88	66.88
PO_4	18.92	23.10	33.33	60.90	65.05

4.2. Isotherm Model

Most of the sorption data were not well described by the Langmuir isotherm model ($R^2 < 0.84$). In contrast, Freundlich isotherm model gave a good representation of the data for both biosorbent dosages under consideration. Correlation coefficient values were greater than 0.96 (Table 4). This is an indication that Freundlich isotherm model is more applicable in adsorption process description than Langmuir model under this experimental condition. Hence, this represents a non-monolayer adsorption process. Similar results were obtained in most adsorption studies (Amuda & Ibrahim, 2006; Pan et al., 2009; Ijaola et al., 2013).

Table 4 Isotherm models for biosorbent

	Freundlich			Langmuir
	R^2	k	n	R^2
100 g				
SO_4	0.9977	0.0242	0.8167	0.8138
NO_3	0.9939	0.0271	0.7402	0.7363
PO_4	0.9987	0.0006	0.4323	0.0246
200 g				
SO_4	0.9944	0.0008	0.5929	0.3879
NO_3	0.9606	0.0024	0.6655	0.8384
PO_4	0.9842	0.0024	0.7377	0.8360

4.3. Pseudo Kinetic Model

The sorption process could not be described by the pseudo-first order equation for both adsorption dosage due to non-linear relationship between log $(Q_e - Q_t)$ and t. Correlation coefficient values were less than 0.30. On the contrary, the values fit better into the second-order pseudo-kinetic model ($R^2 > 0.85$) for most of the contaminants considered (Table 5). The process description also indicates chemisorption mechanism involvement (Pan et al., 2009). Relationship between experimental Qe computed from the plot of t/Q_t against t and calculated Qt values were closely related (Table 5). This is in agreement with Sangodoyin and Ajayi-Banji (2014) observation.

Table 5 Pseudo kinetics for biosorbent

	First order		Second order		
	R^2	K_Q	R^2	Q_e	Q_t
100 g					
SO_4	0.0129	0.0025	0.9788	0.3642	0.3339
NO_3	0.0355	0.0067	0.8920	0.3686	0.3383
PO_4	0.0270	0.0042	0.9931	0.4002	0.3791
200 g					
SO_4	0.0056	0.0056	0.8562	0.5784	0.3122
NO_3	0.2117	0.2117	0.9028	0.3221	0.2391
PO_4	0.0034	0.0339	0.7492	0.4841	0.3083

5. CONCLUSION

The study shows that 100 g of coconut husk char under this experimental condition has a strong affinity for sulphate, phosphate and nitrate ions in mildly polluted surface water. Freundlich isotherm model well describe ions adsorption on coconut husk char. Pseudo-second-order kinetics is applicable in the description of the sorption data. Therefore, the processes involved in the ions sorption are adsorption and chemisorption. Removal efficiency increased with service time, but not with adsorbent dosage. Hence, an increase in the contact time could increase polyatomic ions sorption.

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