Effectiveness of Composites of Corn Cobs, Coconut Husks and Breadfruit Peels in Purifying Selected Paint Effluents

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***Abstract*:- Due to the varying degrees of chemicals used in paint industries, the resulting effluent contains appreciable concentrations of toxic metals and inorganic anions which reduce the quality of the receiving streams, aquatic life and adverse effects on human health. This research aimed at determining the effectiveness of composites of Corn cob, Coconut Husk and bread fruit peels in purifying selected paint effluents through the assessment of their physicochemical properties before and after treatment using column adsorption technique. The experimental conditions observed were pH 4 and 8; adsorbent doses of 1g and 2g. Standard laboratory techniques involving the use of Atomic Adsorption Spectrophotometric method were adopted to determine the physicochemical properties of the effluent samples. The physicochemical results showed that the composites were effective in the removal of total solid, turbidity, colour, phosphate, nitrate, chloride, copper and cadmium while the values of COD, BOD, Lead and sulphate recorded noticeable increase on the treated effluent samples. The best experimental conditions according to the adsorption capacity were pH 4 and 1g adsorbent dose. The efficiency removal for heavy metal and inorganic anions in the effluent samples after treatment was in this order: $Cl^- < Cu < NO_3^- < PO_4^- < Cd$. Considering the values of R^2 for the models fits to the experimental data, it can be concluded that all models can be used reasonably well to describe the behaviour of the adsorption of cadmium, copper, chloride, nitrate and phosphate, except for the partly negative values of Bohart – Adams and Thomas models. This research work shows that the use of corn cob, coconut husks and breadfruit peels as composite is more effective in reducing the concentrations of physicochemical properties of paint effluents.**

Keywords: **Composite, physicochemical properties, paint effluents, purification.**

I. INTRODUCTION

Pollution of water bodies by effluents from industrial processes is a serious problem in most countries. Increased industrial activities have reduced the availability of quality water by the discharging of large amount of effluents into water bodies. Paint industries are among these industries that discharge effluents containing heavy metals. Paints generally consist of organic and inorganic pigments and dyestuffs, extenders, cellulosic and non-cellulosic thickeners, latexes, emulsifying agents, anti foaming agents, preservatives, solvents and coalescing agents. Paint effluent is generated primarily due to cleaning operations of mixers, reactors, blenders, packing machines and floors. Due to the varying degrees of chemicals used, the wastewater contains appreciable concentrations of carbon (Biological Oxygen Demand (BOD) or Chemical Oxygen Demand (COD)), suspended solids, toxic compounds and colour [1]. The discharge of such wastewater into the environment impedes light penetration, damages the quality of the receiving streams and may be toxic to treatment processes, to food chain organisms and to aquatic life [2].

Several wastewater treatment processes such as chemical precipitation, adsorption, ion exchange and membrane filtration, coagulation, lime precipitation, advanced oxidation process and electrolytic methods, have been developed over the years to remove the heavy metals dissolved in industrial wastewaters [3]. However, most of these techniques have disadvantages, such as complicated treatment process, high cost, energy consumption and generation of secondary wastes. Secondary wastes present treatment problems, such as large quantity of sludge generated by precipitation processes. On the other hand, ion exchange, reversed osmosis and adsorption are more attractive processes because the metals values can be recovered along with their removal from the effluents. Reverse osmosis and ion exchange do not seem to be economically feasible because of their relatively high investment and operational cost [4].

Adsorption process is therefore considered better because of convenience, ease of operation and simplicity of design. The major advantages of adsorption over conventional treatment methods include low cost, high efficiency, minimization of chemical and/or biological sludge, and regeneration of biosorbent, no additional nutrient requirement and possibility of metal recovery. The use of agricultural by-products as biosorbent material to purify heavy metal-contaminated water has become increasingly popular during the past decade, because they are less expensive, biodegradable, abundant and efficient. Cost is an important parameter for comparing the sorbent materials. The cost of individual sorbents varies, depending on the degree of processing required and availability. Thus, there is an urgent need that all possible sources of agro-based inexpensive adsorbents are explored and their feasibility for the removal of heavy metals studied in detail [5]-[7].

In the last decades, several agricultural and forest wastes have been studied as low-cost adsorbents. Agricultural adsorbents such grape waste, rice husk [8], [9], tea waste [10], maize corn cob, sugarcane bagasse [11] and pine bark [12], were developed from agro-waste to remove heavy metal ions. Some of these biosorbents (corn cob, rice husk and sugar bagasse) have also been used in the removal of dyes [13]. These findings brought good news and hope for people living in countries where they have to depend on contaminated water from rivers and lakes for their daily water supply.

This research aimed at determining the effectiveness of composite of corn cob, coconut husk and bread fruit peels in purifying selected paint effluents.

II. MATERIALS AND METHODS

2.1 Materials

Corn cob, Bread fruit peels, Coconut husk and Effluents from selected paint industries.

2.2 Methods

Collection of Effluent Samples

Paint effluent samples were sourced from the outlet of paint industries designated as:

1. SP
2. CP
3. DP. The samples were collected using sterilized 1litre rubber container each.

Preparation of Bio-sorbent Precursors

Respective peels, cob and husk were obtained form fresh bread fruit, corns, and coconuts purchased from Umuna daily market Orlu, Imo State, Nigeria. The biomass was oven dried at 50°C and pulverised separately into fine powder using a sterilized milling machine. The agrowaste was then partially carbonized at 280°C using Furner's to remove the fats. The partially carbonized biomass were then sieved using 1.18mm sieve size and stored in air-tight bottle prior to the laboratory investigations at room temperature.

Preparation of the Effluent samples

The pH of 500ml of each of the paint effluents (SP, CP and DP) were adjusted to pH 4 by addition of concentrated H_2SO_4 drop by drop and pH 8 by addition of NaOH.

Experimental Procedure (Effluent Treatment with Bio Sorbents)

Experimental Design

The experimental design as shown in table I represents the untreated samples as the independent variables and the samples after treatment as dependent variable. Each of the untreated effluent samples were adjusted to two pH levels (4 and 8) by addition of concentrated H_2SO_4 for pH4 and NaOH for pH 8 drop by drop, and each level subjected to two adsorbent doses (1g and 2g) and labeled appropriately. Samples 1-4were SP effluent, samples 5-8 were CP effluent while samples 9-12 were DPeffluent subjected to the composites of corn cob, coconut husk and bread fruit peels.

Table I: Experimental design

Untreated Effluents	pH	Adsorbent dose	Samples after Treatment
SP	4	1g	SP4/1
SP	8	1g	SP8/1
SP	4	2g	SP4/2
SP	8	2g	SP8/2
CP	4	1g	CP4/1
CP	8	1g	CP8/1
CP	4	2g	CP4/2
CP	8	2g	CP8/2
DP	4	1g	DP4/1
DP	8	1g	DP8/1
DP	4	2g	DP4/2
DP	8	2g	DP8/2

Fixed Bed Adsorption Study (Packing of Column)

The fixed columns for the treatment of the paint effluent were set up with 250ml burettes held to pivot stands serving as the fixed columns. Sand (2g) obtained from river bank in Owerri was added to each of the twelve columns to form a base. This was to prevent the adsorbent from running off. The sand was washed by pouring deionized water through the column to cover the level of the sand. The water was allowed to drain off the column and the procedure repeated. When properly drained, the columns were packed with their corresponding adsorbent doses according to the experimental design (Table I).

