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Potentials of Consortium of Banana, Orange and Potato Peels as Bio-Sorbents in the Purification of Paint Industrial Wastewater

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ABSTRACT

The research aimed at evaluating the potentials of consortium of banana, orange and potato peels as bio-sorbents in the purification of paint industrial wastewater, using column adsorption technique. The experimental conditions observed were pH 4 and 8 and adsorbent doses 1 g and 2 g. Atomic Adsorption Spectrophotometric method was adopted to evaluate the physicochemical properties of the wastewater samples. Results showed that the consortium were effective in the removal of COD, BOD, total solid, colour, turbidity, nitrate, chloride, copper and cadmium while the values of lead, sulphate and phosphate was observed a noticeable increase on the treated wastewater samples. The best experimental conditions according to the adsorption capacity were pH 4 and 1g adsorbent dose. The efficacy of the percentage removal for heavy metal and inorganic anions in the wastewater samples after treatment were in this order: $Cl^- < Cd < NO_3^- <$ Cu. It can be deduced that all models can be used reasonably well to describe the behaviour of the adsorption of cadmium, copper, chloride and nitrate. The best model for the column adsorption process was observed to be Yoon – Nelson isotherm model which have the highest correlation coefficient values of the study. The results of this study showed that the agrowastes consortium has the potentials in the treatment of industrial wastewater, which is cost effective, economical and eco-friendly.

Introduction

Paint effluents contain high amounts of heavy metals and organic pollutants therefore, the removal of these toxic pollutants from effluent before discharging to the environment and from raw water before public use is essential for the protection of health and environment. The groundwater in industrial areas across the country has undergone severe contamination by industrial wastes, effluents and emissions which are discharged indiscriminately without any regulatory system. However, in the wake of recent industrialization and fast urbanization the quality of groundwater has become an increasing concern due to contamination by various toxic chemicals [1].

Several methods have been adopted for the removal of these pollutants from industrial effluents, which includes: chemical precipitations, conventional coagulation, reverse osmosis, ion-exchange, solvent extraction, membrane filtration, chemical precipitation, electrodialysis and lime coagulation, oxidation and reduction method. However, the selection of wastewater treatment method is based on the concentration of the pollutants in the effluent, the efficiency and cost of the process operation relative to other techniques. These techniques are not only expensive but also inefficient in complete removal, high reagent and energy requirements and generation of toxic sludge. Furthermore, they require high level of expertise to operate and maintain the process.

Adsorption has been found to be the most efficient method for the removal of pollutants from effluents [2]. The effectiveness of an adsorbent depends on the adsorptive properties of their surface. The sorption of these pollutants from aqueous solutions is an important process in wastewater treatment. The use of adsorbents such as banana, potato and orange peels has also been found to circumvent the production of large amounts of sludge usually generated using alternative wastewater treatment techniques. A biosorption process offers a number of advantages when compared to the conventional methods currently used. These include low operating costs, minimization of the volume of chemical and/or biological sludge to be handled, and high efficiency in detoxifying effluents [3][4].

The mechanisms of biosorption are generally based on physico-chemical interactions between metal ions and the functional groups present on the cell surface, such as electrostatic interactions, ion exchange, and metal ion chelation or complexation [5]. Functional groups most commonly implicated in such interactions include carboxylate, hydroxyl, amine and phosphoryl groups present within cell wall components such as polysaccharides, lipids, and proteins [6]. In this case, factors like pH, size of biosorbent, ionic strength and temperature influence the metal biosorption [7].

Therefore, the purpose of this study was to evaluate the potentials of consortium of banana, orange and potato peels as bio-sorbents in the purifications of paint industrial wastewater. The effects of pH and adsorbent dose on their biosorption capacities were also studied.

Materials and Methods

Materials

Orange peels, Banana peels, Potato peels and Effluents from selected paint industries.

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Methods

Collection of Effluent Samples

Paint effluent samples were collected using sterilized 1 litre rubber container from the outlet of paint industries and designated as:

1. SP
2. CP
3. DP

Preparation of Agro-waste Materials

Fresh oranges, ripe bananas and potatoes were purchased from Relief market, Imo State, Nigeria and the peels were obtained. The biomass was oven dried at 50°C and pulverised separately into fine powder using a sterilized milling machine. The agro-waste were then transferred to heating mug and placed in the muffle furnace and partially carbonized for 30 min at temperature of 280°C to remove the fats. The partially carbonized biomass were then sieved using 1.18 mm sieve size and stored in air-tight bottle prior to the laboratory investigations at room temperature.

Experimental Design

The experimental design shows the untreated and treated samples. Each of the untreated effluent samples were adjusted to pH level 4 by addition of concentrated H_2SO_4 drop by drop and pH level 8 by addition of NaOH. And each level subjected to two adsorbent doses (1 g and 2 g) and labeled appropriately. Samples 1- 12 after treatment was designated as SP4/1, SP8/1, SP4/2, SP8/2, CP4/1, CP8/1, CP4/2, CP8/2, DP4/1, DP8/1, DP4/2 & DP8/2 and were subjected to the agrowaste consortium. Where, SP, CP & DP are the paint effluent samples, 4 & 8 are the adjusted pH levels and 1 & 2 are the adsorbent dosage in grams.

Fixed Bed Adsorption Study (Packing of Column)

The fixed columns for the treatment of the paint effluent were set up with 250 ml burettes held to pivot stands serving as the fixed columns. Sieve of sand (2 g) obtained from a river bank in Owerri was added to each of the columns as a form of base. The columns were then packed with their corresponding adsorbent doses according to the experimental design. Some 500 ml each of the adjusted pH effluents of 4 and 8 were introduced to their respective columns. Each effluent was allowed to flow by gravity through the column and treated effluent collected at the bottom and analysed for physicochemical properties.

pH

The pH of the untreated effluent samples was determined using LABTECH pH meter. The pH of the samples was measured by dipping the electrode into each of the samples in turn and rinsing the electrode with distilled water before dipping it into the next sample and the pH reading was obtained from the digital readout.

