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Application of agricultural waste in the treatment of industrial waste water.

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Abstract
The treatment of waste water from soft drink, industry was investigated. Batch adsorption method was employed at various doses of a carbonaceous adsorbent prepared from rice husk via sulphuric acid treatment to determine the effective manganese and iron removal at different metal ion concentrations. Adsorption of Mn^{2+} and Fe^{3+} ions was strongly influenced by adsorbent dose and contact time. The highest manganese and iron adsorption was achieved at adsorbent dose of 100g and contact time of 80min. Also the highest percentage efficiencies of the adsorbent for Mn^{2+} and Fe^{3+} uptake at equilibrium were 17% for mn^{2+} and 95.24% for Fe^{3+} . Isotherms for the adsorption of manganese and iron on RHAC were developed and the equilibrium data for Fe^{3+} uptake fitted well to the Langmuir and Freundlich models.

Keywords: Rice husk, activated carbon, Mn^{2+}, Fe^{3+}, soft-drink industrial wastewater.

1. Introduction

Rapid industrial development and population explosion have created problems of environmental pollution which is gaining severe dimensions day by day all over the world, in general, and in developing countries in particular. While great efforts are being made for industrial development in the developing countries, proper attention is not paid by most of them to take suitable measures for pollution abatement (Pathade, 1995). Due to the fact that treatment plants are expensive, the ability to pay for services is minimal and skills as well as technology are scarce. In order to alleviate the prevailing difficulties, approaches should focus on sustainable waste water treatment systems that are natural, low cost and require minimal maintenance and operator skills. Locally available natural raw materials can be exploited towards achieving sustainable safe environment.

The processes involved in soft drink production range from bottle washing, juice production, cleaning of floors, tanks and pipes, etc. During these processes, waste and by-products are generated. The operating conditions and processes carried out influence the amount and characteristics of the waste and by-products generated (Chipasa, 2001).

Soft-drink waste water is one of the most complex, caramelized and troublesome waste, having very high chemical oxygen demand and biochemical oxygen demand content which are highly toxic to environment with other organic and inorganic constituents (Misra, 1993)

Several methods are available for treatment of waste water from soft drink industry such as coagulation – flocculation, adsorption, reverse osmosis and membrane technology, alkaline chemical precipitation by lime addition, etc (Gupta, 1998). However, the high cost associated with these methods necessitated the use of a low-cost, natural and indigenous adsorbent. In this work the carbonaceous material produced from rice husk was modified with sulphuric acid to produce activated adsorbent. The capability of the adsorbent to remove pollutant ions (Mn^{2+} and Fe^{3+}) from waste water will be tested.

2. Material and Methods

The investigations were carried out on freshly collected wastewater sample from soft-drink industry situated in Anambra State, Nigeria. The wastewater samples were specifically collected from the final discharge points – Syrup production unit and bottling washing / bottling hall units. The rice husk sample was collected from Ayamelum Local Government Area, Anambra State.

2.1. Preparation of modified rice husk

The adsorbent material (1.2kg) was washed with distilled water to remove dirt, dust and any superficial impurities. The rice husk was dried in an open air at room temperature to constant weight. The dried rice husk (1.2kg) was put in a clean dry pot 0.6400ml of 13m husk and the mixture dried and carbonized in a muffle furnace at a temperature of 500°C for 2hrs (Ong, et al., 2007). The black mixture was allowed to cool and filtered. The activated material was washed several times with distilled water to reduce the acidity. At the pH 7 the activated rice husk was kept in an oven to dry at a

temperature of 120°C for 1.30mins and stored in an air – tight container.

2.2. Characterization of wastewater 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 (Tchobangoglous, 1998). Analytical grade reagents were used in all experiments. The wastewater samples were analyzed for; pH, colour, dissolved oxygen (DO), temperature, electrical conductivity, chemical oxygen demand (BOD), total dissolved solids (TDS), total suspended solids (TSS), nitrate, calcium, manganese, iron, total solids (TS),. The tests were carried out using standard methods for the examination of water and wastewater (Eaton, et al., 1998)

2.3. Treatment of wastewater sample

This was achieved using static adsorption process. Static or batch adsorption process was carried out by transferring 100ml of wastewater sample into five different 500cm^3 flasks corked and labeled. Different doses of the adsorbent (100, 150, 200, 250 and 300g's respectively) were weighed and added in each of the flasks and agitated in a shaker for different contact times (20,40,60,80 and 100mins). After each agitation time, it was allowed to settle, a sample of the supernatant was withdrawn and analyzed using U.V-Spectro photometer (Spectrum lab 20 model) with wavelength set at 620µm in each case following a standard procedure for the examination of water and wastewater (Eaton, et al., 1998). The removal efficiency of the adsorbent on the pollutants is defined as

$E(\%) = [(C_i - Ce) / C_i] \times 100$

Where C_i and C_e are the initial and equilibrium concentrations of pollutants (mg/l) respectively.

