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Investigative Study of Kaolin, Sand and Plant Biomass *(Spathodea campanulata)* as Potential Adsorbents for Treating Industrial Effluents

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Abstract

Physico-chemical analysis, Heavy metals determination and improvised treatment processes were carried out on raw effluent collected from an Industrial area in Nigeria. The effluent was treated with a combination of three adsorbents (kaolin, sand and plant biomass) in the form of Adsorbent Y and Z. The Physico-chemical analysis of the raw effluent gave the following results: Total Solids (250 mg/1), Suspended Solids (30 mg/1), Dissolved Solids (220 mg/1), pH (6.75), Turbidity (0.02 NTU), Conductivity (326 µs/cm), Temperature (27°C), Biochemical Oxygen Demand (3.7 mg/l), Chemical Oxygen Demand (4.1 mg/l), Dissolved Oxygen (6.5 mg/l), Sulphate (200 mg/l), Nitrate (18 mg/l), Phosphate (215 mg/l), Chloride (21.87 mg/l), Acidity (31.4 mg/l $CaCO_3$), Alkalinity (185.2 mg/l $CaCO_3$), Hardness (45.5 mg/l $CaCO_3$). The heavy metals concentration are Iron (0.22 ppm), Cadmium (0.01 ppm), Manganese (0.03 ppm), Chromium (0.82 ppm), Copper (0.06 ppm), Nickel (0.05 ppm) and Zinc (0.35 ppm). The values of the treated effluents were considerable lower indicating a measure of treatment. The study showed a greater removal rate for some of the contaminants. Adsorbent-Y showed a relatively high adsorption capacity for many parameters in comparison with Adsorbent-Z. Hence, the prepared adsorbents are highly suitable for the removal of certain pollutants/contaminants in the treatment of wastewater discharged by Industries.

Keywords

Biomass, Adsorbents, Adsorption, Heavy Metals, Environment

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1. Introduction

The discharge of wastewater from various industrial processes into the environment is of great concern to humanity. The continued indiscriminate disposal of these effluents have grossly endangered the relationship between man and his ecosystem: the degradation of flora and fauna, the pollution of the atmosphere, the contamination of groundwater, the destruction of aquatic life and the overall impairment of human health [1].

Therefore, the removal of various contaminants/pollutants in the environment, most especially in aquatic body is of great necessity. Various treatment technologies aimed at mitigating heavy metal contamination and reductions of organic pollutants [2]. These treatment techniques among which are chemical precipitation, oxidation technologies, reverse osmosis, coagulation/flocculation, membrane filtration etc. have been marred with inefficiencies and production of toxic by-products [3].

Thus, the application of adsorption processes for water and wastewater treatment have been productive due to factors such as cost effectivseness, less labour, availability, affordability etc. Adsorption techniques are highly effective in the removal of organics, inorganics as well as treatment of heavy metal contamination. [4].

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Activated Carbon has achieved wide spectrum of application as a commonly-used adsorbent in waste water treatment. Its frequent utilization is predicated on their good adsorptive capacity, porosity, large surface area and fine particle size. However, the high cost of activated carbon and the adoption of an expensive regeneration upon usage have limited its large scale application as an industrial adsorbent [5].

Consequently, many researchers have beamed their search light on the application of low cost adsorbents such as clay materials, non-edible plant biomass in the treatment of domestic and industrial wastewater before discharge into aquatic body. Chukwujike et al. [6] investigated the treatment of wastewater from paint industries using local and calcined clays. They reported high removal efficiencies for Turbidity, Alkalinity, Biochemical Oxygen Demand, and Chemical Oxygen Demand.

Ahmaruzzaman and Gupta [3] also investigated the potential of Rice Husk (a non-edible plant biomass) in the treatment of water and wastewater. They observed greater reduction rate in the concentrations of Ni, Zn, Pb, Mn, Fe and Cd upon treatment.

As a matter of fact, many Researchers have investigated the utilization of clay and sandy materials as well as non-edible biomass in wastewater treatment. However, few research works have enlightened the scientific community about the combination of naturally occurring clay materials and non-edible plant biomass as an adsorbent for removal of contaminants. Hence, this study is aimed at investigating the potential of the combination of kaolin, pods of Flame of the Forest Plant and Sand as an adsorbent in the treatment of wastewater from detergent and disinfectant-producing industries. Literatures have established the high retention potentials of Kaolin, high affinity potentials of biomass to ions and efficient flow rate enhancement through the application of sand. Harnessing these potentials gives this adsorbent high adsorption potential.