Determination of colour

Colour determination was done using Hanna Hi 83200 Multi-parameter bench photometer. A simple colorimetric procedure for apparent colour determinations utilizing platinum-cobalt standards and expressing the results in Hazen units. The method involves assessing the absorbance of a given sample with a colorimeter at wavelength of 455 nm.

Analysis of Heavy Metal Concentrations

The analysis of heavy metals was carried out, using FS240AA Agilent Atomic absorption Spectrophotometer. The AAS was put on and the flame lit up on the burner with acetylene as fuel and compressed air as oxidant at the appropriate flow rates. Standard solutions of each element under investigation were aspirated into the nebuliser-burner assembly via a capillary tube and the absorbance readings taken from the direct read out of the atomic absorption spectrophotometer. It was immediately followed by aspirating the sample solutions into the nebuliser-burner assembly via a capillary tube and the absorbance readings also obtained from the digital read out of the instrument. The hollow-cathode lamp was set at the wavelength of the element (analyte).The concentration of the element under investigation in the sample was obtained by the extrapolation from the standard curve and result recorded in mg/L (ppm).

Biochemical Oxygen Demand (BOD_5) Analysis

Biochemical oxygen demand (BOD_5) was evaluated according to official methods of analysis of the Association of Official Analytical Chemists (AOAC), 2002. The sample was filled in BOD bottle and 1ml of allyl thiourea added to the bottle. The amount of the dissolved oxygen in BOD bottle was determined by titration method and was incubated in an incubator in complete darkness at 20°C for 5 days and the mean reading taken as D_1. Dissolved oxygen reading in the incubated sample was evaluated by titration and the mean reading taken as D_2. The BOD of the effluent was determined by using the formula:

$$BOD_{mg/l} = \frac{D_1 - D_2}{\frac{\text{amount of the sample taken}}{\text{capacity of the BOD bottles}}}$$

Chemical Oxygen Demand (COD)

20 ml of the effluent sample was placed into a 250 ml conical flask and 10 ml of the dichromate solution added. Slowly, 30 ml of concentrated sulphuric acid was added to the solution. The flask was cooled during addition by vortexing in a cold water-containing dish. The mixture was made up to 150 ml of water, and titrated with ferrous ammonium sulphate solution using ferroin indicator. Parallel to this, a blank determination was carried out using 20 ml of distilled water instead of the sample. The COD was calculated as follows:

$$COD\ (mg/litre) = \frac{(B - A)(N)(8000)}{V}$$

Where A = Volume of ferrous ammonium sulphate solution used for sample titration, in ml

B = Volume of ferrous ammonium sulphate solution used for blank, in ml

N = normality of the ferrous ammonium sulphate

V = Sample volume, in ml (i.e. 20 ml)

Turbidity Determination

Turbidity was determined using WGZ-1B Turbidimeter by Xinrui Instruments and Meters Co. Ltd. Shanghai China. Deionized water (15 ml) was poured into the sample as blank. The blank was used to zero the turbidimeter. The turbidimeter was calibrated with a formazine standard turbidity solution of 10 NTU (Normal Turbidity Units) diluted from a stock standard solution of 400 NTU. Some 15 ml of the standard turbidity solution was poured into another cell of the same thickness until a reading of 10 NTU was obtained on the digital read out. Again, 15 ml of the sample was poured into another cell after being shaken vigorously. The sample cell containing the sample was put into the light shield and closed after the blank was removed and the "read" button pressed. The value was then digitally displayed in NTU.

Determination of Total Solids (TS)

20 ml of the effluent samples were measured into a pre-weighed 250 cm^3 beaker. Each beaker and its contents were heated to dryness in oven at 105℃. The beaker and its residue were then weighed again on an electronic weighing balance after cooling. Then the total solid was calculated as follows:

$$TS_{mg/l} = \frac{[(Wf - Wi) \times 1000 \times 1000]}{\text{volume of sample}}$$

Where,

Wi- initial weight of the beaker

Wf- final weight of the beaker

Determination of Inorganic Anions

Inorganic anion concentrations were determined using standard procedures as described by below:

Chloride (Cl^-)

In each case, 25 ml of the effluent was pipetted into a 100 ml conical flask and 1ml Potassium chromate indicator added to the effluent. The solution in the conical flask was titrated with 0.02M Silver nitrate to a reddish brown end point using a micro burette. A blank titration was done as above using deionised water.

$$Chloride, (mg/l) = \frac{(\text{Sample titre} - \text{Blank titre}) \times 0.02M \times 35.5 \times 1000}{\text{Volume of samples}}$$

Phosphate (PO_4^{3-})

In the determination of phosphate, 6.0 g ammonium heptamolybdate was weighed and dissolved in 150 ml distilled water in 250 ml conical flask. Ascorbic acid (2.6 g) was dissolved in 50 ml of distilled water in 1 litre volumetric flask to give 0.0007M ascorbic acid. Potassium antimony tartrate (0.14 g) was also weighed and dissolved in 20ml distilled water (0.0000086M). 1M stock of concentrated sulphuric acid was prepared by dissolving 10 ml of stock in 50 ml distilled water. Then, 12.4 ml of the ammonium molybdate reagents was transferred to a 50 ml volumetric flask, 10ml sulphuric acid added, swirled, and 2.3 ml of antimony potassium tartrate added. The mixture was swirled properly to mix and made up to the mark with distilled water. Spectrophotometric determination was carried out by adding 0.4 ml molybdate reagent to 20 ml of standard or sample in a test tube and swirled to mix. Also, 0.4 ml of L-ascorbic acid was added and swirled. The light absorption of the solution was measured at 820 nm wavelength. The final concentration of phosphate was determined using the following formula:

$$P_{(\frac{mg}{l})} = \frac{\frac{mg}{l} \text{from the curve} \times 50ml}{\text{initial volume used (ml)}}$$

Nitrate (NO_3^-)

The effluent sample was passed through a copper-coated Cadmium reduction column. Nitrate in the sample is reduced to nitrite in a buffer solution. The nitrite was then determined by diazotizing with sulfanilamide and coupling with N-1-naphthylethylenediamine dihydrochloride to form acolorazo dye. The absorbance was measured at 540 nm which is linearly proportional to the concentration of nitrite plus nitrate in the sample. Nitrate concentrations were obtained bysubtracting nitrite values, which have been separatelydetermined without the cadmium reduction procedure, from the nitrite + nitrate values.