Furthermore, 500ml each of the pH adjusted effluents of pH 4 and pH 8 were introduced to their respective columns. Each effluent was allowed to flow by gravity through the column and treated effluent was collected at the bottom and analysed for physicochemical properties.

Sample analyses

The effluent samples (untreated and treated) were analysed for physical properties, inorganic anions and heavy metals according to Standard Method for the Examination of Water and Waste water, and official methods of analysis of the Association of Official Analytical Chemists (AOAC).

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 was determined 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 entails measuring the absorbance of a sample with a colorimeter at 455nm wavelength.

Analysis of Heavy Metal Concentrations

The analysis of heavy metals was carried outusing FS240AA Agilent Atomic absorption Spectrophotometer. FS240AA Agilent Atomic absorption Spectrophotometer 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. This 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 determined according to official methods of analysis of the Association of Official Analytical Chemists (AOAC).The sample was filled in BOD bottle and 1ml of allylthiourea 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 5days and the mean reading taken as D_1. Dissolved oxygen reading in the incubated sample was estimated by titration and the mean reading taken as D_2. The BOD of the effluent was determined by using the formula:

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

Chemical Oxygen Demand (COD)

Effluent sample (20 ml) was placed into a 250ml conical flask and 10 ml of dichromate solution added. Slowly, 30ml 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 150ml of water, and titrated with ferrous ammonium sulphate solution using ferroin indicator. Parallel to this, a blank determination was carried out using 20ml of distilled water instead of the sample. The COD was calculated as follows:

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

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. 20ml)

Turbidity Determination

Turbidity was determined using WGZ-1B Turbidimeter by Xinrui Instruments and Meters Co. Ltd. Shanghai China. Deionized water (15ml) 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 10NTU (Normal Turbidity Units) diluted from a stock standard solution of 400NTU. Some 15ml of the standard turbidity solution was poured into another cell of the same thickness until a reading of 10NTU was obtained on the digital read out. Again, 15ml 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)

Effluent samples (20 ml) were measured into a pre-weighed 250cm^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:

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

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 below:

Chloride (Argentometric Method): In each case, 25ml of the effluent was pipetted into a 100ml 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.

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

*Phosphate (Ascorbic acid Method)***:** In the determination of phosphate, 6.0g ammonium heptamolybdate was weighed and dissolved in 150ml distilled water in 250ml conical flask. Ascorbic acid (2.6g) was dissolved in 50ml of distilled water in 1 litre volumetric flask to give 0.0007M ascorbic acid. Potassium antimony tartrate (0.14g) was also weighed and dissolved in 20ml distilled water (0.0000086M). 1M stock of concentrated sulphuric acid was prepared by dissolving 10ml of stock in 50ml distilled water.

After, 12.4ml of the ammonium molybdate reagents was transferred to a 50ml volumetric flask, 10ml sulphuric acid added, swirled, and 2.3ml 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 0.4ml molybdate reagent to 20ml of standard or sample in a test tube and swirled to mix. Also, 0.4ml of L-ascorbic acid was added and swirled. The light absorption of the solution was measured at 820nm wavelength. The final concentration of phosphate was determined using the following formula:

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

Nitrate (NO_3^-) (Colorimetric Method): The effluent sample was passed through a copper-coated Cadmium reduction column. Nitrate in the sample was 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 by subtracting nitrite values, which have been separately determined without the cadmium reduction procedure, from the nitrite + nitrate values.

*Sulphate (SO_4^{2-}) (Turbidometric Method):*Deionised water (100ml) 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 420nm 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 adsorbents composites (CH, BFP and CC) was investigated with 1g and 2g of the adsorbents in 500ml 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; using needle valve at 10ml/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 (1g & 2g), and 500ml effluent sample allowed to flow by gravity through the bed. The flow rate was controlled by using needle valve at 10ml/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.

III. RESULTS

3.1 Physical Properties

Physical properties of SP, CP and DP effluent before and after treatment using agro-waste composites are shown in table II. Mean total solid and turbidity values of the treated effluent samples were observed to decline while COD, BOD and colour recorded noticeable increase after treatment.

3.2 Inorganic anions

Mean inorganic anion concentrations of treated paint effluent samples of Chloride, Nitrate and Phosphate were observed to decline compared to the untreated effluent samples but sulphate treated samples were observed to increase when compared to the untreated samples as shown in table III.

3.3 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 IV.

Table II: Mean values for Physical properties of Paint Effluents before and after treatment

	SP Effluent					CP Effluent					DP Effluent				
	Untreated		Treated			Untreated		Treated			Untreated		Treated		
Parameters	SP4/1	SP8/1	SP4/2	SP8/2		CP4/1	CP8/1	CP4/2	CP8/2		DP4/1	DP8/1	DP4/2	DP8/2	
COD (mg/l)	3545.6±0.13	6240.3±0.11	6594.8±0.22	6736.6±0.31	6169.4±0.20	3049.2±0.15	5814.8±0.32	2198.3±0.12	5814.8±0.10	2978.3±0.20	3332.9±0.11	6169.3±0.21	3261.9±0.10	5885.7±0.23	3616.5±0.20
BOD (mg/l)	1276.4±0.29	2246.5±0.24	2374.2±0.11	2425.2±0.12	2220.9±0.21	1097.7±0.25	2093.3±0.23	791.38±0.30	2093.3±0.22	1072.1±0.23	1199.84±0.40	2220.9±0.26	1174.3±0.28	2118.9±0.24	1301.9±0.50
Total solid (mg/l)	68000±0.47	30000±1.25	50500±0.82	37500±0.94	42000±1.30	60500±0.50	43500±1.24	42500±0.90	33500±1.12	41500±1.60	54000±1.40	16500±0.92	42000±1.70	18000±1.41	51000±1.00
Colour (PCU)	2928±0.80	1368±0.50	1750±0.47	740±1.0	7440±1.20	485±0.94	420±0.50	293±1.60	370±1.20	460±0.90	744±0.51	336±0.94	268±0.51	481±1.70	354±1.40
Turbidity (NTU)	14.14±0.40	1.59±0.14	8.66±0.20	5.93±0.19	10.76±0.23	16.22±0.14	6.65±0.21	6.02±0.05	7.61±0.30	2.65±0.22	10.48±0.22	3.53±0.20	2.90±0.25	1.45±0.23	3.90±0.19

Note: Values are Mean±SD of triplicate determination; pH=4 & 8, Adsorbent doses= 1g & 2g

Table III: Mean values for Inorganic anions of paint effluents before and after treatment

