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Analysis of Adsorptive Treatment of Brewery Effluent with Activated Black Date Seed Carbon

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ABSTRACT
Black date seed shell, an abundant, biodegradable and inexpensive natural resource was used as a precursor to bio-adsorbent production for the removal of suspended and dissolved particles (SDP) from initially coagulated Brewery Effluent (BRE). Influence of key parameters such as contact time, bio-adsorbent dose, pH and temperature were investigated using batch method. The adsorption of SDP on H_3PO^4-and NH_4Cl-treated seeds were examined at specified temperatures. This investigation demonstrated that black dateseed could be utilized as low cost, renewable, ecofriendly bio-adsorbent for the removal of SDP from BRE.

Keywords: Brewery effluent analysis; black date seed; Suspended and dissolved particles

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1. Introduction

Brewing is an intensive water consuming activity, besides utilizing a wide variety of chemicals. Expectedly, large volumes of effluent is discharged into water courses of brewery bearing communities, leaving in its wake a polluted aquifer (Khuo-Omoregbe *et al*., 2005; Menkiti, 2010). Increasing concentration of these organic/non-organic enriched BRE in the water constitute a severe health hazard to both plants and animals, thus impeding the functionality of the ecosystem. The situation is typical of the BRE receiving aquatic system in Nigeria, where much of the water resources cannot be utilized without a form of treatment, following effluent discharges with negligible consideration for environmental control (Menkiti and Onukwuli 2011a). BRE, generated from lager beer production, contains large amount of SDP (Menkiti and Onukwuli, 2010). Typically, the organic contents of BRE consists of sugars, soluble starch, ethanol, volatile fatty acids and solids which are mainly spent grains, yeast and trub (Driessen and Vereijken, 2003). Untreated BRE quantitatively contains suspended solids (100–1500 mg/l), chemical oxygen demand (300–800 mg/l), nitrogen (30–100 mg/l) and phosphorus (10–30 mg/l) (Menkiti *et al.*, 2011a, World Bank Group, 1998).

Over the years, significant attention has been given tothe environmental cleanup of such contaminated aqua system using varieties of techniques such as precipitation, ion-exchange, coagulation, reverse osmosis and adsorption (Hameed and El-Khaiary, 2008; Larous *et al.*, 2005; Menkitiet al. 2011b; Menkiti and Onukwuli, 2011b). Among thedifferent treatments listed above, adsorption technology is attractive due to its merits of efficiency, even at low concentration of contaminants (Meena *et al.*, 2008; Yakubu *et al.,* 2008), economy, simple operation and insensitivity to toxic substances (Grini 2005; Feng *et al.,* 2010; Menkiti and Onukwuli 2011b).

The common adsorbents primarily include zeolite, clays, polymeric materials and natural agricultural materials which provided

the focus of this study (Asasian and Kaghazchi 2013; Jiang *et al.,* 2012; Amirnia *et al.,* 2012).

These natural materials have potential to be used as low cost bio-adsorbent, as they represent unused resources, abundantly available and known to be eco-friendly (Deans and Dioxn 1992). Progressively, much attention has been focused on techniques of converting these waste materials into useful adsorbents. Among these agricultural wastes are saw dust (Meena et al. 2008) palm ash (Ahmad et al. 2007).

Canarium schweinfurthii seed shell, considered in thisstudy, is of tropical forest tree of genus *Canarium schweinfurthii*, family of sapotacae and order of ericales. The fruit is large berry containing round seeds with a hard inside shell (Bada, 1997). Significant quantities of these seeds shells are produced annually in Nigeria without being put to useful ends industrially. According to the author's knowledge, no attempt has been made until now to use this seed shell for the treatment of natural organic aqueous waste, such as BRE. Therefore, it was of interest to experiment with such a promising biomaterial for the adsorptive removal of SDP from initially coagulated BRE by batch technique. The work further seeks to investigate the influence of contact time, adsorbent dosage, temperature and effluent pH on the adsorptive uptake of SDP from the BRE. Finally, material characterization and analyses were conducted to present the characteristic properties changes associated with the adsorption study.