Sulphate (SO_4^{2-})

Deionised water (100 ml) was poured into a clean and acid-washed beaker with 50ml of buffer solution, and then transferred into a clean, 125-ml Erlenmeyer flask containing a clean magnetic stirring bar. Some 10ml of deionised water, 6 ml of buffer reagent, and 10ml of the standard solution were added into the flask. It was vortexed gently to ensure mixing. About 0.1g - 0.2 g of $BaCl_2$ was added to the flask which was immediately placed on the magnetic stirrer and stirred for 58 to 62 seconds. After a minute of stirring, the solution was allowed to stand undisturbed for ~2 minutes. The absorbance was measured by a spectrophotometer at the wavelength of 420 nm and sulphate concentration determined by comparison of the reading with a standard curve.

Experimental Conditions

Effect of pH

The effect of pH on metal adsorption by the agrowaste consortium was investigated with 1g and 2 g of the adsorbents in 500 ml effluent sample with adjusted pH 4 and 8 using either 1N H_2SO_4 or NaOH solution and was allowed to flow by gravity through the bed. The flow rate was controlled by using needle valve at 10 ml/min. the treated effluent sample was collected at the bottom and analyzed for physicochemical properties.

Effect of Adsorbent Dosages

The effect of adsorbent dosage was investigated with two different doses (1 g & 2 g), and 500 ml effluent sample allowed to flow by gravity through the bed. The flow rate was controlled by using needle valve at 10 ml/min. The treated effluent was collected at the bottom and analyzed for physicochemical properties.

Treatment Efficiency Calculation

Treatment efficiency was calculated on the heavy metal ions and inorganic ions as percentage removal. This was computed by subtraction of the initial concentration from the final concentration multiplied by 100 divided by the initial concentration.

Adsorption Isotherm Study

Adsorption isotherm studies were conducted by considering the effects of pH and adsorbent dosage on the adsorption capacity of the adsorbent of the heavy metals. The equilibrium data was fitted with Bohart-Adams, Thomas and Yoon-Nelson isotherm models and the applicability judged with the coefficient of determination (R^2).

Calculation of Metal Uptake

The quality of biosorbent was judged by the metal uptake (biosorption capacity), q. Amount of metal bound by the biosorbent which disappears from the solution was calculated based on the mass balance for the biosorbent in the system.

$$q = \frac{V(C_i - C_f)}{S}$$

q = Metal ion uptake capacity (mgg^{-1})

Ci = Initial concentration of metal in solution, before the sorption analysis (mgL^{-1}).

C_f = Final concentration of metal in solution, after the sorption analysis (mgL-1).

S = Dry weight of biosorbent (g)

V = Solution volume (L)

The difference between the initial metal ion concentration and final metal ion concentration was assumed to be bound to the biosorbent.

Results

Physical Properties

Physical properties of SP, CP and DP effluent before and after treatment using the consortium are shown in Table 1. The mean physical properties values of the treated effluent samples were observed to decline when compared to the untreated.

Inorganic anions

The treated effluent samples of nitrate and chloride recorded a noticeable decrease when compared to untreated effluent but sulphate and phosphate recorded an increase compared to the untreated effluent samples as shown in table 2.

Table 1. Mean values for Physical properties of Paint Effluents before and after treatment with agrowaste consortium.

	SP Effluent					**CP Effluent**					**DP Effluent**				
Parameters	**Untreated**	**Treated**				**Untreated**	**Treated**				**Untreated**	**Treated**			
		SP4/1	**SP8/1**	**SP4/2**	**SP8/2**		**CP4/1**	**CP8/1**	**CP4/2**	**CP8/2**		**DP4/1**	**DP8/1**	**DP4/2**	**FP8/2**
COD (mg/l)	3545.6±0.13	3106.1±0.21	3297.4±0.18	2907.4±0.22	3084.7±0.25	3049.2±0.15	2786.9±0.20	2255.0±0.12	2552.9±0.16	2411.0±0.14	3332.9±0.11	**2467.9±0.19**	**2552.9±0.28**	**2517.4±0.24**	**2588.3±0.17**
BOD (mg/l)	**1276.4±0.29**	**1118.2±0.23**	**1187.1±0.20**	**1046.7±0.28**	**1110.5±0.32**	**1097.7±0.25**	**1002.9±0.24**	**811.8±0.21**	**919.0±0.25**	**867.9±0.26**	**1199.8±0.40**	**888.4±0.32**	**191.0±0.29**	**906.3± 0.33**	**931.8±0.35**
Total solid (mg/l)	**68000±0.47**	**50000±0.50**	**16000±0.81**	**53000± 0.90**	**10000±0.94**	**60500±0.50**	**38000±0.94**	**14000±1.24**	**44500±0.82**	**14000±0.47**	**54000±1.40**	**36000±1.70**	**16000±1.60**	**18000±1.30**	**22000±1.63**
Colour (PCU)	**2928±0.80**	**440±0.91**	**435±0.10**	**788±0.53**	**722±1.2**	**485±0.94**	**348±1.21**	**121±1.61**	**388±1.42**	**355±1.88**	**744±0.51**	**207±0.92**	**30±1.23**	**580±1.70**	**353±1.40**
Turbidity (NTU)	**14.14±0.40**	**6.28±0.10**	**5.74±0.30**	**7.84±0.12**	**12.72±0.29**	**10.48±0.24**	**6.34± 0.26**	**8.14± 0.16**	**6.05± 0.19**	**7.80± 0.20**	**10.48±0.22**	**7.49±0.14**	**9.70±0.42**	**8.33±0.24**	**7.02±0.54**

Note: Values are Mean±SD of triplicate determination

pH =4 & 8, Adsorbent doses= 1 g & 2 g

Table 2. Mean values for Inorganic anions of paint effluents before and after treatment with agrowaste consortium