2. Materials and Methods

2.1. Sample Collection and Preparation

The effluent sample was collected from Ikeja Industrial area (the effluent was adjudged to be a blend of waste water from different Industries). The effluent sample collected was a representative of the bulk and various on-site analysis and quality control measures were taken which include measurement of pH and preservation of the ions by the addition of 2ml Nitric acid per litre of sample collected. The sample was transported to the site of analysis bearing in mind various quality control measures. Before carrying out the analysis in the laboratory, the sample was allowed to equilibrate with the temperature and condition of the laboratory in order to obtain reliable and accurate results.

2.2. Sample Analysis

Analysis of the raw effluent and the treated samples were carried out using the standard and established analytical methods [7, 8]

2.3. Temperature, pH, Electrical Conductivity and Turbidity

The temperature, pH, electrical conductivity (EC) and Turbidity of raw and treated effluents were analyzed using degree-calibrated thermometer, Universal Handheld pH meter, conductivity meter, Turbidometer according to the standard methods referenced [8].

2.4. Total Suspended Solids (TSS), Total Dissolved Solid (TDS) and Total Solids (TS) Determination

The TSS, TDS and TS content of the water samples were analysed by standard methods as described by APHA, 1989 [9].

2.5. Total Hardness, Total Alkalinity and Acidity Determination

The total hardness, total alkalinity and acidity of the water samples were analysed using standard methods [7]

2.6. Phosphate Sulphate and Nitrate Determination

The Phosphate, Sulphate and Nitrate content of the water samples were analysed by standard methods as described by Manivaskam [10].

2.7. Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Dissolved Oxygen (DO) Determination

The BOD, COD and DO of the water samples were analysed by standard methods [8]

2.8. Heavy Metals Determination

The water samples were prepared according to the method described by Joel and Amajuoyi [11]. The resulting solution was analyzed for the following heavy metals (Fe, Cd, Mn, Cr, Cu, Ni, Zn and Pb) using Bulk scientific 10/211 VGP Atomic Absorption Spectrophotometer.

2.9. Adsorbent Collection and Preparation

Pure Kaolin samples were collected from the Department of Industrial Design, Federal University of Technology, Akure. The collected samples were dried, pulverized and passed through an appropriate mesh of 18mm to obtain a uniform particle size.

The pods of Flame of the Forest Plant (*Spathodea campanulata)* was obtained from Department of Crop and Pest Management, Federal University of Technology, Akure. The seed of the pods were removed and the pods dried in the oven for several hours at 105°C until constant weight. The dried pods were pulverized and passed through an 18mm mesh size sieve. The powdered pod was washed with tap water, followed by dilute sulphuric acid and then rinsed with distilled water.

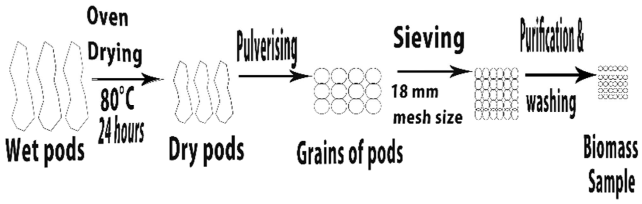

Figure 1. Biomass preparation and purification steps.

The sand stone was collected from the Department of Department of Chemistry, Federal University of Technology, Akure. It was passed through a 18mm mesh size sieve. The resultant sand stone was washed with tap water and then distilled water.

2.10. Adsorbent Experiment

Table 1 showed the proportion of the compounds in the adsorbents. Adsorbent-X is a mixture of Kaolin and Sand; Adsorbent-Z is a mixture of Kaolin, Biomass and Sand stone.

Table 1. Percentage of Compounds in the packed adsorbents.

Packed column	Kaolin (%)	Sand (%)	Biomass (%)
Adsorbent-Y	66.67	33.33	0
Adsorbent-Z	33.33	33.33	33.33

Two columns, A and B made of glass with length and diameter of 80cm and 34 mm were used for the experiment. Column A was packed with 60g of adsorbent-Y, and Column B was packed with 60g of adsorbent-Z. Each column was packed with sizeable quantity of glass wool and incorporated with a flow regulator in order to monitor the flow rate and ensure effective treatment of the effluent.