3. Results and Discussions

3.1. Parameters

The following values were obtained from the analysis carried out:

Table 1 – Quality characteristics of wastewater sample before treatment.

Parameters	Values	FMEHUD Max Limit
pH	6.0	6.90
Colour (Hazen disc)	9.0	7.0
Dissolved oxygen (DO) (mg/l)	1.377	≤ 5.0
Temperature (°C)	45	≤ 40
Electrical conductivity (Ωcm^{-1})	2.25 x 10^4	100
Chemical oxygen demand (COD) mg/l)	1200	20
Sulphate (mg/l)	85.30	NS
Biochemical Oxygen Demand (BOD) (mg/l)	1201.37	50
Total Dissolved Solids (TDS) (mg/l)	460	2000
Nitrate (mg/l)	16.07	20
Chloride (mg/l)	1.2126	NS
Specific gravity	0.418	NS
Manganese (mg/l)	840.00	5.0
Total Solids (mg/l)	380.00	2030
Total Suspended Solid (mg/l)	285.00	20
Alkalinity (mg/l)	553.80	NS
Calcium (mg/l)	100.00	200
Iron (mg/l)	0.420	0.20
Acidity (mg/l)	97.50	NS
Oil and Gas (mg/l)	ND	10

Table 2 – Quality characteristics of wastewater sample after treatment

Parameters	Values	FMEHUD Max Limit
pH	4.0	6.90
Colour (Hazen disc)	8.0	7.0
Dissolved oxygen (DO) (mg/l)	1.378	≤ 5.0
Temperature (°C)	42	≤ 40
Electrical conductivity (Ωcm^{-1})	2.25 x 10^4	100
Chemical oxygen demand (COD) mg/l)	1195	20
Sulphate (mg/l)	85.30	NS
Biochemical Oxygen Demand (BOD) (mg/l)	1101.37	50
Total Dissolved Solids (TDS) (mg/l)	207.2	2000
Nitrate (mg/l)	1.2029	20
Chloride (mg/l)	1.2126	NS
Specific gravity	0.416	NS
Manganese (mg/l)	1.3780	5.0
Total Solids (mg/l)	430.20	2030
Total Suspended Solid (mg/l)	97.00	20
Alkalinity (mg/l)	94.45	NS
Calcium (mg/l)	144.288	200
Iron (mg/l)	0.003	0.20
Acidity (mg/l)	97.50	NS
Oil and Gas (mg/l)	ND	10

Key:
NS = not stated
ND = not detected

3.2. Effect of adsorbent dosage

The adsorbent dosage has been shown to be one of the important factors in adsorption processes. In this study, the adsorbent different doses of (100 – 300g) were used to determine the effects of activated rice husk (RHAC) dosage on manganese (Mn) and iron (Fe) adsorption capacity. Fig 1, showed that uptake of Mn^{2+} and Fe^{3+} ions respectively decreased with increasing the

adsorbent dosage, (even though, an increase in adsorbent dosage, generally, increase the uptake of the substances). This phenomenon is attributable to the interference between the binding sites of the rice husk biomass (adsorbent), in agreement with previous work (Peruze, 2001, Esposto, et al., 2001 and Veglio, et al., 1997). The manganese and iron adsorption onto activated rice husk decreased with increasing adsorbent dosage owing to decreasing surface area that decreased the binding sites. In this work, the optimum uptakes of manganese and iron were 1.378mg/l and 0.30mg/l, respectively at 100g adsorbent dosage.

3.3. Effect of Contact Time

The adsorption of manganese and iron with respect to adsorbent contact time is shown in figs. 2 and 3 over the range of 20 – 100 mins. The adsorption of Mn^{2+} and Fe^{3+} was rapid in the first 80mins followed by a steep decline as evidenced in fig 2. A similar result was also obtained in fig 3, where the percentage efficiency of the adsorbent in adsorption of Mn^{2+} and Fe^{3+} increased with increasing contact time from 20 – 80mins. The highest Mn^{2+} and Fe^{3+} ions uptake registered at equilibrium were 17% for Mn^{2+} and 95.24% for Fe^{3+}, while the lowest were recorded at 6% for Mn^{2+} and 33.33% for Fe^{3+}.

The adsorption profiles in respect of figs 2 and 3 can be interpreted as follows: the first 80mins witnessed a rapid increase both in the amount of Mn^{2+} and Fe^{3+} ions adsorbed and the percentage efficiency; then contact time of 80mins, which is the plateau, indicates the optimum level where equilibrium has been attained.