	SP Effluent					CP Effluent					DP Effluent				
Parameters	Untreated	Treated				Untreated	Treated				Untreated	Treated			
		SP4/1	SP8/1	SP4/2	SP8/2		CP4/1	CP8/1	CP4/2	CP8/2		DP4/1	DP8/1	DP4/2	FP8/2
Sulphate SO_4^{2-}(mg/l)	86.98±0.13	132.09±0.11	119.60±0.14	125.64±0.12	318.94±0.09	151.42±0.12	6.44±0.10	86.98±0.13	3.22± 0.18	1723.97±0.45	283.50±0.12	9.66±0.15	16.11±0.11	3.22±0.13	144.97±0.10
Phosphate PO_4^3	61.06±0.35	209.52±0.22	3.92±0.33	256.02±0.39	0.00	54.90±0.42	313.71±0.24	0.00	331.09±0.37	0.00	53.78±0.35	337.82±0.20	0.00	443.69±0.37	15.13±0.35
Nitrate NO_3^- (mg/l)	64.73±0.50	40.81±0.38	1.92±0.34	54.55±0.27	59.89±0.42	61.89±0.30	42.87±0.36	4.91±0.43	38.81±0.38	54.77±0.27	61.32±0.32	35.39±0.18	8.90±0.42	51.06±0.44	14.67±0.22
Chloride Cl- (mg/l)	5422.62±0.77	5325±0.28	4961.12±0.41	5325±0.35	5280.62±0.29	7588.12±0.52	4260±0.45	5316.12±0.36	10650±0.43	7366.25±0.30	5919.62±0.56	4260±0.46	5671.12±0.44	4260±0.37	5884.12±0.51

Note: Values are Mean±SD of triplicate determination

pH =4 & 8, Adsorbent doses = 1 g & 2 g

Table 3. Mean values for heavy metal of paint effluents before and after treatment with agrowaste consortium.

	SP Effluent					**CP Effluent**					**DP Effluent**				
Parameters	**Untreated**	**Treated**				**Untreated**	**Treated**				**Untreated**	**Treated**			
		SP4/1	**SP8/1**	**SP4/2**	**SP8/2**		**CP4/1**	**CP8/1**	**CP4/2**	**CP8/2**		**DP4/1**	**DP8/1**	**DP4/2**	**FP8/2**
Copper, Cu (ppm)	0.103±0.04	0.159±0.07	0.00	0.084±0.03	0.00	0.83±0.38	0.115±0.05	0.00	0.056±0.03	0.00	0.064±0.02	0.063±0.029	0.00	0.00	0.00
Nickel, Ni (ppm	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Lead, Pb (ppm)	0.013±0.01	0.437±0.20	0.00	0.175±0.08	0.00	0.004±0.002	0.228±0.12	0.00	0.129±0.06	0.00	0.178±0.08	0.393±0.18	0.025±0.01	0.476±0.22	0.00
Cadmium, Ca (ppm)	0.022±0.01	0.003±0.001	0.003±0.002	0.011±0.001	0.020±0.002	0.028±0.013	0.015±0.01	0.016±0.01	0.011±0.0	0.013±0.006	0.018±0.011	0.009±0.002	0.016±0.01	0.024±0.01	0.00

Note: Values are Mean±SD of triplicate determination

pH =4 & 8, Adsorbent doses=1 g & 2 g

Heavy Metals

Mean heavy metals concentrations of treated paint effluent samples of copper and cadmium were observed to decline compared to the untreated paint effluent samples. But the treated effluent samples of Lead values were observed to increase compared to untreated paint effluent samples. However, nickel was not detected in the untreated effluent samples as shown in table 3.

Efficiency of Bio-sorbent Consortium

Efficiencies removal of heavy metals and inorganic anions of the consortium on the paint effluent samples were calculated. The results showed that efficiency removal of copper was highest in samples of SP8/1, SP8/2, CP4/1, CP8/1, CP8/2, DP4/2, DP8/1 and DP8/2 while cadmium was highest in SP4/1, SP4/2, CP4/2 and DP4/1. The result of efficiency removal of inorganic anions shows that Nitrate was highest in SP4/1, SP8/1, SP4/2, SP8/2, CP8/1, CP8/2, DP4/1, DP8/1 and DP8/2 while chloride was highest in CP4/1, CP4/2 and DP4/2. The dose of peels at which purification was best achieved was also ascertained by the efficiency calculation. It was observed that 1g of the consortium was the best dose for purification as it appeared that the higher the dose the lower the purification efficiency (Fig. 1 & 2).

Heavy Metals

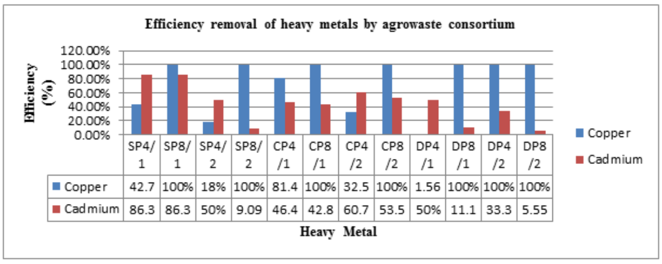

Fig 1. Efficiency removal of heavy metals by agrowaste consortium.

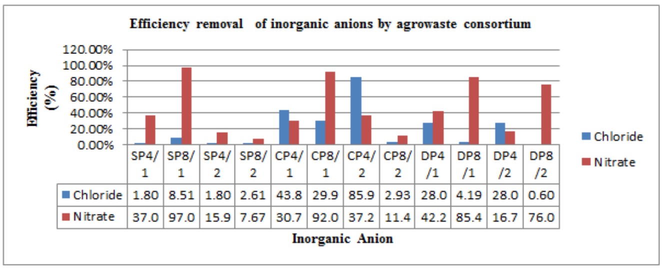

Fig 2. Efficiency removal of inorganic anions by agrowaste consortium

Experimental conditions

Effect of pH

pH effect on adsorption of heavy metals shows Cu, 46.03% and Cd, 100% at pH4 and Cu, 100% and Cd, 34.76% at pH8. Adsorption of inorganic anions, chloride and nitrate shows 31.5%, and 8.13% and 29.99%, and 61.63% at pH 4 and 8 respectively (fig. 3 & 4).