2. Materials collection

2.1. Brewery effluent

Brewery effluent was obtained from a beer brewery at 9th Mile Corner Udi, Enugu Sate Nigeria and stored in black plastic container to preserve and further prevent changes in the characteristics of the effluent (Clesceri *et al.*, 1999).

2.2. Date seeds

The precursor for the preparation of the bio-adsorbents, date seeds were obtained as a waste material from Nsugbe, Anambra State of Nigeria. Pretreatment of the seeds was done by thorough washing with distilled water to remove the impurities was done and the washed sample dried in an air circulating oven at 40°C for 14 hours. The seed samples were blended, sieved and particles that ranged between 2 and 3 mm were obtained and stored in a desiccator for use in the experiments. Two portions of the seed samples, of known weights, were immersed in 60% solutions of ammonium chlorideand phosphoric acid, respectively, for 24 hours. The carbonization of the seed samples were carried out in a muffle furnace at 600°C for 4 hours, washed with distilled water to pH 7, dried at 110°C for 8 hours and subsequently sieved to desired diameter using standard sieves.

2.3. Materials characterization

Characteristics of H_3PO^{4-}treated date seed (ADSA) and NH_4Cl treated date seed (ADSS) carbons characterized are depicted in table 1 below.

Table 1: Characteristics of H_3PO^{4-} and NH_4Cl treated black date seed carbon

Parameters	H_3PO^{4-}	NH_4Cl
BET Surface area (m^2/g)	270.532	134.086
Total pore volume (cm^3)	25501	2.011
Bulk density (g/cm^3)	0.3775	0.4901
% Ash content	2.412	1.600
Oil content (%)	0.8541	0.8511
Moisture content (%)	2.421	2.422

3. Adsorption experiments

Batch adsorption experiments were performed in Erlenmeyer flask according to the methods reported by Sivakumar and Palanisamy (2009) and Yeddou and Bensmaili (2005). In a typical experiment, 20 ml of effluent sample was mixed with the appropriate amount of adsorbents (types ASAA and ASAS) in the range of 10-50 g/l and then shaken for a period of time ranging from 5 to 60 min at 20 rev/s. The temperatures of adsorption measurements ranged between 20 and 30°C and the appropriate value was applied accordingly as required. The sample was then filtered using Whatman no 42 filter paper having fine porosity and particle retention of 2.5 micrometer at slow flow rate in a glass funnel. The filtered liquid was analyzed with respect to particle (SDP) content.

3.1 Analytical method

Filtrate from adsorbed BREsamples were taken at specified time range of 5–60 min, and then analyzed using a Spectronic (Milton Roy Company) 21 UV-visible spectrophotometer. The maximum uncertainty of the analytical methods was estimated at 5% level. The adsorption capacity, qt (mg/g), and the percentage SDP removal, % Rem, were calculated using Equations 5 and 6, respectively.

$$q_t = \frac{C_0 - C_t}{D_A} \quad (5.0)$$

$$\%Rem = \left(\frac{C_0 - C_t}{C_0}\right) 100 \quad (6.0)$$

where: C_0, C_t and D_A are initial constant effluent concentration (mg/l), effluent concentration at any time, t and adsorbent dose (g/l), respectively.

4. Results and discussion

4.1. Characterization of results

4.1.1. Physiochemical and biological characteristics

The results of the physiochemical and biological characteristicsof the coagulated BRE, along with the regulatory standard (FEPA-Federal Environmental Protection Agency 1991), are presented in Table 2. The major characteristics (turbidity, total dissolved solid, total suspended solid, biological oxygen demand) contributing to the cloudiness of the fluid were relatively in low concentrations, but significant enough to promote adsorption process in the medium. Usually low concentration of contaminant is one of the key conditions that favor the application of adsorption (Meena *et al.*, 2008; Yakubu *et al.*, 2008). Meanwhile, the characteristics of adsorbents presented in Table 1showed that ADSA had larger surface area/pore volume than the ADSS, an indication of likely better adsorptive performance of the former.