	SP Effluent					CP Effluent					DP Effluent				
	Untreated		Treated			Untreated		Treated			Untreated		Treated		
Parameters	SP4/1	SP8/1	SP4/2	SP8/2		CP4/1	CP8/1	CP4/2	CP8/2		DP4/1	DP8/1	DP4/2	DP8/2	
Sulphate SO_4^{2-}(mg/l)	86.98±0.13	125.64±0.12	186.85±0.15	106.31±0.16	199.74±0.11	151.42±0.12	177.19±0.18	0.00	141.75±0.14	0.00	283.50±0.12	112.76±0.16	183.63±0.13	128.86±0.17	241.62±0.19
Phosphate PO_4^{3-} (mg/l)	61.06±0.35	15.13±0.11	22.41±0.13	7.76±0.11	38.2±0.29	54.90±0.42	29.13±0.31	0.00	27.73±0.61	8.96±0.29	53.78±0.35	0.00	31.93±0.15	0.00	52.10±0.90
Nitrate NO_3^- (mg/l)	64.73±0.50	21.76±0.82	7.76±0.92	27.13±0.34	26.71±0.38	61.89±0.30	24.85±0.51	7.90±0.47	33.11±0.89	23.57±0.30	61.32±0.32	36.32±0.27	5.20±0.33	33.83±0.38	23.86±0.41
Chloride Cl^- (mg/l)	5422.62±0.77	5316.12±0.41	3825.12±0.38	5325.00±0.51	3967.12±0.39	7588.12±0.52	14910.0±0.42	17386.12±0.36	14910.0±0.40	6168.12±0.39	5919.62±0.56	44730.00±0.89	5316.12±0.36	3195.00±0.91	5671.12±0.41

Note: Values are Mean±SD of triplicate determination; pH= 4 & 8, Adsorbent doses= 1g & 2g

Table IV: Mean values for heavy metal of paint effluents before and after treatment

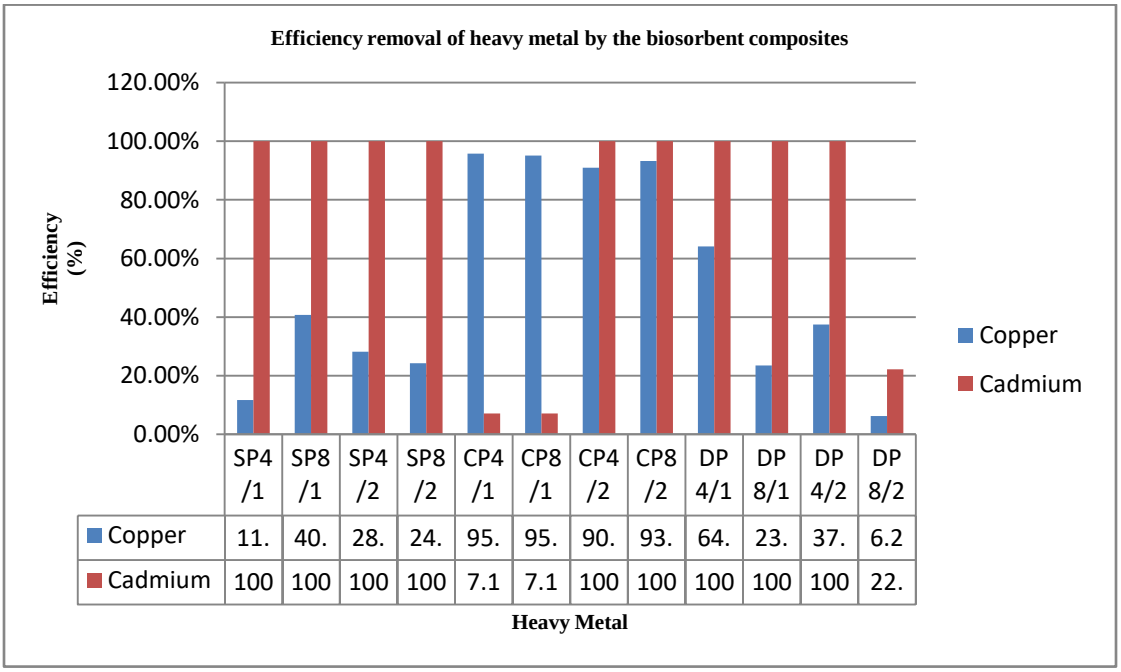
	SP Effluent					CP Effluent					DP Effluent				
	Untreated		Treated			Untreated		Treated			Untreated		Treated		
Parameters	SP4/1	SP8/1	SP4/2	SP8/2		CP4/1	CP8/1	CP4/2	CP8/2		DP4/1	DP8/1	DP4/2	DP8/2	
Copper, Cu (ppm)	0.103±0.04	0.091±0.03	0.061±0.01	0.132±0.06	0.0078±0.00	4 0.83±0.38	0.035±0.01	60.041±0.02	0.075±0.03	0.056±0.01	0.064±0.02	0.023±0.01	0.049±0.03	0.040±0.01	80.060±0.04
Nickel, Ni (ppm)	0.00	0.011±0.01	0.068±0.03	0.017±0.01	0.050±0.02	0.00	0.109±0.05	0.117±0.10	0.054±0.03	0.033±0.02	0.00	0.060±0.03	0.037±0.01	70.100±0.05	0.007±0.003
Lead, Pb (ppm)	0.013±0.01	0.00	0.00	0.329±0.15	0.00	0.004±0.002	0.00	0.346±0.20	0.382±0.18	0.350±0.25	0.178±0.08	0.240±0.11	0.165±0.07	0.404±0.19	0.699±0.32
Cadmium, Ca (ppm)	0.022±0.01	0.00	0.00	0.00	0.00	0.028±0.013	0.00	0.026±0.01	20.026±0.013	0.00	0.018±0.011	0.00	0.00	0.00	0.014±0.012

Note: Values are Mean±SD of triplicate determination; pH= 4 & 8, Adsorbent doses= 1g & 2g

Efficiency of Bio-sorbent Composites

Efficiencies of removal of heavy metals and inorganic anions by the biosorbent composites in the paint effluent samples were calculated. The results showed that efficiency of removal of cadmium was highest on samples SP4/1, SP8/1, SP4/2, SP8/2, CP4/2, CP8/2, DP4/1, DP8/1, and DP4/2. Meanwhile, Copper recorded highest efficiency of removal on CP4/1, CP8/1 and DP8/2 samples. The results of efficiency removal of inorganic anions shows that Nitrate were highest on samples SP8/1, SP4/2, SP8/2, DP8/1 and DP8/2. Phosphate recorded highest on SP4/1, CP8/1, CP4/2, DP4/1 and DP4/2 samples. While Chloride was highest on samples CP4/1 and CP4/2. The dose of peels at which purification was best achieved was also ascertained by the efficiency calculation. It was observed that 1g of the composite was the best dose for purification (Figures 1&2).