The general fact is that the increase in the amount of Mn^{2+} and Fe^{3+} ions adsorbed and the percentage efficiency of the adsorbent respectively are attributable to the fact that at early minutes into the adsorption process, the active sites of the adsorbent appear fresh, therefore much of the solutes will be adsorbed rapidly and a steep decline is observed when the adsorbent becomes saturated with adsorbates.

3.4. Adsorption Isotherm Analysis

The nature of the adsorption isotherm was evaluated on the bases of Langmuir Isotherm equation (Langmuir, 1918) and Freundlich Isotherm equation (Freundlich, 1906). The Langmuir Isotherm is written as follows.

$$q_e = \frac{QbC_e}{1 + bC_e} \quad (1)$$

The linearized form of this equation is given by

$$C_e = \frac{1}{Qb} + \frac{1}{Q}\left(\frac{C_e}{Q_e}\right)$$

Where C_e is the equilibrium concentration of the adsorbate (mg/l), q_e is the amount of the adsorbate adsorbed per unit mass of adsorbate mg/g, Q is the amount of the metal adsorbed per unit weight of the adsorbent (on dry basis) for monolayer coverage of the surface (monolayer capacity) and b is the adsorption. C_e/q_e was plotted against C_e, straight line with slope 1/Q was obtained (fig 4), indicating that the adsorption of iron (Fe^{3+}) on the RHAC followed the Langmuir Isotherm, while fig 5 did not.

The values of 'Q' and 'b' were calculated from this Isotherm and recorded in table 3.

Table 3: Langmuir and Freundlich Isotherm constants

Longmuir Isotherm	Iron	Manganese
Q(mg g^{-1})	0.027	-125
b(mg^{-1})	12.7	0.381
R^2	0.935	0.837

Freundlich Isotherm	Iron	Manganese
K_f (L/mg)	26.98	56.49
n	2.37	0.374
R^2	0.731	0.447

The high values of R^2 for Fe^{3+} indicate that adsorption followed Langmuir model (fig 4). Equally, the highest coefficient b, was obtained for Fe^{3+} as 12.78 mg^{-1} which is related to the affinity between the adsorbent and adsorbate. A large value of b, indicates strong bonding.

3.5. Freundlich Isotherm

The Freundich adsorption isotherm is $q_e = K_f\ C_e\ \frac{1}{n}$ the equation can be linearized by taking logarithms to find the parameters K_f and n, i.e.

$$\text{Log } q_e = \text{Log } K_f + \left[\frac{1}{n}\right] \text{Log } C_e \quad (3)$$

where K_f and $\frac{1}{n}$ are constants, which are considered to be the relative indicators of adsorption capacity and adsorption intensity respectively.

q_e is the amount of the adsorbate adsorbed per unit mass of adsorbate (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l).

The plot of $\frac{1}{n}$. (fig 6) showed that the adsorption of Fe^{3+} with R^2 of 0.731 followed the Freundlich isotherm, while fig 7 showed that the adsorption of Mn^{2+} with low R^2 = 0.447 did not follow the Freundlich isotherm. The calculated Freundlich constants (K_f and n) are shown in table 3.

Comparatively the obtained R^2 values are more satisfactory for Langmuir Isotherm than for Freundlich isotherm (table 3). In addition, the R^2 values obtained suggest that the adsorption of Fe^{3+} onto RHAC adsorbent favours monolayer

formation. This is in agreement with the assumption of Langmuir adsorption isotherm (which is based on the monolayer coverage of the adsorbate on the surface of adsorbent (Singh, et al., 2006).

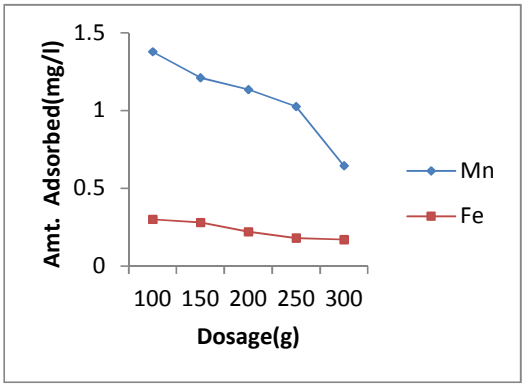

Fig 1: Effect of adsorbent dosage on the adsorption of iron and manganese.