Table 2: Characterization result of Brewery Effluent and FEPA standard

Parameters	Value	FEPA Limit
pH	2.3300	6-9
Turbidity (NTU)	37.0000	-
Total hardness	140.0000	-
(mg/l)	46.7000	-
Ca^{2+} (mg/l)	12.5000	-
Mg^{2+} (mg/l)	0.2000	-
Fe^{2+} (mg/l)	64.5200	-
SO_4^{2-}(mg/l)	0.2100	20
NO_3^{2-}(mg/l)	624.9088	<1
Cl^- (mg/l)	159.2000	400-800
E. Cond	9.2360	<2000
(μm/m^2)	2.0500	15-30
TDS (mg/l)	Nil	-
TSS (mg/l)	0.8900	-
T. Coliform	Nil	-
Plate Count	5.7401	10-50
E-Coli		
BOD_3		

4.2. Influence of contact time and adsorbent dosage on adsorptive removal of SDP from BRE

The results for adsorptive removal of SDP with respect to time and adsorbent doses are shown in Figures 5, 6, 7 and 8 over the range of 10–50 g/l. Figures 5 and 6 indicated that SDP removal increased with increase in adsorbent dosage. From the profiles of the Figs., the particle retention increased rapidly and tended towards constant after equilibrium time of 30 min for both ADSA (Figure 5) and ADSS (Figure 6). From Figure 5, the percentage removal recorded for ADSA at 10 g/l were 60.5978 and 69.8369% for the time of 5 and (30– 60) min, respectively. For ADSA (Figure 5) at 50 g/l, 63.3152 and 74.1168% were recorded for 5 and (30–60) min, respectively. Similar trends were depicted in Figure 6 (ASAS) where 52.4456 and 66.1005% were achieved for time of 5 and (30–60) min, respectively at 10 g/l dose. For 50 g/l ADSS dose, 55.095 and 67.527% removal were achieved at 5 and (30–60) min, respectively. The results demonstrated that ADSA performed better than the ADSS at the conditions of this experiment.

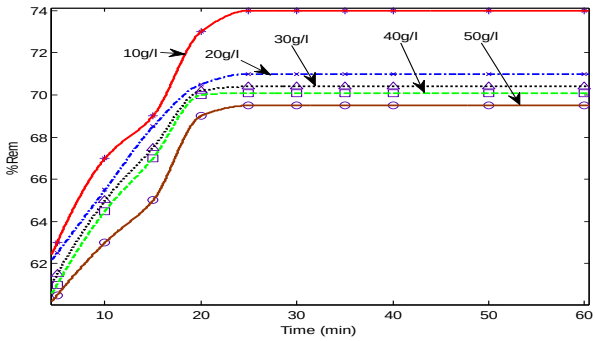

Figure 5: Influence of contact time and varying ADSA dose on the % removal of SDP from BRE (BRE volume =20 ml, C0 = 161.92 mg/l, initial BRE pH, original temperature = 25°C).

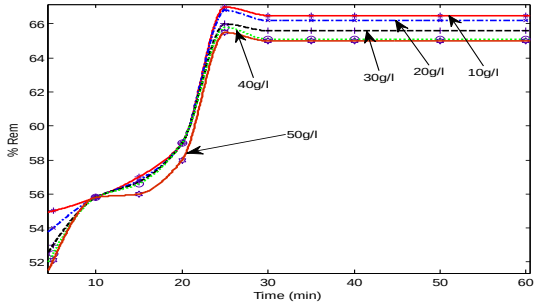

Figure 6: Influence of contact time and varying ADSS dose on the % removal of SDP from BRE (BRE volume =20 ml, C0 = 161.92 mg/l, initial BRE pH, original temperature = 25°C).

