

## Treatment of wastewater from vegetable oil industry using modified laterite adsorbent

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### Abstract

The treatment of vegetable oil refining wastewater using modified laterite adsorbent was undertaken. The effluent quality parameters of interest were; colour, electrical conductivity, chlorides, iron, copper, nitrates, manganese, lead, chemical oxygen demand (COD) Biochemical oxygen demand (BOD), dissolved oxygen (DO), total dissolved solids (TDS), total suspended solids (TSS), oil and grease. Effluent waste water samples were treated in an adsorption column set-up using different dosages of low-cost laterite adsorbent. Results obtained after the treatment process showed that all the parameters tested conformed to the Federal Ministry of Environment, Housing and Urban Development (FMEHUD) specification guidelines, with exception of the following parameters which the values were astronomically - BOD (179.425 mg/l) TSS (111.25 mg/l), oil and grease (4.20 mg/l) and electrical conductivity ( $1.26 \times 10^3 \Omega\text{cm}^{-1}$ ). The maximum percentage reduction of the pollutants was achieved at a high dosage of laterite (350g). The adsorption process also obeyed the Freundlich and Langmuir Isotherms and modified laterite was also found to be a promising adsorbent for heavy metal uptake from vegetable oil refining wastewater.

*Keywords:* Removal; Pollutants; Vegetable oil refining wastewater; Laterite adsorbent

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### 1. Introduction

The problem of considerable contamination of the aqueous environment with the pollutants in the industrial effluent water still requires the development of quick and simple methods for waste water effluent treatment prior to discharge. The processes involved in vegetable oil production range from pre-treatment of oilseeds, manufacturing, refining and modification of oils. During these processes, waste and by-products are generated. The operating conditions and processes carried out influence the amount and characteristics of the wastes and by-products generated (Chipasa, 2001). Vegetable oil refining waste waters are known to contain chemical compounds like phenol, heavy metals from bleaching earth, catalysts used in the hydrogenation process, oxidizable substances and fats and oils. Due to quantity and characteristic variations and complexity, wastewater treatment to meet the desired effluent standards is complicated and the choice of methods of wastewater treatment depends on many local conditions and therefore, cannot be standardized. The principal parameters of concern are, pH, electrical conductivity, colour, sulphates, phosphates, chlorides,

total solids, total suspended solids, total dissolved solids, acidity, alkalinity dissolved oxygen, biochemical oxygen demand, lead, chemical oxygen demand, temperature etc.

Several methods are available for treatment of wastewater effluents, such as alkaline chemical precipitation by lime addition, adsorption, ion-exchange process, reverse osmosis, etc. (Gupta, 1998). However, the high cost associated with these methods results in the need for a low-cost and indigenous adsorbent. In this work the feasibility of using modified laterite which is a low-cost adsorbent obtained from natural laterite soil extensively found in several parts of Nigeria is examined.

### 2. Material and methods

The investigations were carried out on freshly collected wastewater samples from a vegetable oil industry situated at Anambra State, Nigeria. The wastewater samples were specifically collected from the final discharge points –refinery and solvent extraction sections of the factory. The laterite sample was collected from Agu-Awka in Anambra state.

### 2.1. Preparation of modified laterite adsorbent

The adsorbent material, locally available lumps of laterite 6kg was milled into smaller particles and sieved using the mechanical sieve of 1.8mm mesh. The sieved sample was stored in a cool dry place prior to activation. Subsequently the laterite sample was weighed into a pot and then 2kg of concentrated sulphuric acid was added (ie in the proportion of 2:1 mass ratio) into the same pot following by addition of 500ml of distilled water to form slurry. The slurry was heated in an electric oven at a temperature of 400°C for 3hours after which it was allowed to cool. Then distilled water was used to wash the activated laterite severally to reduce the acidity. At the normal P<sup>H</sup>, the activated laterite was kept in an oven to dry at a temperature of 100°C for 2 hours and stored in an air – tight container.