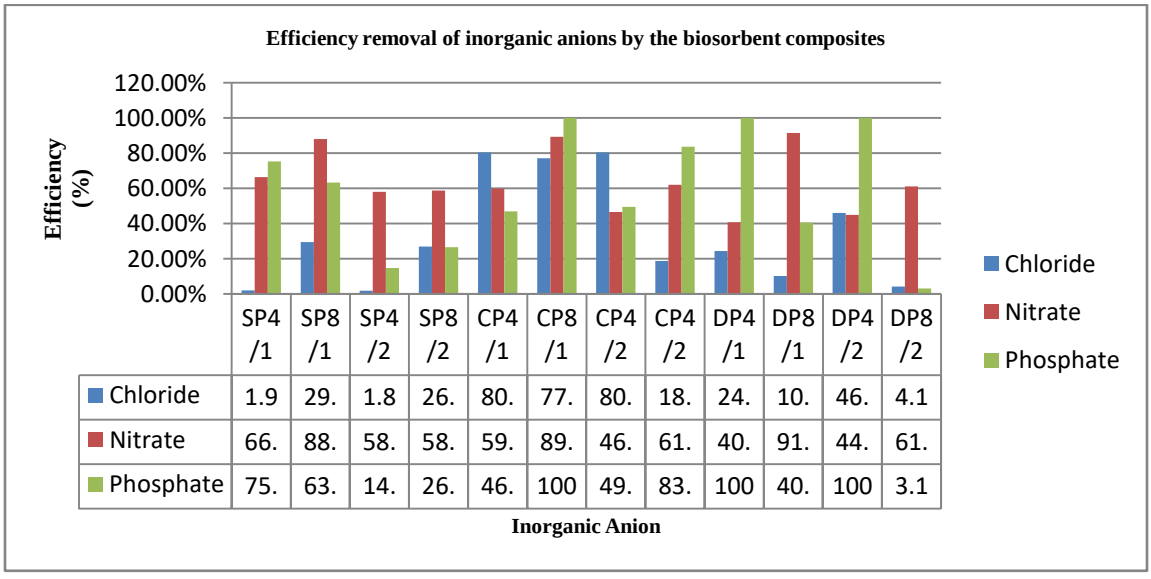
Heavy Metals



	SP4/1	SP8/1	SP4/2	SP8/2	CP4/1	CP8/1	CP4/2	CP8/2	DP 4/1	DP 8/1	DP 4/2	DP 8/2
Copper	11.	40.	28.	24.	95.	95.	90.	93.	64.	23.	37.	6.2
Cadmium	100	100	100	100	7.1	7.1	100	100	100	100	100	22.

Fig. 1: Efficiency removal of heavy metal by the biosorbent composites

Inorganic Anions



	SP4/1	SP8/1	SP4/2	SP8/2	CP4/1	CP8/1	CP4/2	CP4/2	DP4/1	DP8/1	DP4/2	DP8/2
Chloride	1.9	29.	1.8	26.	80.	77.	80.	18.	24.	10.	46.	4.1
Nitrate	66.	88.	58.	58.	59.	89.	46.	61.	40.	91.	44.	61.
Phosphate	75.	63.	14.	26.	46.	100	49.	83.	100	40.	100	3.1

Fig. 2: Efficiency removal of inorganic anions by the biosorbent composites

Experimental Conditions

Effect of pH

pH effect on adsorption of heavy metals by the composite shows that at pH 4, adsorption was Cu, 54.68% and Cd, 84.52% while at pH8, it was 47.17% and 71.56% for Cu and Cd respectively. Adsorption of inorganic anions by the composite shows chloride, 39.15% and 27.75%, nitrate, 52.72% and 75.07%, and phosphate, 64.38% & 52.89% at pH 4 and 8 respectively (figures 3 & 4).

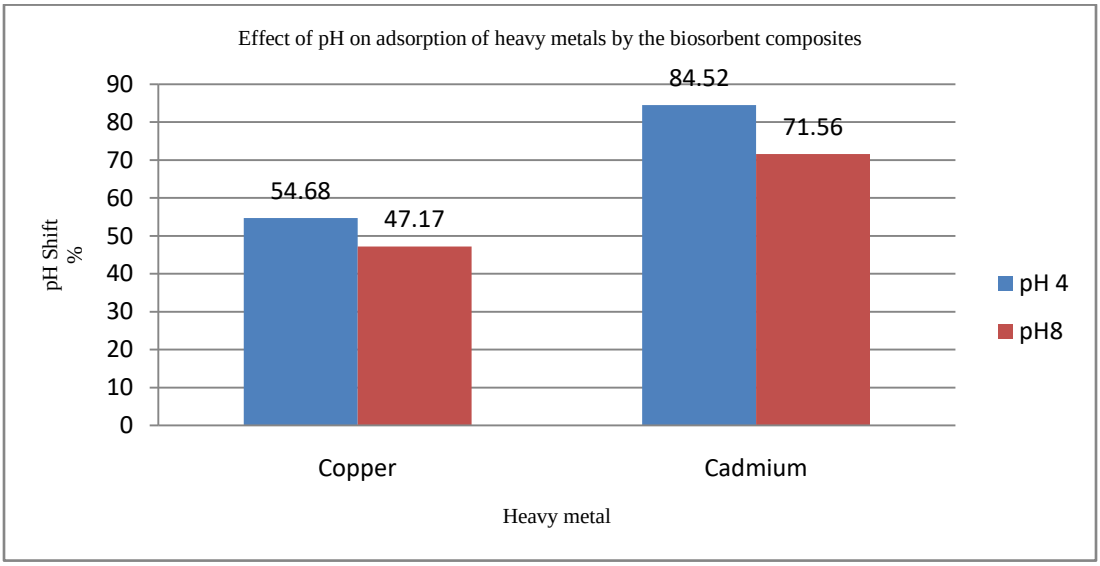


Fig. 3: Effect of pH on adsorption of heavy metals by the biosorbent composites

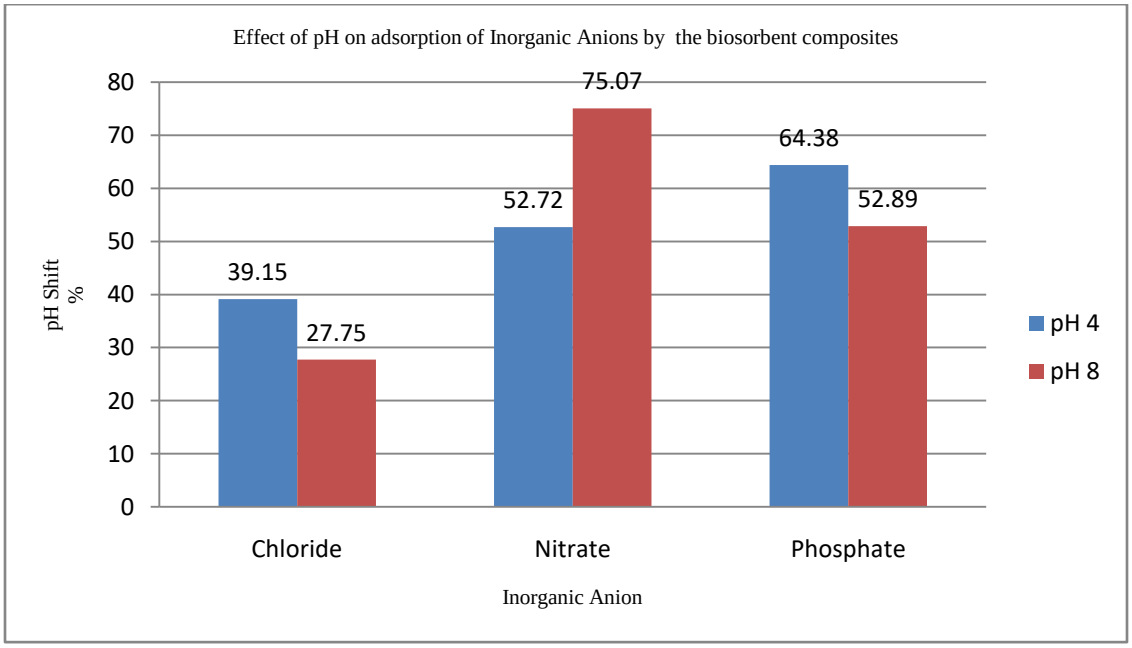


Fig. 4:Effect of pH on adsorption of Inorganic Anions by the biosorbent composites

Effects of Adsorbent Dose

The effect of adsorbent dose on adsorption of heavy metals by the composite shows, 1g dose recorded 55.13% treatment efficiency and 2g, 46.73% for copper; 1g (69.05%) and 2g (87.04%) for cadmium. Adsorption of Inorganic anions by the biosorbent composites shows chloride was removed by dose 1 g at efficiency of 37.25% and 2g, 29.65%; Nitrate, 1g (72.61%) and 2g (55.20%), and Phosphate, 1g (71.01%) and 2g (46.25%) as shown in figures 5 & 6.