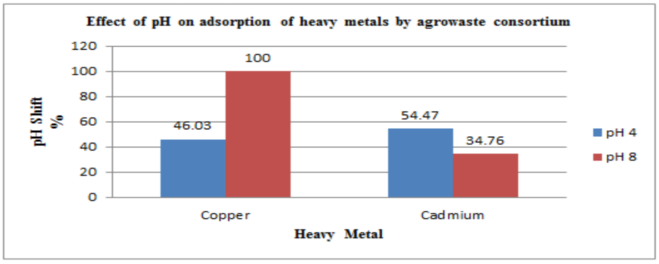

Fig 3. Effect of pH on adsorption of heavy metals by agrowaste consortium

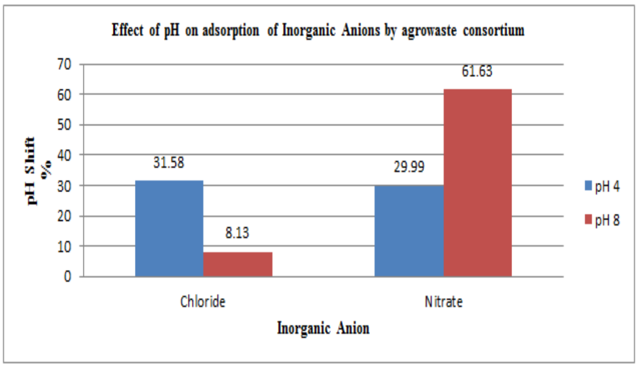

Fig 4. Effect of pH on adsorption of Inorganic Anions by agrowaste consortium

Effects of Adsorbent Dose

The effect of adsorbent dose on adsorption of heavy metals shows, 1 g (70.95%) and 2 g (75.09%) for copper and 1 g (53.88%) and 2 g (35.37%) for cadmium. Adsorption of chloride, 1 g (19.39%) and 2 g (20.32%) and Nitrate, 1 g (64.11%) and 2 g (27.52%) as showed in fig. 5 & 6.

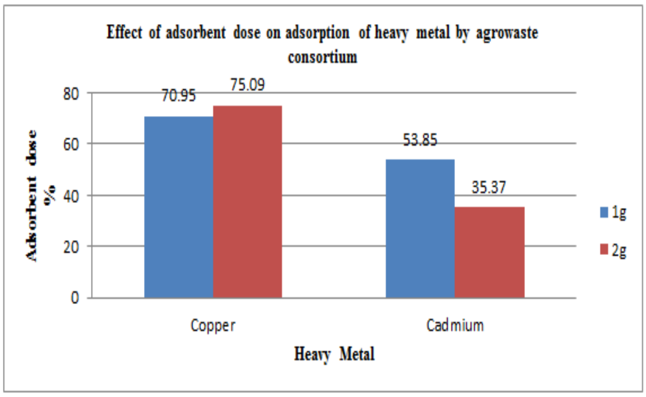

Fig 5. Effect of adsorbent dose on adsorption of heavy metal by agrowaste consortium

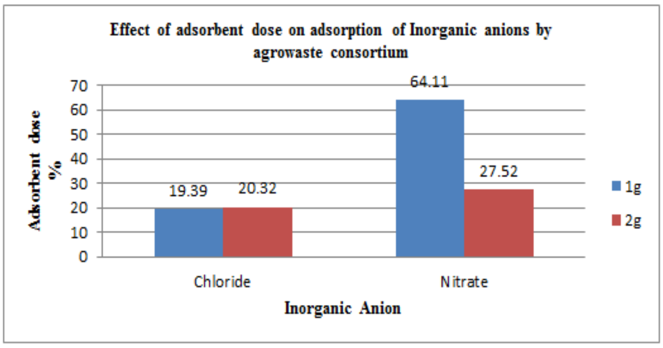

Fig 6. Effect of adsorbent dose on adsorption of Inorganic anions by agro-waste consortium

Adsorption Isotherm Study

The adsorption isotherm study was conducted and the equilibrium data was fitted into Boharts – Adams, Thomas and Yoon – Nelson isotherm models and the applicability was judged with the correlation coefficient (R2) as shown in Table 4. Considering the values of R2 for the models fits to the experimental data, it can be observed that all models can be used reasonably well to describe the behaviour of the adsorption of cadmium, copper, chloride and nitrate, except for partly negative values of Bohart – Adams and Thormas models. But best model for the column adsorption process was observed to be Yoon – Nelson isotherm models which had the highest correlation coefficient values of the study. The constants of the isotherm models were evaluated from slope and intercepts (Fig. 7 to 17).

Table 4. Parameters for isotherm models for adsorptions of heavy metals and inorganic anions

Isotherm Models	Parameters	Cd	Cd	NO_3^-	Cl^-
1.Bohart – Adams $In\frac{C}{C_o} = K_{AB}C_ot - K_{AB}N_o\frac{Z}{U_o}$	N_o	.21	1.4	0.8	-0.83
	K_{AB}	0.25	0.5	0.1	0.04
	R^2	0.65	0.48	-1.21	-1.02
2.Thomas $In\left(\frac{Co}{Ct} - 1\right) = \frac{K_{Th}\ q_o M}{Q} - K_{Th}\ C_o t$	q_o	1.51	2.9	-1.7	-3.5
	K_{Th}	3.0	3.0	1.60	3.9
	R^2	1.24	13.0	-1.52	-1.4
3. Yoon – Nelson $In\left[\frac{C_t}{C_o} - C_t\right] = K_{YN}t - \pi K_{YN}$	π	1.7	3.54	-5.9	-2.35
	K_{YN}	1.89	3.4	4.9	10
	R^2	11.24	1.7	-22.2	0.96

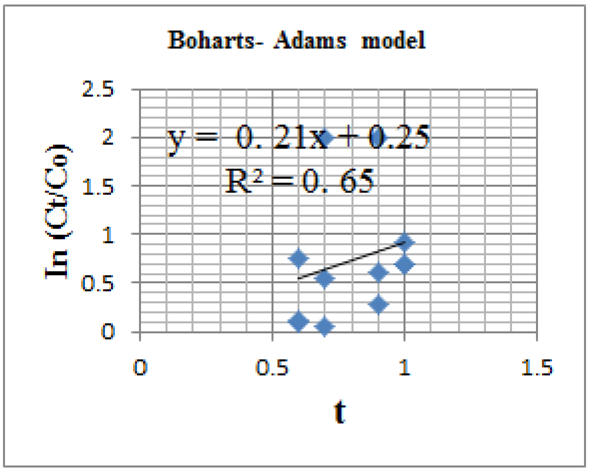

Figure 7. Boharts- Adams model for Cd.