### 2.2. Characterization of waste water effluent sample

The wastewater samples were characterized on the same day of collection, when this was not possible, they were preserved at 4°C following standard procedures obtained from literature (Tchobangoglous, 1998). Analytical grade reagents were used in all experiments. The wastewater samples were analysed for; electrical conductivity temperature, pH, total dissolve solids, acidity, alkalinity, chlorides, copper, iron, nitrates, magnesium, calcium, lead, aluminium, chemical oxygen demand(COD), dissolved oxygen (DO) biochemical oxygen demand BOD. The tests were

carried out using standard methods for the examination of water and waste water (Eaton et. al., 1998).

### 3. Treatment of wastewater

The adsorption column used was a glass tube (100 x 14cm) made of a Perspex material with a coarse sintered glass disc and a tap at the bottom. The column was prepared by careful filling of activated laterite (200g), the bed length being 40cm. A fixed volume of the effluent water sample was allowed to pass through the column from the 2800ml capacity wastewater storage tank. After about 2 hrs the treated wastewater started dropping from the tap into the beaker. The samples were collected at the time intervals of 20mins, 40mins, 60mins, 80mins, 100mins, till it got to a point at which the laterite stopped adsorbing wastewater (i.e adsorbent equilibrium point or saturation point) at 110mins. The concentration of the pollutants in the treated sample determined following the standard procedure. The whole process was repeated using different dosages of activated laterite - 250g, 300g and 350g respectively, and the various concentrations of the pollutants in the treated samples were determined accordingly.

### 4. Results and discussions

The following values were generated from the analysis carried out (before and after treatment)

Table 1  
Quality parameters of wastewater effluent sample before treatment and FMEHUD standard

| <i>Parameters</i>                              | <i>Effluent sample before treatment</i> | <i>FMEHUD specification</i> |
|--|---|-----------------------------|
| Colour (hazen disc )                           | 70                                      | 7.00                        |
| pH   | 6.0                                     | 6.9                         |
| Electrical Conductivity $\Omega\text{cm}^{-1}$ | $2.8 \times 10^3$                       | 100                         |
| Total solids (TS) (mg/l)                       | 3204                                    | 2030                        |
| Alkalinity (mg/l)                              | 350                                     | -                           |
| Chlorides (mg/l)                               | Nil                                     | -                           |
| Copper (mg/l)                                  | 4.35                                    | -                           |
| Iron (mg/l)                                    | 0.418                                   | 0.20                        |
| Nitrates (mg/l)                                | $0.273 \times 10^3$                     | 20.0                        |
| Maganese (mg/l)                                | 8.5524                                  | 5.0                         |
| Lead (mg/l)                                    | 18.36                                   | $\leq 1.0$                  |
| Temperture (°C)                                | 50                                      | $\leq 40$                   |
| Chemical Oxygen Demand COD (mg/l)              | 352                                     | 20.0                        |
| Biochemical Oxygen Demand(BOD) (mg/l)          | 358.49                                  | 50.0                        |
| Specific Gravity                               | 1.0763                                  | -                           |
| Acidity (mg/l)                                 | 400                                     | -                           |
| Total dissolve solids (TDS) (mg/l)             | 2432                                    | 2000.00                     |

|                                    |         |        |
|------------------------------------|---------|--------|
| Total suspended solids(TDS) (mg/l) | 772     | 20.00  |
| Calcium (mg/l)                     | 380.76  | 200.00 |
| Aluminium (mg/l)                   | 0.56668 | 3600   |
| Oil and grease (mg/l)              | 27.40   | 10.00  |
| Dissolved Oxygen (DO) (mg/l)       | 6.49    | ≤ 5.0  |