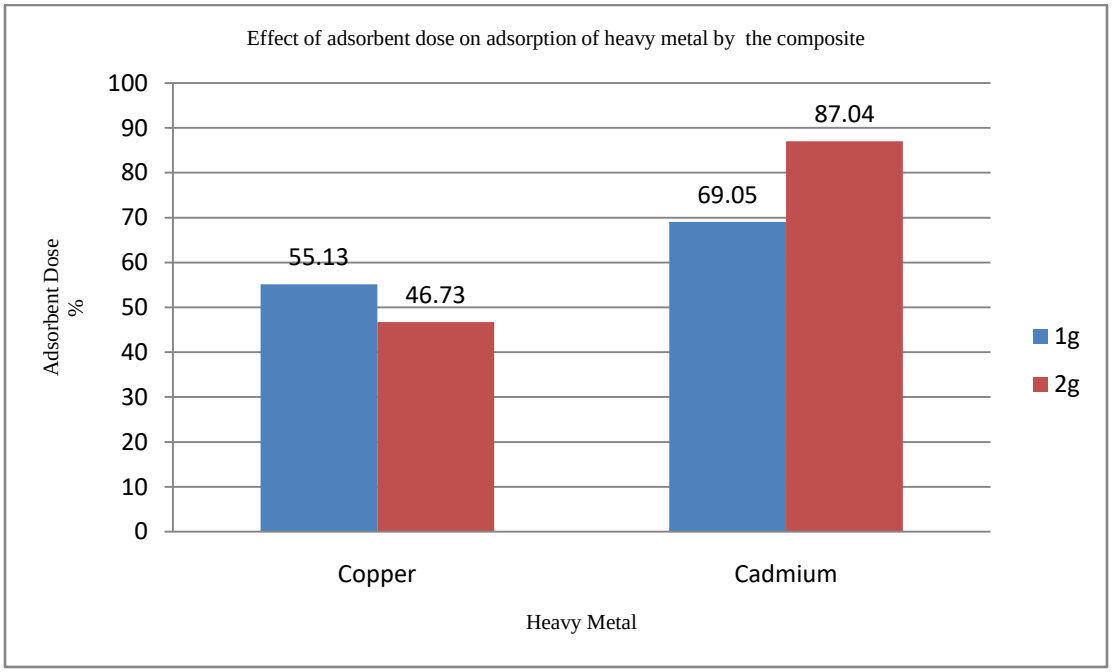


Fig. 5:Effect of adsorbent dose on adsorption of heavy metal by 1 g and 2 g composite doses

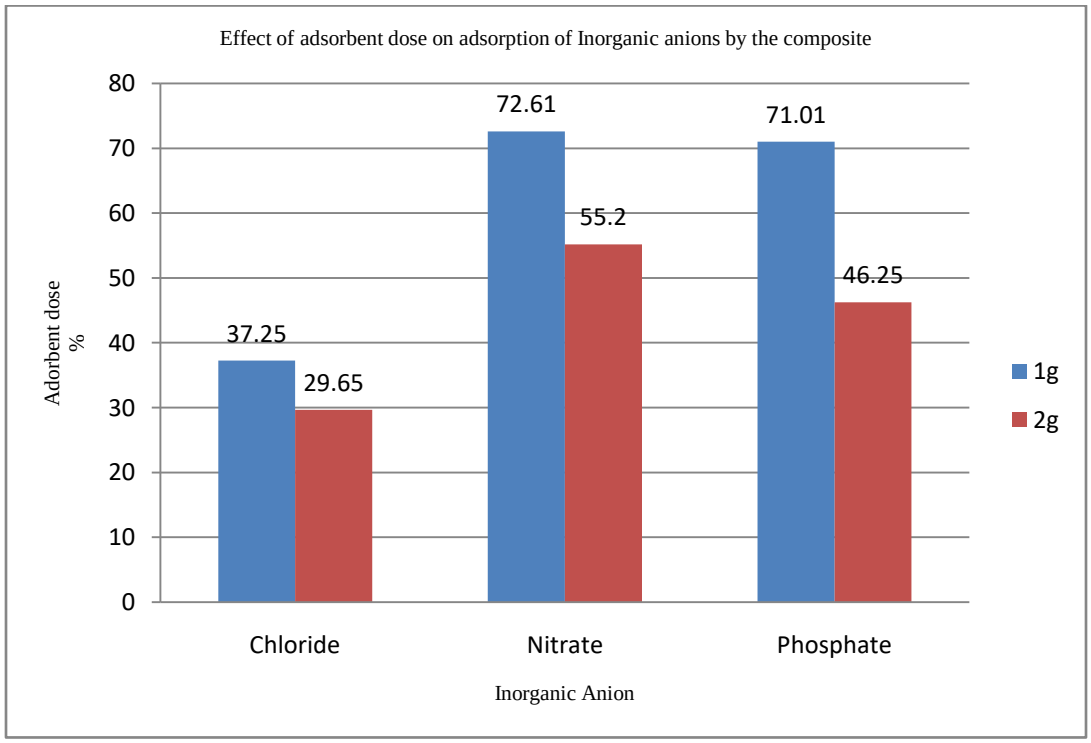


Fig. 6:Effect of adsorbent dose on adsorption of inorganic anions by 1 g and 2 gcomposite doses

Adsorption Isotherm Study

The adsorption isotherm study was conducted and the equilibrium data was fitted into Bohart – Adams, Thomas and Yoon – Nelson isotherm models and the applicability was judged with the correlation coefficient (R^2) as shown in Table V. Considering the values of R^2 for the models fit to the experimental data, it can be observed that Yoon – Nelson isotherm models had the highest correlation coefficient values. The constants of the isotherm models were evaluated from slope and intercepts (Figures 7-21).