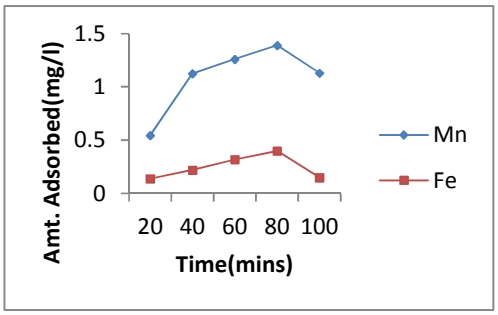

Fig 2: Effect of contact time adsorption of iron And manganese

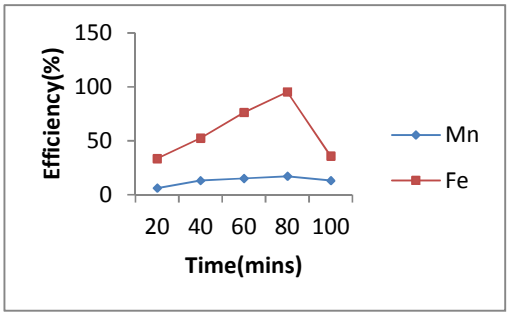

Fig 3: Effect of contact time on efficiency (E%) of adsorption of iron and manganese.

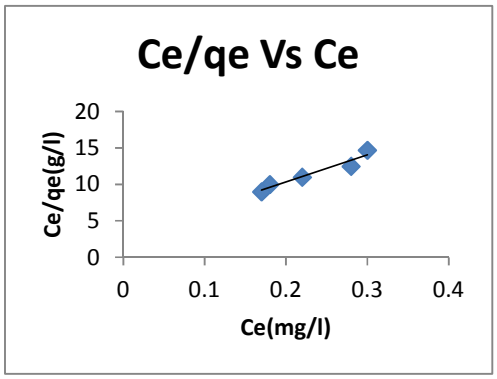

Fig 4: Langmuir isotherm for iron uptake on modified rice husk

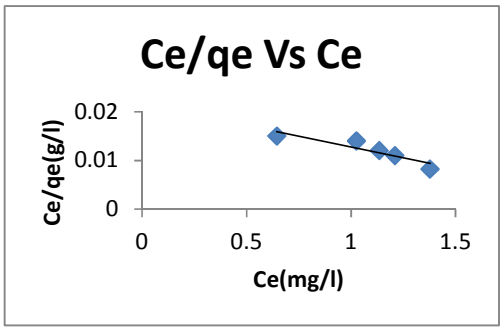

Fig 5: Langmuir isotherm for manganese uptake on modified rice husk.

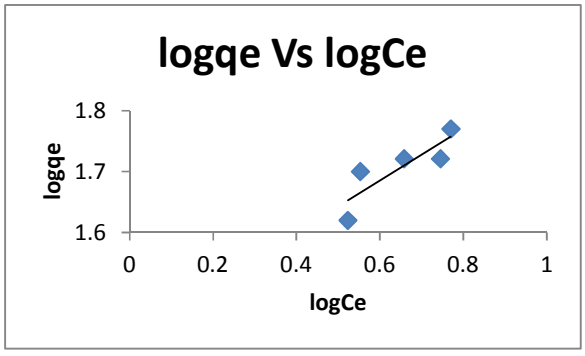

Fig 6 : Freudlich isotherm for iron uptake on modified rice husk.

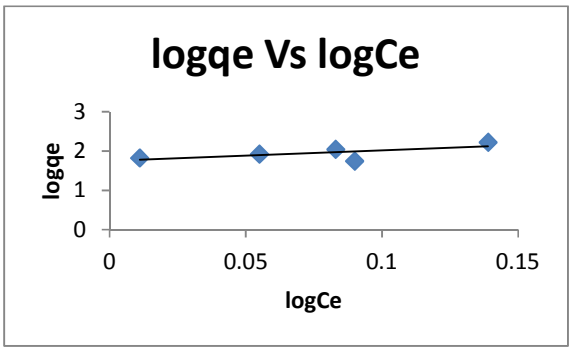

Fig 7 : Freundlich isotherm for manganese uptake on modified rice husk.

4. Conclusion

Within the experimental conditions, the computed results fitted into Freudlich and Langmuir isotherm models respectively, well described the adsorption of iron (Fe^{3+}) onto RHAC adsorbent. The high removal efficiency of 95.24% recorded presents the potential of RHAC as an agricultural bio-mass applicable in large scale wastewater and water treatment.

Nomenclature

C_e = Equilibrium iron and manganese concentration (mg/l)
q_e = Adsorption Capacity at equilibrium (mg/g)
K_f = Freundlich Isotherm constant L mg $^{-1}$
n = Freundlich exponent related to adsorption intensity (dimensionless)
b = Sorption equilibrium constant
Q = Amount of adsorbate per unit weight of the adsorbent (mg/g)
R^2 = Squared regression correlation coefficient
RHAC = Rice husk activated Carbon.

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