The observed adsorption dynamic profiles depicted byFigures 5 and 6 can be divided into three regimes (Ncibi *et al*., 2008):

(i) a linear increase in adsorption with time,

(ii) a transition regime where the rate of adsorption levels off, and

(iii) a plateau regime. First regime (initial steep slope) indicated instantaneous adsorption (overshoot phenomena) ability of effluent particles onto the surface of the adsorbents. The second regime indicated a phase of gradual attainment of equilibrium where the apparent fall in SDP adsorption rate might be due to utilization of active sites on adsorbents surface. Plateau regime indicated phase where equilibrium had been achieved (Mohan et al. 2007).

One general phenomenon was the perceived increasein SDP uptake with increase in adsorbent dose. It shouldalso be observed that the % Rem for doses considered in Figures 5 and 6 ranged closely; with only apparent difference noticed for 50 g/l (Figure 5). This could be attributed to the greater availability of close number of exchangeable sites or surfaces in the adsorbents (Meena *et al.*, 2008). Following optimal results obtained at 50 g/l and 30 min, the rest of the work was carried out at the stated results, unless otherwise indicated.

Figures 7 and 8, present results similar to Figures 5 and6 in respect of the variation of adsorption capacity qt(mg/ g) with contact time and adsorbent dose. It was evident that qt increases with decreasing adsorbent dose and increasing contact time before leveling-off. The highest and lowest qt were recorded at 10 and 50 g/l, respectively for both ADSA (Figure 7) and ADSS (Figure 8). In specific terms, qt at 10 g/l increased from 9.812 to11.308 mg/g for 5 and (30–60) min, respectively as shown in Figure 7. Also, the qt at 50 g/l ADSA increased from 2.0504 to 2.4002 mg/g for 5 and (30–60) min, respectively. Figure 8 indicated that qt at 10 mg/l recorded increment from8.4920 to 10.703 mg/g for 5 and (30–60) min, respectively while that of 50 g/l increased from 1.7842 to 2.1868 mg/g for 5 and (30–60) min, respectively. The results indicated also that the ADSA performed better than ADSS.

The apparent decrease in adsorption density (amount adsorbed per unit mass of the adsorbent) with increase in adsorbent dose was due to progressive unsaturation of adsorption sites through the adsorption reaction. Another reason might be due to the particle interaction, such as aggregation, usually resulting from high adsorbent concentration. Such aggregation would lead to decrease in total surface area of the adsorbent and on increase in the diffusional path length (Shukla *et al.,* 2002). Particle interaction might also desorb some of theadsorbate that was only loosely and reversibly bound to the adsorbent surface.

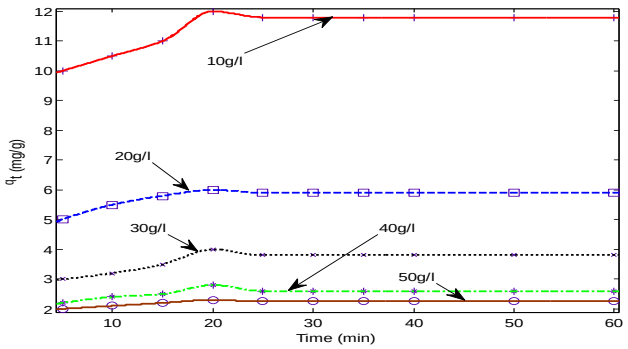

Figure 7: Influence of contact time and varying ADSA dose on the adsorptive capacity (BRE volume =20 ml, C0 = 161.92 mg/l, initial BRE pH, original temperature = 25°C).