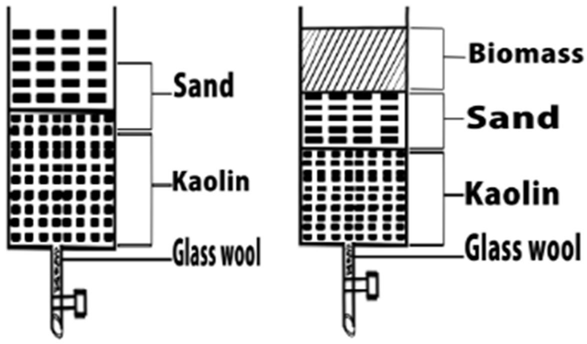

Figure 2. Column Preparation and Adsorbents stratification.

3. Result and Discussion

The results of the Physicochemical Parameters and heavy metals composition of Sample X, Y and Z in comparison with Federal Environmental Protection Agency Standard were summarized in Tables 2 and 3 respectively.

Table 2. Physicochemical Parameters of raw effluent, treated effluent and Federal Environmental Protection Agency (F. E. P. A) Standard.

PARAMETERS	X	Y	Z	F. E. P. A STANDARD
TOTALSOLIDS (mg/l)	250±3.5	30±2.3	36±2.1	N/A
DISSOLVED SOLIDS (mg/l)	220±3.0	28±1.5	34±2.2	2000
SUSPENDED SOLIDS (mg/l)	30±1.8	2±0.3	3±0.2	50
pH	6.75±0.05	6.45±0.03	6.50±0.05	6.5 – 8.5
ALKALINITY (mg/l)	185.2±3.2	151±3.3	148±2.8	160
ACIDITY (mg/l)	31.4±1.2	22.1±0.8	25.5±1.1	29.3
CONDUCTIVITY (µs/cm)	326±2.4	110±2.0	282±2.5	900
HARDNESS (mg/l $CaCO_3$)	45.5±1.3	10.5±0.9	8.6±0.4	200
PHOSPHATE (PO_4^{3-}) (mg/l)	215±2.1	116±1.8	100±2.3	N/A
NITRATE (NO_3^-) (mg/l)	18±1.5	5.1±0.8	6±0.7	20
SULPHATE (SO_4^{2-}) (mg/l)	200±3.3	32±2.4	49±2.9	1000
CHLORIDE (Cl^-) (mg/l)	21.9±1.2	5.6±0.6	15.1±0.9	200
D. O (mg/l)	6.5±0.4	5.5±0.4	2.8±0.1	
B. O. D (mg/l)	3.7±0.2	2.1±0.1	2.8±0.1	50
C. O. D (mg/l)	4.1±0.2	2.3±0.1	3.7±0.1	6-9
TEMPERATURE °C	28±0.1	27±0.1	27.2±0.1	< 40
TURBIDITY (NTU)	0.02±0.003	0.001±0.0002	0.01±0.001	10

N/A = Not Available.
Values given as Mean ± Standard deviation.
Raw effluent = Sample X.
Effluent treated with kaolin and sand = Sample Y.
Effluent treated with kaolin, biomass and sand = Sample Z.

3.1. Physicochemical Parameters of Raw Effluent, Treated Effluent

The results of the physicochemical analysis of the raw and treated effluents were presented in Table 2. Generally, the result showed an apparent reduction in all the measured parameters of the raw effluent (Sample X) as compared with effluent treated with Kaolin and sand (Sample Y) and the effluent treated with Kaolin, Sand and biomass (Sample Z).

The temperature of sample X, Y and Z ranged from 27-27.2 which is below the required standard (<40) by FEPA. Same trend was observed for pH values, this is an indication that the adsorbents did not contribute significantly to change in pH. The inability maybe attributed to the fact the adsorbents are ineffective in acidic medium. Lower pH values may lead to tuberculation and corrosion while higher pH values may result to incrustation, sediment, deposition etc. [12].