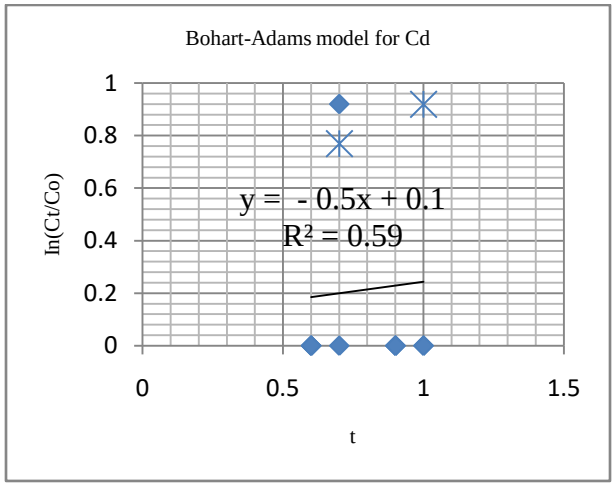


Fig. 7: Bohart-Adams model for Cd

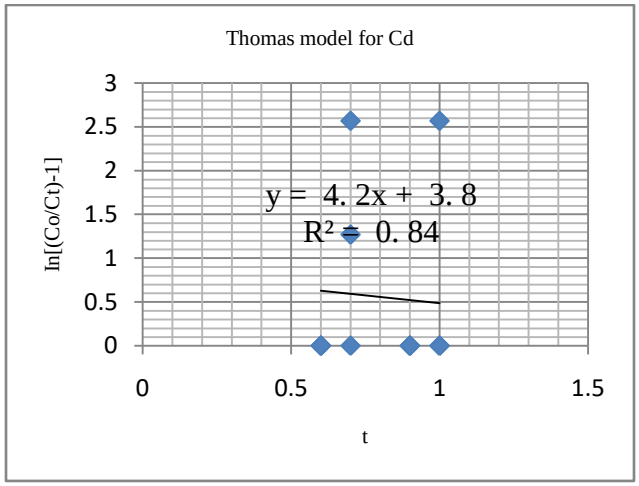


Fig. 8: Thomas model for Cd

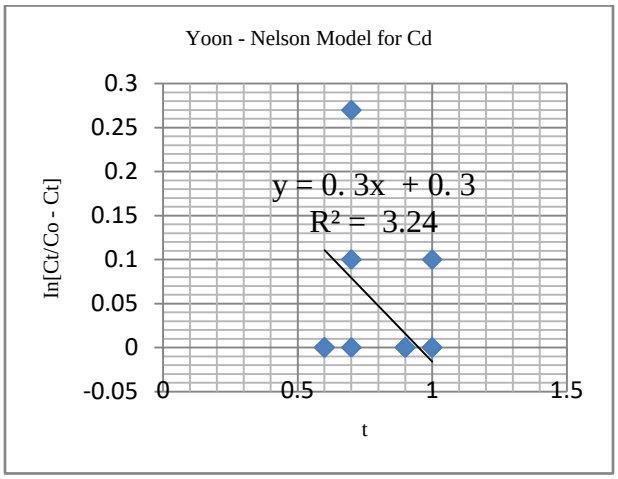


Fig. 9:Yoon - Nelson Model for Cd

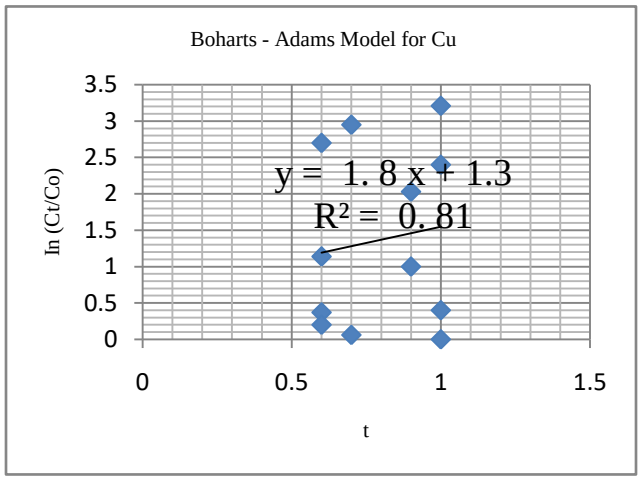


Fig. 10:Boharts - Adams Model for Cu

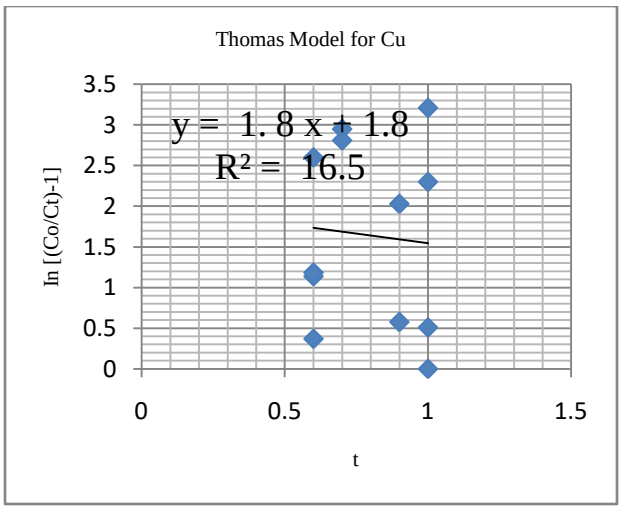


Fig. 11:Thomas Model for Cu

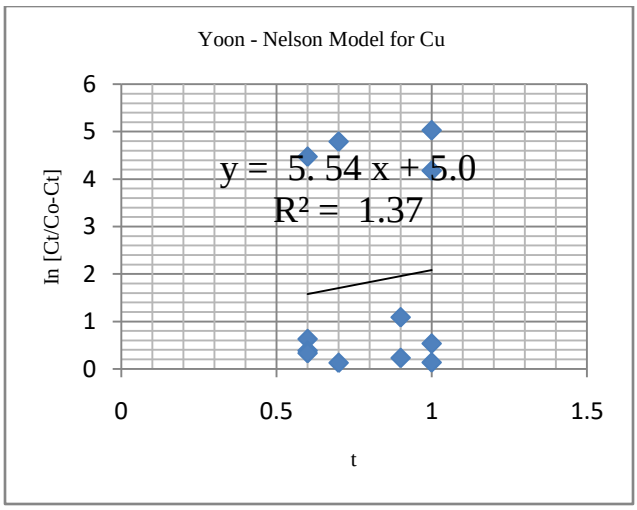


Fig. 12:Yoon - Nelson Model for Cu

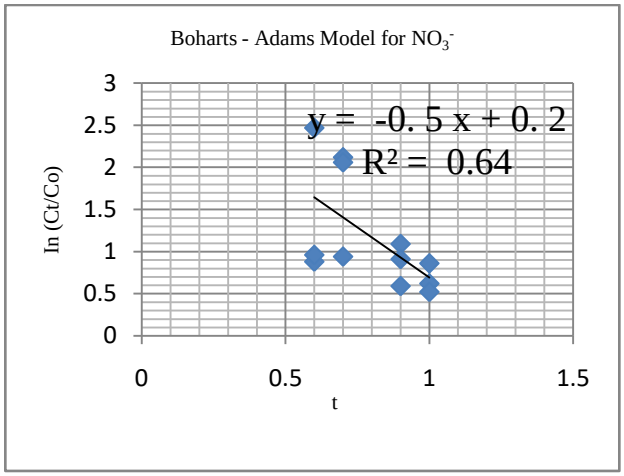


Fig. 13: Boharts - Adams Mode for NO_3^-

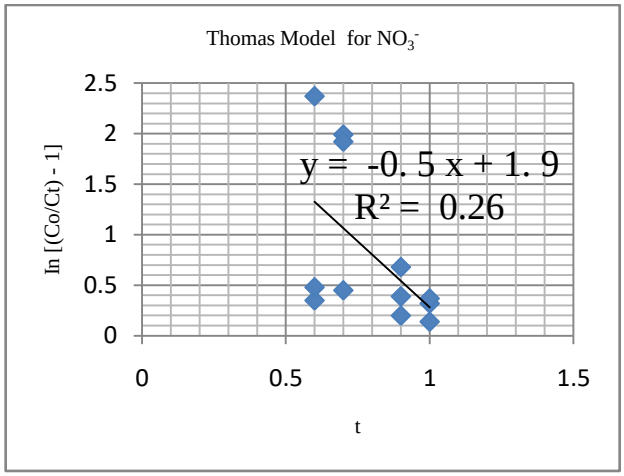


Fig. 14: Thomas Model for NO_3^-

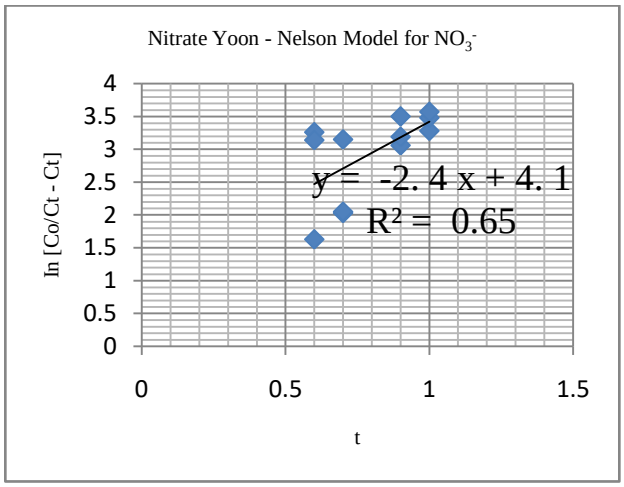


Fig. 15:Yoon - Nelson Model for NO_3^-

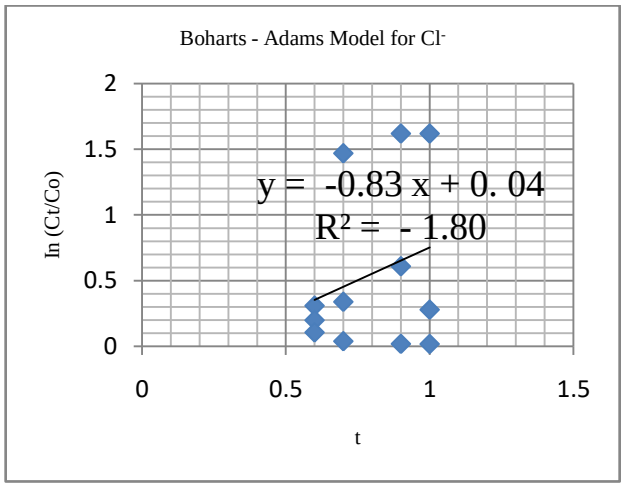


Fig. 16: Boharts - Adams Model for Cl^-

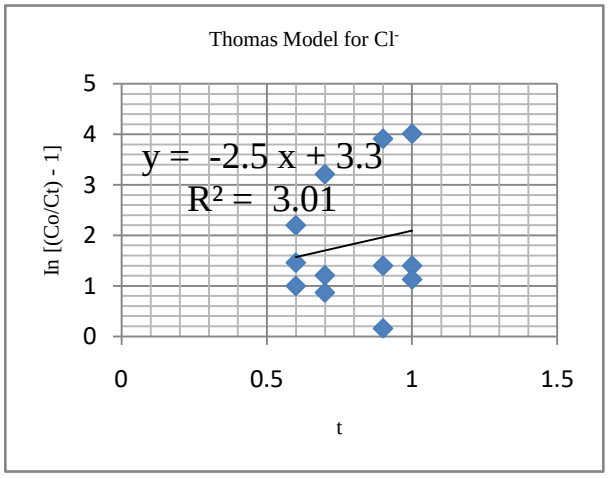


Fig. 17: Thomas Model for Cl^-

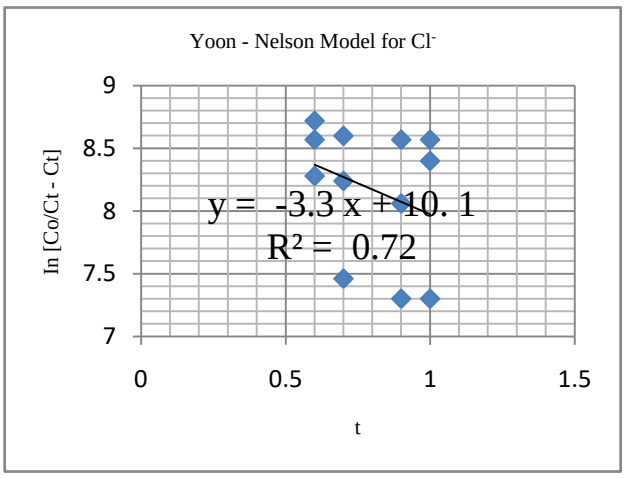


Fig. 18:Yoon - Nelson Model for Cl^-

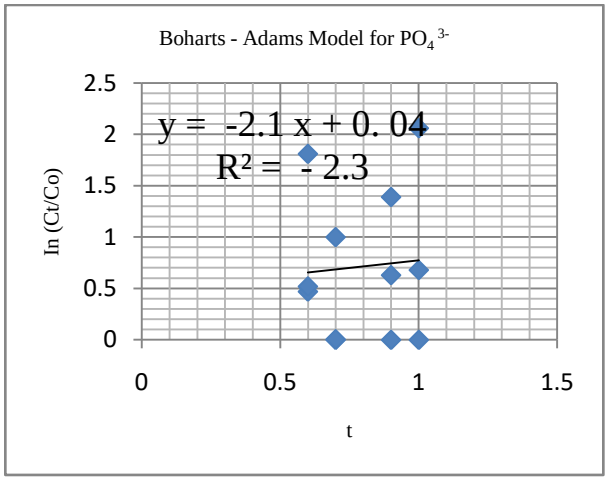


Fig. 19: Boharts - Adams Model for PO_4^{3-}

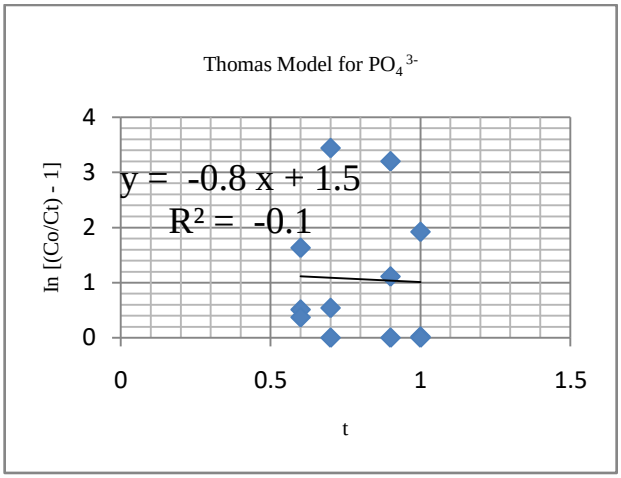


Fig. 20:Thomas Model for PO_4^{3-}

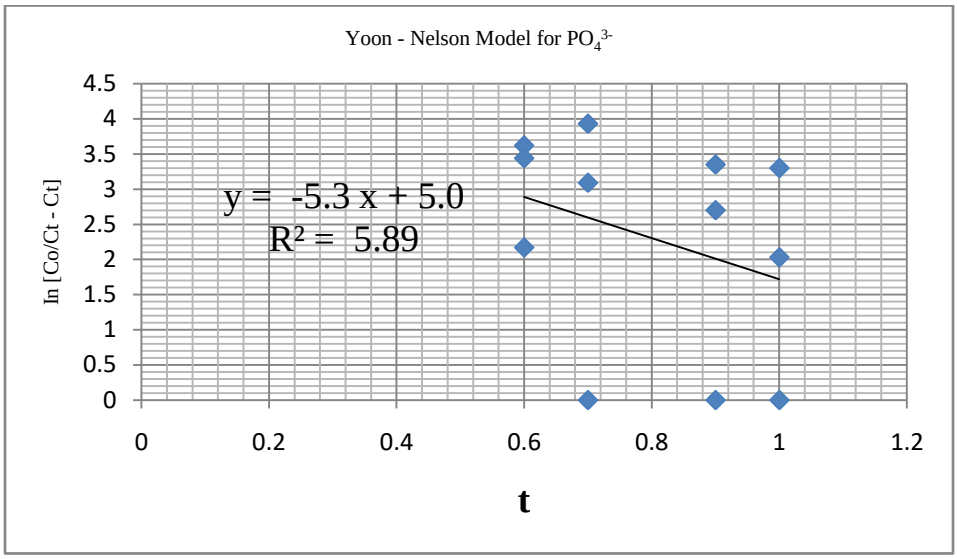


Fig. 21: Yoon - Nelson Model for PO_4^{3-}

Table V: Parameters for isotherm models for adsorptions of heavy metals and inorganic anions

Isotherm Models	Parameters	Cd	Cu	NO_3^-	Cl^-	PO_4^{3-}
Bohart – Adams $In\frac{C}{C_o} = K_{AB}C_o t - K_{AB}N_o\frac{Z}{U_o}$	N_o	0.5	1.8	-0.5	-0.83	-2.1
	K_{AB}	0.1	1.3	0.2	0.04	0.04
	R^2	0.59	0.81	0.64	-1.80	-2.3
Thomas $In\left(\frac{Co}{Ct}-1\right) = \frac{K_{Th}\,q_o\,M}{Q} - K_{Th}\,C_o\,t$	q_o	4.2	1.8	-0.5	-2.5	-0.8
	K_{Th}	3.8	1.8	1.9	3.3	1.5
	R^2	0.84	16.5	0.26	3.01	-0.1
Yoon – Nelson $In\left[\frac{C_t}{C_o} - C_t\right] = K_{YN}\,t - \pi\,K_{YN}$	π	0.3	5.54	-2.4	-3.3	-5.3
	K_{YN}	0.3	5.0	4.1	10.1	5.0
	R^2	11.24	1.37	0.65	0.72	5.89

IV. DISCUSSION

4.1 Physical Properties

The Biochemical Oxygen Demand is a measure of the amount of biodegradable matter in the wastewater. It is a very essential parameter in water quality assessment. The result revealed that there was a noticeable increase in BOD and COD levels on the treated paint effluent samples compared to the untreated effluent samples. This high level of BOD and COD observed were probably due to the presence of high organic matters of the composites of the agrowaste. It also could be as result of the adjusted pH levels, as pH 4 samples showed higher BOD and COD values than pH 8 samples. This showed that treatment was not effective in removing COD and BOD from the effluent sample. Individually, all the adsorbents in previous studies have shown high percentage removal of both COD and BOD with corn cobs having 83.3% removal of COD [14], and