Table 2

Quality Parameters of wastewater effluent sample after treatment for different adsorbent dosages

| Parameters                          | 200g                   | 250g                    | 300g                    | 350g                    |
|-------------------------------------|------------------------|-------------------------|-------------------------|-------------------------|
| Colour Hazen disc                   | 5.0                    | 5.0                     | 5.0                     | 5.0                     |
| pH                                  | 4.0                    | 3.8                     | 3.7                     | 3.5                     |
| Aluminium (mg/l)                    | 0.5604                 | 0.5594                  | 0.5580                  | 0.5570                  |
| Conductivity (scm <sup>-1</sup> )   | 1.45 x10 <sup>3</sup>  | 1.3 x10 <sup>-3</sup>   | 1.2 x10 <sup>-3</sup>   | 1.0 x10 <sup>-3</sup>   |
| Temperature °C                      | 25                     | 25                      | 25                      | 25                      |
| Dissolved Oxygen (DO) (mg/l)        | 5.40                   | 5.10                    | 5.23                    | 5.33                    |
| Total Solids (TS) (mg/l)            | 645                    | 650                     | 655                     | 674                     |
| Alkalinity (mg/l)                   | Nil                    | Nil                     | Nil                     | Nil                     |
| Chloride (mg/l)                     | Nil                    | Nil                     | Nil                     | Nil                     |
| Copper (mg/l)                       | 1.50                   | 1.40                    | 1.35                    | 1.32                    |
| Iron (mg/l)                         | 0.340                  | 0.335                   | 0.330                   | 0.322                   |
| Nitrates (mg/l)                     | 0.273x10 <sup>-3</sup> | 0.273 x10 <sup>-3</sup> | 0.273 x10 <sup>-3</sup> | 0.273 x10 <sup>-3</sup> |
| Manganese (mg/l)                    | 3.140                  | 4.80                    | 4.60                    | 4.30                    |
| Lead (mg/l)                         | 0.228                  | 0.222                   | 0.218                   | 0.212                   |
| Chemical Oxygen demand (mg/l)       | 60.0                   | 55.50                   | 55.0                    | 55.0                    |
| Specific gravity                    | 1.0147                 | 1.0134                  | 1.0134                  | 1.0139                  |
| Acidity (mg/l)                      | 3568.0                 | 3578.0                  | 3600.0                  | 3625.0                  |
| Total dissolved solids (TDS) (mg/l) | 570.10                 | 560.0                   | 500.70                  | 494.0                   |
| Total suspended solids (TSS) (mg/l) | 142.0                  | 121.0                   | 98.00                   | 84.0                    |
| Calcium (mg/l)                      | 701.40                 | 701.40                  | 701.40                  | 701.40                  |
| Oil and Grease                      | 10.0                   | 9.0                     |                         | 6.50                    |
| Biochemical oxygen demand (mg/l)    | 190.15                 | 185.02                  | 172.50                  | 170.0                   |

Table 3

Variation of effluent water quality after treatment with time (on adsorbent dosage of 350g)

| Parameters                | 20mins | 40mins | 60mins | 80mins | 100mins |
|---------------------------|--------|--------|--------|--------|---------|
| TSS (mg/l)                | 181.00 | 183.00 | 189.00 | 204.00 | 184.00  |
| DO (mg/l)                 | 5.20   | 5.30   | 5.35   | 5.37   | 5.20    |
| p <sup>H</sup>            | 3.50   | 3.60   | 3.70   | 3.75   | 3.65    |
| Copper (cu) (mg/l)        | 1.11   | 1.15   | 1.17   | 1.18   | 1.12    |
| (BOD) <sub>5</sub> (mg/l) | 185.00 | 192.30 | 195.00 | 195.00 | 191.00  |
| COD (mg/l)                | 54.40  | 58.00  | 60.20  | 62.40  | 59.00   |
| TDS (mg/l)                | 500.10 | 520.20 | 570.00 | 580.03 | 572.10  |
| Iron (mg/l)               | 0.320  | 0.322  | 0.324  | 0.324  | 0.323   |
| Aluminium (mg/l)          | 0.5560 | 0.5571 | 0.5574 | 0.5580 | 0.5550  |
| Specific gravity          | 1.0122 | 1.0133 | 1.0134 | 1.0134 | 1.0134  |
| Lead (mg/l)               | 0.20   | 0.211  | 0.212  | 0.214  | 0.210   |