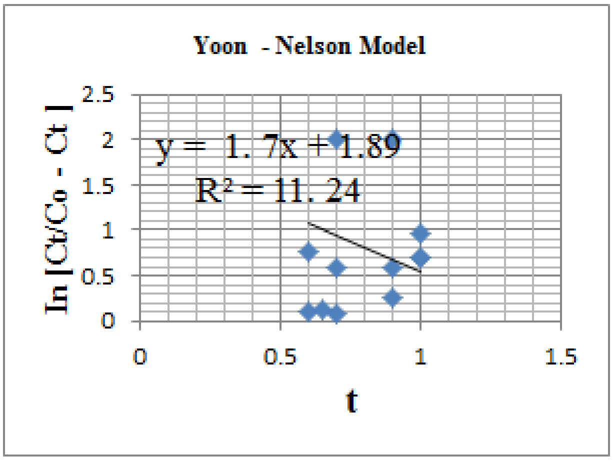

Figure 8. Yoon - Nelson Model Cd.

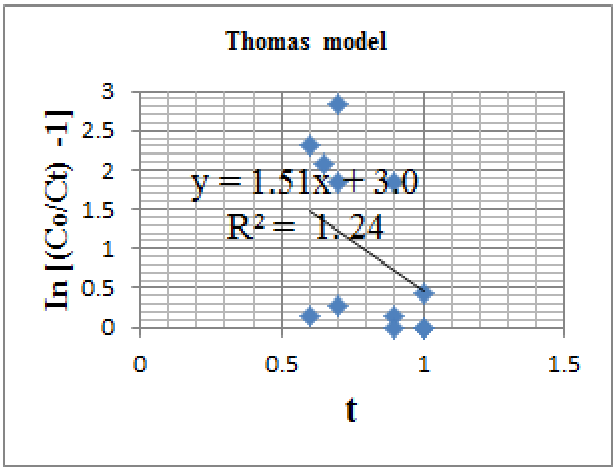

Figure 9.Thomas model for Cd.

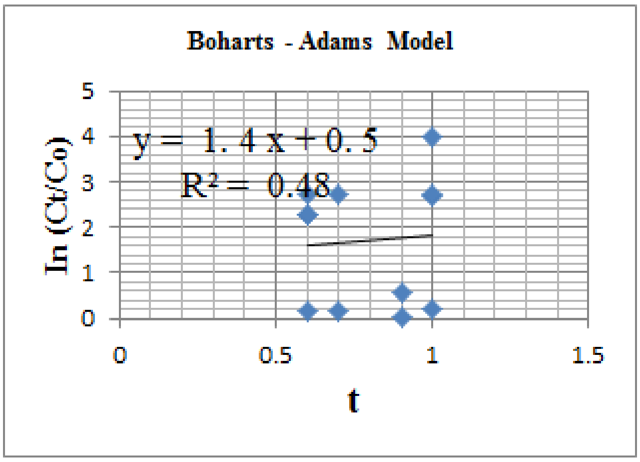

Figure 10. Boharts-Adams model for Cu.

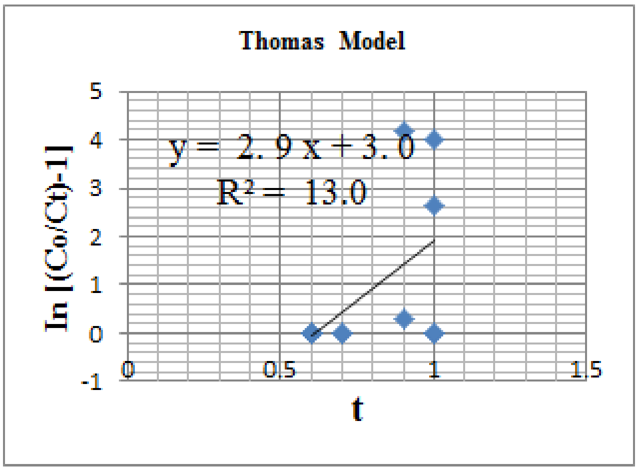

Figure 11. Thomas Model for Cu.

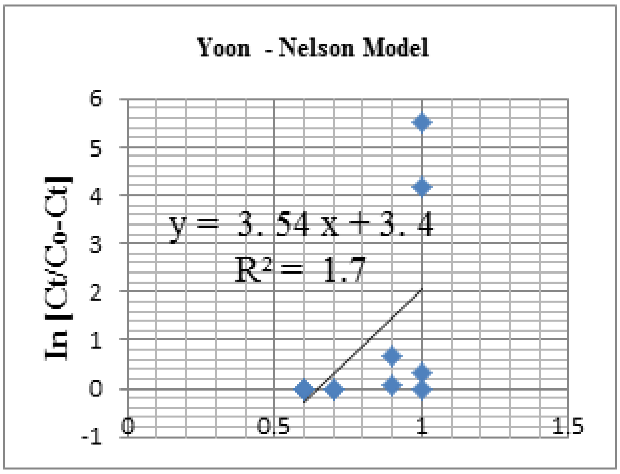

Figure 12. Yoon-Nelson model for Cu.