coconut husk having 68% removal [15]. The mean turbidity values for the untreated effluents showed the highest value as 16.22 NTU and the least value as 10.48NTU. The highest mean turbidity value for the treated sample with composite A was 10.76NTU and the least, 1.59NTU as shown in Table II. The values reported in this work are consistent with findings of reference [16]. Total Dissolved Solids (TDS) describes the amount of dissolved compounds in the water and is similar to conductivity. Water is a good solvent and picks up impurities easily. 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 works of reference [14]. Colourvalues were observed to decrease after treatment when compared with the untreated paint effluent samples which are synonymous with the finding of reference [17].

4.2 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 80.35%. The result is in agreement with the reports of reference [18]. Phosphate can be present as dissolved or particulate matter. The mean phosphate results were observed to decrease with maximum efficiency removal of 100%.The discharge of nitrate presents several water quality concerns. Nitrate contributes to eutrophication of water bodies, which eventually leads to depleted dissolved oxygen levels. For Nitrate, the results show that the treated effluent samples were observed to decrease compared to the untreated effluent samples. The maximum efficiency removal was 91.51%. The result is in accordance with works of reference [19].

4.3 Heavy Metal

The removal efficiency for Cadmium was 100%. Studies by reference [20] reported removal efficiency of 45% using corn cob while reference [21] achieved similar results using coconut coir. The removal efficiency of copper was between 95.78%.Studies carried out by reference [22] using composite of corn cob, groundnut husk and breadfruit peels showed similar adsorption percentage levels. According to reference [23], the biosorption ability of breadfruit peels are efficient towards heavy metals ions, Cd (II) and Cu (II), is so strong that sorption equilibrium attains efficiently. This easily explains the removal of copper and cadmium from the treated effluent samples. Studies carried out by reference [24] revealed that corn cob has potentials, as adsorbent to remove toxic heavy metal like Lead (Pb) from industrial waste water. Therefore, the increase of Lead values in the treated effluent samples can only be explained in terms of the leaching out in either of the adsorbents during treatment with the help of the adjusted pH levels

Effects of pH