The results obtained from the analysis carried out both before and after treatment show that most of the parameters tested for before the treatment were very much above the (FMEHUD) specified standard but after treating with the activated laterite a high percentage reduction was achieved with respect to the following parameters; COD, temperature, Colour, lead, total solids, total dissolved solids, iron, manganese, sulphate and chloride, BOD and TSS (Tables 1 and 2). However, there was no appreciable effect on conductivity and calcium values respectively,

#### 4.1. Effect of laterite dosage on adsorption

The minimum amount of laterite corresponding to the maximum solute sorption at a definite solute concentration was taken as the optimum dose. Laterite dose was varied from 200 to 350g and there was increase in the percent uptake of pollutant ions as seen from Tables 1 and 2. Also the amount of the pollutants ions adsorbed was seen to be a function of adsorbent dosage. Hence increase in the adsorbent dosage increased the amount of ion adsorbed except for the

nitrate and calcium contents of the wastewater which showed no effects.

#### 4.2. Effect of contact time on adsorption

The effect of contact time on the adsorption operation process can be seen from Table 3. It shows that the amount of adsorbate increases as the contact time increases. This is because at a longer time more of the pollutants are adsorbed on the adsorbents. The adsorption of most pollutants on the adsorbents were found to be more at the contact time of 80mins and gradually decreased until at the contact time of 110mins where the laterite stopped adsorbing wastewater (i.e equilibrium point or saturation point).

#### 4.3. Effect of temperature on adsorption

Temperature is an important parameter in the context of adsorption on solid phase. An increase in the percent adsorption was observed corresponding to the increase in temperature from 25–50°C (Tables 1 and 2).

#### 4.4. Effect of pH on adsorption

Adsorption of solute on a solid surface is known to be dependent on the pH of the solution. The results indicate that protonated pollutants were more effectively adsorbed than uncharged pollutants. Pollutants adsorption increased with decreasing pH exhibiting the typical sorption behaviours of anions (the adsorption of anions is coupled with the release of OH<sup>-</sup>). This is in agreement with other works reported in literature (Stumm, 1996). Maximum pollutants adsorption on the other hand was recorded at the pH of 3.5 and declined abruptly at both higher pH values under the experimental conditions used. The observed pH dependence of the pollutants removal was attributed to several factors that are reported in detail in literature (Genc, 2003a; Genc et. al., 2004b; Gupta et. al., 2001).

#### 4.5. Adsorption equilibrium and adsorption isotherms

The ability of laterite to extract solute from aqueous solution was evaluated by measuring uptake of metal ions on the modified laterite adsorbent, correlating the equilibrium adsorption amount on laterite and equilibrium concentration in solution. The Langmuir and Freundlich isotherms for uptake of Cu, Fe, Mn, Pb and Al from the aqueous solution of the wastewater effluent are shown in Figs 1 - 10. The laterite type adsorption behaviour, predicted from the equilibrium data in the present system suggests favourable adsorption and also a strong tendency of monolayer formation.

#### 4.6. Mechanism of solute–laterite interaction

Laterite is primarily composed of silica alumina and iron (III) oxides. When it is soaked in water for several hours the oxides get converted to oxohydroxides of silica, aluminium and iron. The Si-O and Al-O bonds are much stronger than Fe-O bonds. The governing

reaction for metal ion-laterite is expected to be of ion exchange type, probably through replacement of weak Fe (III) sites. However, since the results obtained in this work (Tables 1 and 2) showed no appreciable change in conductivity of the wastewater effluent samples before and after treatment, it was concluded that the process was of adsorptive nature rather than of exchange nature.