The percentage reduction rate of total solids for Adsorbent-Y and Adsorbent-Z were 88% and 86% respectively. Similarly, the reduction rate of total dissolved solids for Adsorbent-Y and Adsorbent-Z were 88% and 85% respectively. Also, the reduction rate of total suspended solids for Adsorbent-Y and Adsorbent-Z are 93% and 90%. This revealed that adsorbent-Y had a better adsorption potential for total solids, total dissolved solids and total suspended solids than adsorbent-Z. The increased efficiency of adsorbent-Y over adsorbent-Z for solid content reduction may be attributed to its large absorptive capacity [13]. In addition, this can be as a result of the finer particle sizes of the components of adsorbent Y. Adsorptive capacity depends on the interface between the pollutants in the raw effluent and the prepared adsorbent [14]. Chukwujike et al. [6] reported a relatively high total dissolved solids reduction of 93% for the treatment of paint effluent using dried local clay. The difference in adsorption efficiency may be as a result of difference in adsorbent dosage, physical affinity and chemical structure of the adsorbents. The amount of total dissolved solid is proportional to the extent of pollution (Nasrullah et al [15].

The values of Acidity and conductivity are lower in the output sample Y (22.1mg/l and 110µs/cm) than sample Z (27.5mg/l and 282µs/cm) whwn compared to the raw effluent - sample X (31.4mg/l and 326µs/cm). Hence, it was observed that Adsorbent-Y significantly reduced the acidity and conductivity content of the raw effluent at an adsorption rate of 30 and 66% respectively as compared to adsorbent-Z. The greater absorption efficiency of Adsorbent-Y over Adsorbent-Z may be as a result of larger particle size of the latter [16]. Conductivity is a measure of the amount of total dissolved salts in a sample.

After the treatment, Sample Y is clearer than sample Z because Turbidity reduction for Adsorbent-Y (95%) is greater than Adsorbent-Z (50%). Adsorbent-Z has high surface area and this may be responsible for relatively large turbidity reduction. The surface area of an adsorbent is directly proportional to its porosity [17]. The adsorption efficiency obtained by Adsorbent-Y in the reduction of turbidity is similar to the 96% removal rate observed for the treatment of paint effluent using calcined clay [6].

From the results obtained for Hardness of the treated effluent although there was excellent reduction, it is quite evident that the output of sample Y contains more salts than sample Z. Adsorbents for sample Z performed better due to the presence of latent functional groups present in the biomass that attracts the magnesium (Mg^{2+}) and calcium (Ca^{2+}) ions responsible for water hardness. Hardness of water is a measure of the amount of calcium or magnesium salts in sample. A very low alkalinity reduction rate for Adsorbent-Y and Adsorbent-Z was achieved. This suggests that the adsorbent little effect on alkalinity of the treated effluent.

Adsorbent Y and Z achieved 84% and 76% reduction respectively for the Sulphate content of the raw effluent indicating that both adsorbents have significant reduction potential of Sulphate ions. The adsorption rate of the phosphate and nitrate content of the raw effluent reduced considerably as shown in Table 2. Upon treatment of the raw effluent, Adsorbent-Y achieved greater Chloride reduction of 74% compared with 31% reduction achieved by Adsorbent-Z. The greater removal efficiency of Adsorbent-Y over Z in the treatment of PO_4^{3-}, NO_3^-, SO_4^{2-} and Cl- may be attributable to its affinity for the ions. High chloride ion is an indication of organic pollution in the water [18].

The COD and BOD values which are of paramount importance are lower in sample Y (2.3mg/l and 2.1mg/l) than in sample Z (3.7mg/l and 2.8mg/l). It was observed that Adsorbent-Y achieved 46% reduction for the DO content compared to Adsorbent-Z with 57% reduction. The percentage reduction reported for BOD using Adsorbent-Y is higher than those reported for BOD (39%) using raw clay [6]. The relatively high adsorption efficiency of Adsorbent-Y may be as a result of the addition of the biomass. Patel and Vashi [19] reported a relatively high COD reduction of 57.3% using 1g/L Activated Carbon in the treatment of detergent effluent. There are several factors such as pH, concentration of adsorbent, concentration of adsorbates etc. that may affect the efficiency of removal. COD, BOD and DO are parameters that measure various biochemical changes in aquatic ecosystem and their attendant influence on metabolic activities of organisms [20].