pH variation is one of the most important parameters controlling uptake of heavy metals and inorganic anions from wastewater. Figures 3 & 4 showmaximum uptake of Cadmium (84.52%), chloride (39.15%) and phosphate (64.38%) at pH 4 as against pH 8 which was Cd (71.56%), chloride (37.75%) and phosphate (52.89%). This behavior can be explained by taking into account that at low pH value, the dissociation of carbonyl groups and hydroxide are affected by reducing the sorption capacity of the biomass. This result is consistent with findings of reference [25].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. This finding is in agreement with the works of reference [26].

Effect of Adsorbent Dose

The results for adsorptive removal of heavy metals and inorganic anions with respect to adsorbent dose are shownin Fig.5 & 6. It was observed that optimum adsorption was obtained at 1g adsorbent dose on chloride, phosphate and nitrate compared to 2g adsorbent dose. The increase in adsorption is attributed to the increase of the available biosorption surfaces and sites [27]. It was observed that adsorption capacity was found decreasing further with increase in dosage which is in consistent with the findings of reference [16].

Adsorption Isotherm Models

The study of isotherms helps in describing the adsorption mechanisms of heavy metals and inorganic anions, where they are characterized by specific constants which express the surface properties of affinity of the composite by ions in effluent. Bohart-Adams, Thomas and Yoon- Nelson models were adopted in the present study. The experimental data fitted marginally was satisfactory to Thomas and Bohart-Adams models but the correlation coefficient between the experimental values and the adsorption isotherm was considered high on Yoon-Nelson model. Therefore, the

experimental behavior is best explained by the Yoon-Nelson isotherm model which is in agreement with reference [20].

V. CONCLUSION

The results obtained in this study indicated that the corn cob, coconut husk and bread fruit peels composites have good performance as bio-sorbents in the removal of heavy metals and inorganic anions from paint effluent. This study has also shown that varying experimental conditions such as pH and adsorbent dose, affects adsorption process for example, cadmium, chloride and phosphate 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 1g which means that the lower the adsorbent dose the more effective the treatment. In addition, it was observed that Yoon-Nelson adsorption isotherm model was able to describe the equilibrium data.T his research work shows that the use of corn cob, coconut husks and breadfruit peels as composites reveals high efficiency in reducing the concentrations of physicochemical properties of paint industrial effluents.

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