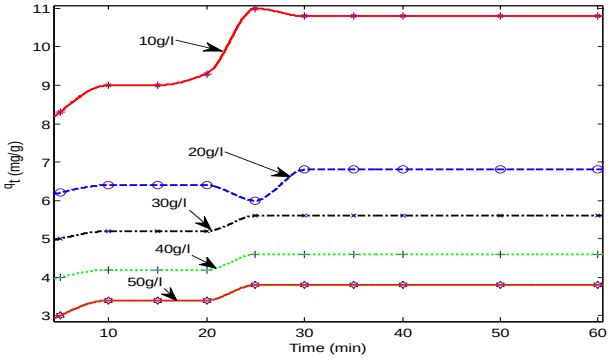

Figure 8: Influence of contact time and varying ADSS dose on the adsorptive capacity (BRE volume =20 ml, C0 = 161.92 mg/l, initialBRE pH, original temperature = 25°C.

4.3. Influence of temperature on the adsorptive removal of SDP from BRE

The removal of SDP from BRE onto ADSA and ADSS was investigated at following conditions: temperatures of 20, 25 and 30°C, 50 g/l adsorbent dose and contact time of 30 min. The effects, represented for only 20 and 30°C, are illustrated by the results in Figure 9. The Figure indicated that the percentage removal of SDP increased for ADSA and ADSS as the temperature of the system increased. Figure 10 shows the results obtained at 20, 25 and 30°C for the final SDP uptake from BRE onto ADSA and ADSS at 30 min of contact time. Quantitatively, at 20°C, 65.683 and 70.76% SDP removal were achieved for 5and 30 min, respectively for ADSA (Figure 9). For ADSA at 30°C, 68.74 and 77.21% were obtained for 5 and 30 min, respectively. Results obtained for ADSS (Figure 9) indicated that 65.021 and 69.12 % were recorded for 5 and 30 min, respectively at 20°C. At 30°C, ADSS recorded 67.02 and 74.100% for 5 and 30 min, respectively. Figure 10 indicated that when the temperature of BRE is placed at 20, 25 and 30°C, the ultimate achievable percentage of SDP removal in respect of ADSA, were 70.76, 75.10 and 77.21%, respectively. In respect of ADSS, the SDP removal achieved at 20, 25 and 30°C were 69.12, 71.13 and 74.10%, respectively.

Both Figures 9 and 10 indicated that the retention ofSDP by the adsorbents increased while the temperature and time increased. The perceived increase of SDP uptake with temperature might be due to the acceleration of some originally slow adsorption steps or the creation of some active sites on the adsorbent surface (Hashem, 2007; Nasssar and Magdy, 1999). The enhanced mobilityof SDP from the bulk solutions towards the adsorbentsurface should also be taken into account (Hashem, 2007; Yubin *et al.,* 1998). Increased temperature encouraged the process of agglomeration and widening adsorbent pore resulting in certain activation of the surface of the solid support (Larous *et al.,* 2005). Obtained results indicated clearly that the adsorption process under study was an endothermic process. This fact was illustrated in Section 3.6. Results similar to the one of this study had been reported by Khalid and Ahmad (1998).

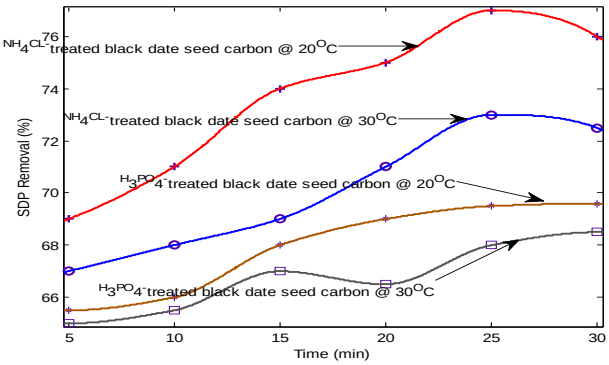

Figure 9: Influence of temperature on the % removal of SDP from BRE onto ADSS and ADSA (adsorbent dose = 50 g/l, BRE volume = 20 ml, C0 = 161.92 mg/l, initial BRE pH, contact time = 30 min).