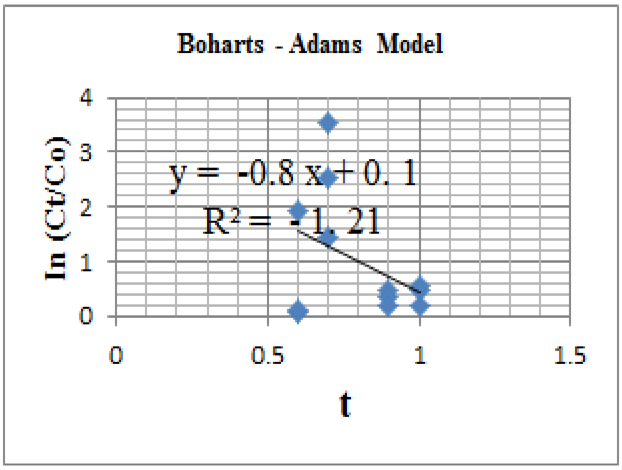

Figure 13. Boharts-Adams model for nitrate.

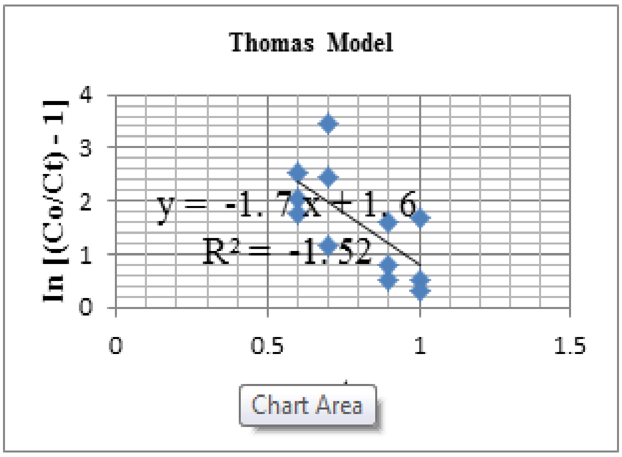

Figure 14. Thomas model for nitrate.

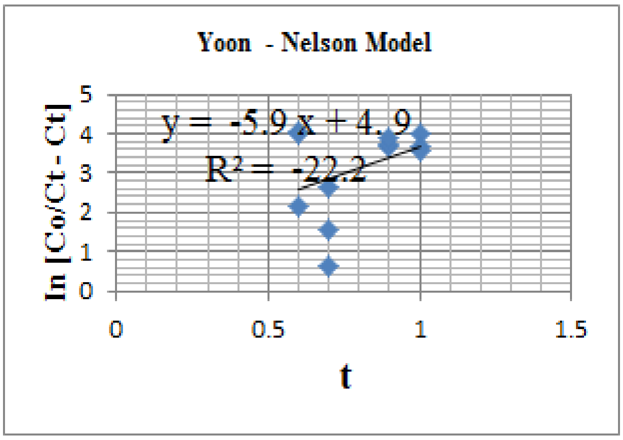

Figure 14. Yoon-Nelson model for nitrate.

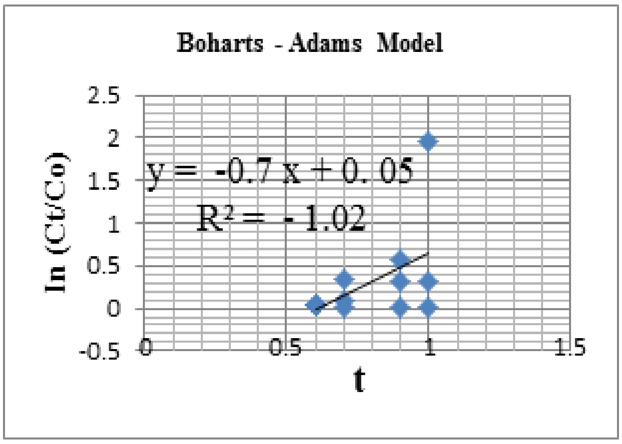

Figure 15. Boharts-Adams model for chloride.

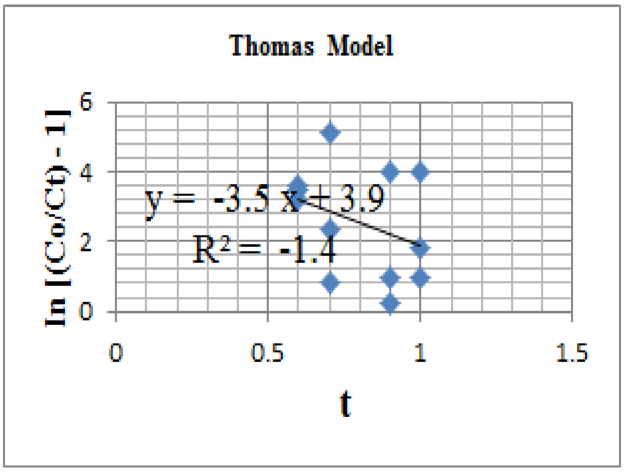

Figure 16. Thomas model for chloride.

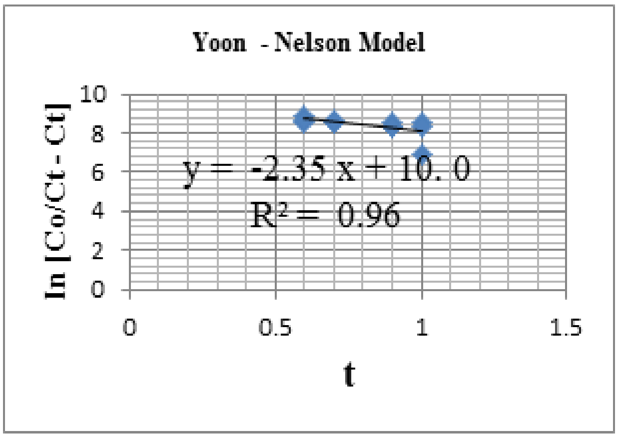

Figure 17. Yoon-Nelson model for chloride.