All the analyzed parameters of Sample X are below the permissible limit of FEPA standard.

Table 3. Heavy metal composition of raw and treated effluent in comparison with FEPA Standard.

SAMPLES	Iron (Fe)	Cadmium (Cd)	Manganese (Mn)	Chromium (Cr)	Copper (Cu)	Nickel (Ni)	Zinc (Zn)	Lead (Pb)
X	0.22	0.01	0.03	0.82	0.06	0.05	0.35	BDL
Y	0.09	BDL	0.01	0.21	0.03	0.01	0.10	BDL
Z	0.10	BDL	0.01	0.37	0.02	0.02	0.09	BDL
FEPA STANDARD	20	< 1	5	< 1	< 1	< 1	< 1	< 1

ppm = Part per million (Unit of measurement); BDL = Below Detection Limit.

3.2. Heavy Metal Composition of Raw and Treated Effluent

The results of heavy metals (Fe, Cd, Mn, Cr, Cu, Ni, Zn and Pb) content of the raw and treated effluents are presented in Table 3. Generally, the result showed an apparent reduction in the level of the heavy metals present in the raw effluent (Sample X) with the exception of few that increased upon treatment.

The result of the heavy metal level measured in ppm (parts per million) were in the order of Cr > Zn > Fe >Cu >Ni > Mn > Cd > Pb for sample X; Cr > Zn > Fe > Cu > Mn = Ni > Cd = Pb for sample Y; and Cr > Fe > Zn > Cu = Ni > Mn > Cd = Pb for sample Z.

The two adsorbents (Y and Z) achieved significant adsorption rate of Fe in the raw effluent. In addition, Adsorbent-Y achieved relatively high removal efficiency for Mn (67%) and Cr (76%) in comparison with Adsorbent-Z which is 67% for Mn and 55% for Cr. A study reported 36% reduction of Cr using Egyptian raw Kaolin [21]. Furthermore, a relatively high adsorption efficiency of 76% was reported for the removal of Mn using Calcined clay [6]. Also, near 100% removal rate was observed for the treatment of Cd using Adsorbent-Y and Z. Talaat et al. [21] observed 47% removal of Cd using Egyptian kaolin in the treatment of heavy metals in wastewater. Similarly, greater removal rate of 80% Ni was observed using Adsorbent-Y viz-a-viz 60% Ni for Adsorbent-Z. The removal efficiency of rice husk for nickel removal was 51.8% for dilute solutions at an adsorbent dose of 20 g/L [22]. Generally, the differences in adsorption efficiencies for Adsorbent Y and Z maybe due to the disparity in the degree of affinity for the adsorbate metals and presence of attendant functional groups to bond to metal ions [23].

According to the result presented in Table 3, the level of Cu in Sample X reduced from 0.06 to 0.02 ppm upon treatment with Adsorbent Z while Cu content of Sample X reduced from 0.06 to 0.03 ppm after treatment with Adsorbent Y. The Zn content of Sample Y is 0.14 ppm, which is indicative of 71% reduction in the Zn level upon treatment with Adsorbent-Y while the Zn content of Sample Z is 0.09 ppm, which mirrors a 74% decrease in the Zn level upon treatment with Adsorbent Z. An adsorption efficiency of 78% and 62% was observed for the removal of Cu and Zn respectively in a synthetic wastewater using Ca-Benotitte as the adsorbent [21]. All the analyzed heavy metals are at a level below the permissible limit of FEPA standard and other monitoring agencies.

4. Conclusion

The application of adsorbents (Kaolin, Sand and Plant Biomass) in the removal of contaminants from industrial effluent has been studied. The utilization of Adsorbent Y (Kaolin and Sand) and Adsorbent Z (Kaolin, Sand and Plant Biomass) proved to be effective in the treatment of effluent from Industries. This has opened an alternative remediation method for waste water treatment using locally sourced, affordable and available materials

Adsorbent Y showed higher degree of treatment of the majority of the physico-chemical parameters and heavy metal contaminations compared to Adsorbent Z.

The study also showed that majority of the analyzed parameters of the treated effluents were below the permissible limit. These adsorbents can be used as primary treatment approach before the effluents are discharged into water ways. This approach is cheap, easy to set up and sustainable.

Conflict of Interest

The Authors declare that there are no conflicts of Interest.

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