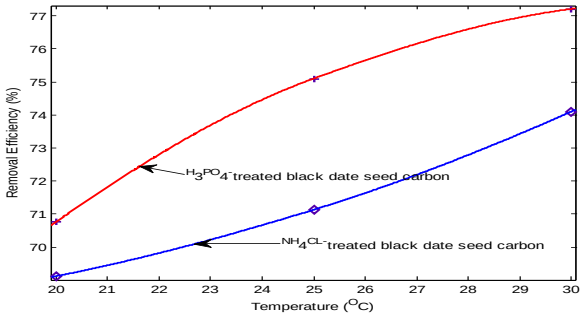

Figure 10: Influence of temperature on removal efficiency of SDP on to ADSS and ADSA at contact time of 30 min (adsorbent dose = 50 g/l,BRE volume =20 ml, C0 = 161.92 mg/l, initial BRE pH).

4.4. Influence of pH on the adsorptive removal of SDP from BRE

The pH of the aqueous solution was a vital controllingfactor in the adsorption process and thus the impact of pH has been studied in the range of 2–8 as depicted graphically in Figure 11. As a general trend, the increase in pH, increased adsorption in a very determined sense, until a certain pH limit, beyond which the process became steady. This pH limit could be regarded as the optimal value.

In quantitative terms, the percentage SDP removalincreased with pH from 2 to about 6.95 and remained unchanged thereafter. In respect of ADSA and ADSS, the SDP removal increased from 69.5768% at pH 2 to 73.0839% at pH 6.95 and 66.3161% at pH 2 to 70.4231% at pH 6.95, respectively. At pH greater than 6.95, the SDP removal remained constant till pH 8. The gentle decrease at about pH 3–6 of the initial rapid adsorption of SDP was presumed to be due to competitive adsorption between hydrogen ion and particles of the BRE. The adsorption at near neutral pH values could be attributed to the cellulose component of adsorbents where site binding adsorption might be occurring. This could be due to surface complex phenomena of functional groups present in the adsorbent (Hashem, 2007; Menkiti *et al.,* 2011a).

Graphical results of Figure 11 could be linked stronglyto the influence of pH, in addition to the functional groups on the adsorbent and their ionic state at a particular pH (Mohan et al. 2007; Genc *et al.,* 2003). Equally, the apparent increment in adsorption with pH was believed to result from corresponding increase in the number of negatively charged sites. Consequently, the electrostatic attraction between the negative surfaceand the cationic BRE molecules increased with pH and reached saturation at about pH 6.95. Sivakumar and Palanisamy (2009) and Noroozi, *et al.*, (2007) had reported similar results for the adsorption of basic red 29 onto Euphorbia antiquorum L. and BR 41 onto silkworm pupa, respectively.

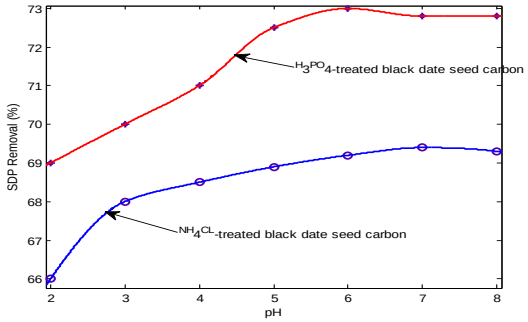

Figure 11: Influence of pH on the adsorption of SDP from BRE on to ASAS and ADSA (adsorbent dose = 50 g/l, BRE volume = 20 ml,C0 = 161.92 mg/l, Temperature 30°C, contact time = 30 min).

5. Conclusion

African date seed biomass (ADSA and ADSS) was able to adsorb SDP from brewery effluent (BRE). The removal of SDP from BRE using ADSA and ADSS was a function of contact time, bio-adsorbent dosage, temperature and pH. Adsorption capacity increased with increasing temperature. The optimum SDP removals were achieved at pH 6.95, 50 g/l dose and 30°C

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