## 5. Conclusion

Activated carbon is considered as universal and most efficient adsorbents for treatment of water contaminated by a wide range of pollutants<sup>(3)</sup>. But its higher cost limits its use. Therefore more research is directed towards the search of alternative adsorbents. In Nigeria, laterite is readily available in large quantity, as a large area is covered by laterite. Therefore laterite filter media can be used as alternative for some metal ions pollutants and other vegetable oil wastewater pollutants removal/reduction. Moreover, the capacity of laterites filter media in suitable experimental condition is more or less comparable to activated carbon, at least for some solutes. Furthermore, the laterite media can be extended for the development of a simple household filter. The laterite media can be used in conjunction with other treatment methods (as pre-treatment) for vegetable oil refining wastewater effluents before ultimate discharge into the environment.

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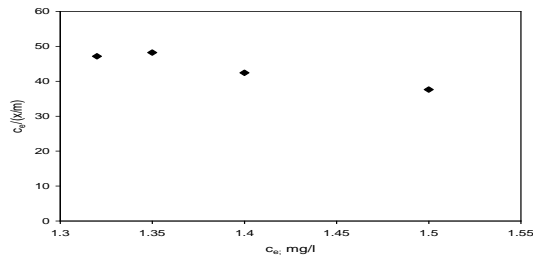


Fig. 1. Langmuir isotherm for Cu uptake on modified laterite adsorbent.

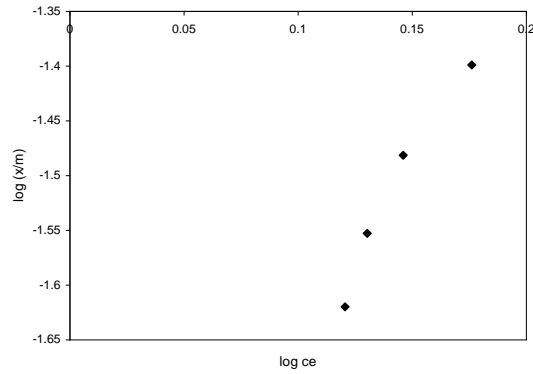


Fig. 2. Freundlich isotherm for Cu uptake on modified laterite adsorbent.

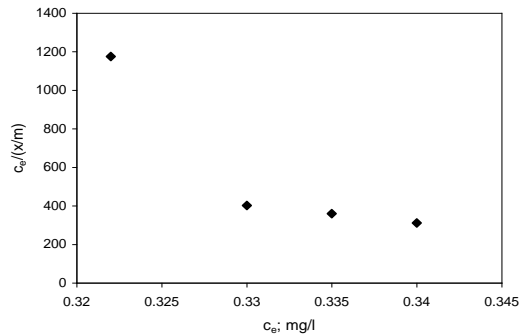


Fig. 3. Langmuir Isotherm for Fe uptake on modified laterite adsorbent.

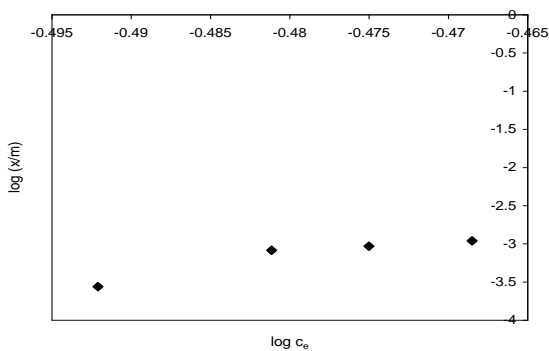


Fig. 4. Freundlich Isotherm for Fe uptake on modified laterite adsorbent

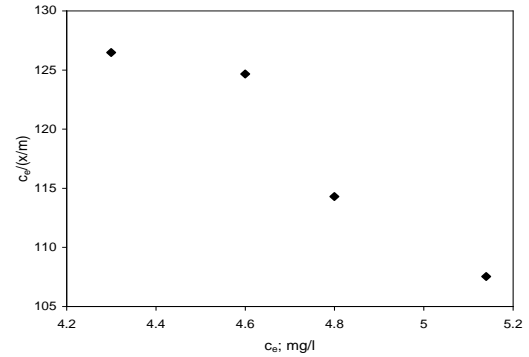


Fig. 5. Langmuir Isotherm for Mn uptake on modified laterite adsorbent.