Discussion

Physical Properties

Biochemical Oxygen Demand (BOD_5) and Chemical Oxygen Demand (COD) tests are useful in determining the relative waste loading and higher degree indicates the presence of large amount of organic pollutant with consequent depletion of oxygen content. The result revealed that COD and BOD were observed to decrease on the treated effluent sample compared to the untreated effluent samples. This result is in agreement with works of others on composites of banana peels and fish scale [8], and composites of Orange and Potato peels [9].

Turbidity in water is caused by the presence of suspended matter such as clay, silt, and finely divided organic and inorganic matter. The highest turbidity value of the treated samples was 12.77 NTU and least was 5.74 NTU, which is less than the untreated effluent samples. The values reported in this work are consistent with findings of "[9]". Also, the study showed a decrease in the initial mean value of the Total solids present in the effluent. As such, the percentage removal of Total solids was 38.46% which is in line with the work of "[10]". The mean colour values were observed to decrease after treatment when compared with the untreated paint effluent samples. This finding is synonymous with the finding of "[11]" and "[8]".

Inorganic Anions

The mean Chloride levels of the treated effluents samples were observed to decrease when compared to the untreated effluent. The maximum efficiency removal was 85.96%. According to "[12]", low cost adsorbents are effective in the removal of Chloride using both column adsorption studies. The result is in agreement with removal of inorganic anions in brewery effluent using banana peels, were chloride had efficiency removal of 36.36% as reported by "[13]". The mean phosphate results on treated effluent samples were observed to increase when compared with untreated effluent values. However, studies by "[14]" and "[13]" using banana peels and orange peels show contrary report. This increase in phosphate value might be from the agrowaste consortium.

For Nitrate, the results show that the treated effluent samples were observed to decrease compared to the untreated effluent samples. The maximum efficiency removal for the agrowaste consortium was 97.04%. Meanwhile, "[15]" and "[13]" reported similar results, nitrate removal efficiency of 80% and 95.28% using banana peels. According to "[16] and "[17]" reported 80% removal efficiency using orange peels. The result is in accordance with works of "[18]", reported the maximum adsorption capacity of 43.1mg/g.

Heavy Metal

The removal efficiency for Cadmium was 86.36%. "[19]" conducted a study on efficiency evaluation of food waste materials for removal of metals and metalloids from complex Multi-Element solutions. It was concluded that cadmium had 92%, 88% and 17% efficiencies for Orange, banana and potato peels respectively. Similar studies was also carried out by "[20]" with efficiency of 86.36% using potato peels, "[21]" with efficiency of 98% using banana peels. Separate studies by "[22]"and "[23]" using banana peels achieved 73.15% and 98% efficiencies respectively. Comparing the studies of the above researchers with the present work, agrowaste consortium shows better adsorption capacity than single adsorbents.

The removal efficiency of copper was 100%. "[24]" studied the removal of Cu (II) and Fe (II) from industrial wastewater using orange peel as adsorbent in batch mode operation. It was concluded that copper had removal efficiency of 87%. Different studies carried out by "[25]" "[26]" and "[27]" using Potato and banana peels, shows similar adsorption percentage levels.

Effects of pH

pH is one of the most important environmental factor that controls the adsorption process of metal onto any adsorbent. Accordingly, different pH values were studied (4 and 8) with constant adsorbent dosage and particle size. The maximum uptake of Cadmium (84.52%), and chloride (39.15%) was achieved at pH 4 as against pH 8 which was Cd (71.56%), and chloride (37.75%). This behavior can be explained by taking into account that at low pH value, the surface of adsorbent would also be surrounded by hydronium ions, which decrease the copper ion and nitrate interaction with binding sites of the adsorbents by greater repulsive forces and therefore lower adsorption takes place. This result is in consistent with findings of "[16]".

Contrary to this, the maximum uptake of copper (100%) and Nitrate (75.07%) was achieved at pH 8 as against pH 4 which was 54.68% for Cu, and 52.72% for Nitrate. This result also means that as the pH was increased, the competing effect of hydrogen ions decreased and more ligands were available. Therefore, at high pH value, the overall surface on the consortium became more negative and adsorption increased as shown in the fig. 3 and 4. This finding is in agreement with the works of "[24]"and "[23]".

Effect of adsorbent dose

Adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. It was observed that optimum adsorption was obtained at 1g adsorbent dose on chloride and nitrate compared to 2g adsorbent dose. The increase in adsorption is attributed to the increase of the available biosorption surfaces and sites [17]. However, copper and cadmium was observed to have better adsorption at 2 g adsorbent dose as shown in fig. 3 and 4.

Adsorption Isotherm models

The experimental data fitted marginally satisfactory to Bohart-Adams and Thomas models as shown by the correlation coefficient R^2 values (table 5). The values of the rate constants, k_{AB} and N_o calculated from Bohart-Adams model were observed to increase in copper ion they were similar with those observed for other adsorbates and adsorbents [28]. The values obtained for qo from Thomas model are similar to the findings of "[29]" and "[12]". The above adsorption capacities were the highest estimated by Thomas model in the experiments. The experimental data fitted very satisfactorily to Yoon-Nelson model because of the high correlation coefficient values. The rate constant k_{YN} were observed to increase in both heavy metals and inorganic anions but more on the inorganic anions as shown in table 5.

Conclusion

The result of this research shows that the agrowaste consortium was very effective in the treatment of paint effluents when compared to single agro-waste. Specifically, it can be used to reduce the concentrations of heavy metals, inorganic anions and other physical properties in industrial effluents. This study has also shown that varying experimental conditions such as effect of pH and adsorbent dose affects adsorption process for example cadmium and chloride achieved their maximum adsorption at pH 4 while copper and nitrate achieved their maximum adsorption at pH 8. This explains that different heavy metals and inorganic anions achieve their maximum uptake at pH range of 4 - 8. In adsorbent dose it was observed that optimum adsorption was obtained at 1 g which means that the lower the adsorbent dose the more effective the treatment. Considering the values of R^2 for the models fits to the experimental data, it can be concluded that Yoon- Nelson isotherm model was the best model for the column adsorption process. The cost implication of using conventional methods of industrial effluent treatment is extremely high compared to using agrowastes consortium since they are readily available in our environment which is observed to be cost effective, economical and eco-friendly.

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