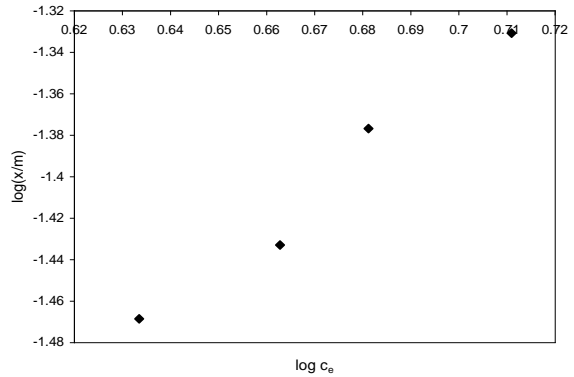


Fig. 6. Freundlich Isotherm for Mn uptake on modified laterite adsorbent.

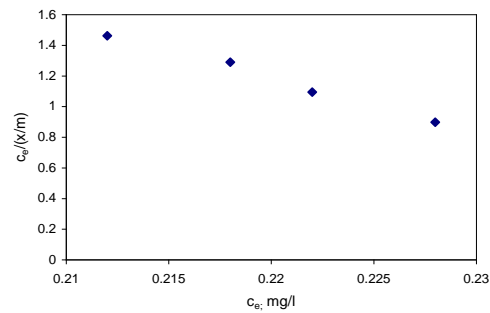


Fig. 7. Langmuir Isotherm for Pb uptake on modified laterite adsorbent.

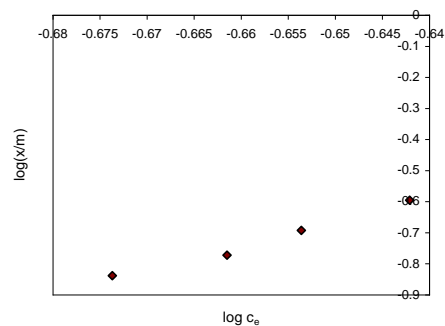


Fig. 8 - Freundlich Isotherm for Pb uptake on modified laterite adsorbent

Fig. 8. Freundlich Isotherm for Pb uptake on modified laterite adsorbent.

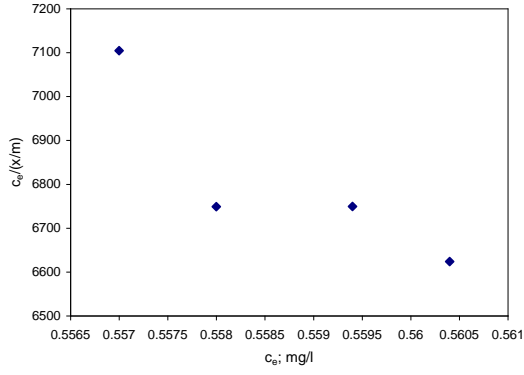


Fig. 9. Langmuir Isotherm for Al uptake on modified laterite adsorbent..

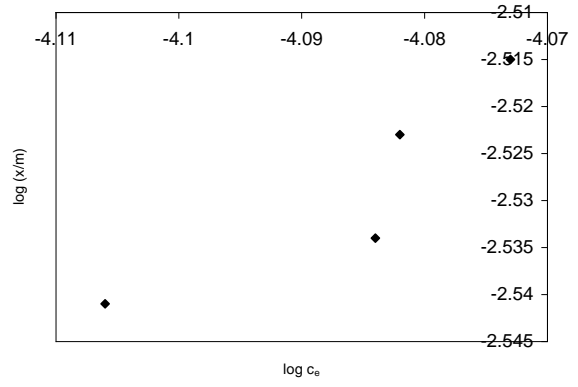


Fig. 10. Freundlich Isotherm for Al uptake on modified laterite adsorbent.