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ارزیابی و کنترل پساب کارخانه آبجو سازی: سینتیک جذب و انتقال فلزات

آدامز دوجی آیتودو*، رافوس شاتو، جانسون ایدوکو آداجی

۱. گروه شیمی، دانشگاه فدرال کشاورزی، نیجریه

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Brewery Wastewater Evaluation and Remediation: Metal Sorption Kinetics and Transport

Adams Udoji Itodo*, Rufus Sha'Ato, Johnson Idoko Adaji

1. Department of Chemistry, Federal University of Agriculture, PMB 2373 Makurdi, Nigeria

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چکیده

این مطالعه شامل جذب فلزات سمی پساب کارخانه آبجوسازی با استفاده از زیست توده گیاه براسوس آتیاپوم به طریق شیمیایی اصلاح‌شده (TDA) و اصلاح شده از نظر سایز (UAD) می‌باشد. مطالعه اولیه و بررسی خروجی کارخانه آبجوسازی با استفاده از جاذب‌های مذکور نشان داد که پارامترهای مربوط به کیفیت آب بیشتر از حد مجاز می باشد. تکنیک‌های دستگاهی و کلاسیکی بکار رفته برای بررسی جاذب نتایج معتبر و قابل قبولی ارائه دادند. مطالعات سینتیکی همراه با تغییر شرایط مانند غلظت پساب، pH، زمان و دما که بر روی جذب کادمیوم و کروم مؤثر بودند، بررسی شد. مدل سنتیکی شبه مرتبه دوم با ضریب همبستگی بالایی برای داده ها مطابقت داشت و qₑ تجربی و تئوری با کمترین خطا برای این مدل بدست آمد. مراحل انتقال توسط نفوذ داخل ذره‌ای، که تنها عامل محدودکننده سرعت نبود، توصیف گردید. بطور کلی زیست توده به طریق شیمیایی اصلاح‌شده کارآیی خیلی خوبی برای حذف فلزات نشان داد که می‌تواند قابل رقابت با کربن فعال تجارتی باشد.

واژه‌های کلیدی

جذب سطحی؛ فلزات؛ آبجوسازی؛ گیاه براسوس آیتاپوم.

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Abstract

The study involves the adsorption of potentially toxic metals from brewery effluent (Beff), using size modified (UAD) and chemically modified (TAD) Borassus aethiopum biomass. Preliminary study and characterization of both brewery effluent and the derived adsorbents were recorded, with result showing some water quality parameters greater than threshold limits set by legislation. Both classical and instrumental techniques adopted for Sorbent characterization show valid outcome. Batch kinetic studies were monitored along with the role of varying conditions (Effluent concentration, pH, time and temperature) that could influence cadmium (Cd) and chromium (Cr) adsorption. Model applicability test supported the Pseudo second-order, with a high correlation coefficient, least error sum and high precision in qe. cal./exp. The mode of transport is best explained with intra-particle diffusion, not as the only rate limiting process. Generally, the chemically treated biomass exhibited metal removal efficiencies that could compete with the function of commercial activated carbon (CAC).

1. INTRODUCTION

The release of large quantities of industrial and municipal effluent into the water body has shown environmental problems in a large extent as a result of their persistence and non-biodegradability. This may strike a known danger to environmental and human health, depending on the nature and quantity of the metal ingested [1]. Their toxicity is related to the formation of complexes with proteins, in which carboxylic acid (–COOH), amine (–NH2), and thiol (–SH) groups are involved. When metals bind to these complexes, important enzyme and protein structures are affected.

Heavy metal removal technologies, including chemical Precipitation, coagulation, ion-exchange, electrochemical methods, membrane process and ultra-filtration, have been documented among others [2,3,4]. Treatment such

as chemical precipitation, ion exchange and adsorption can be used for the removal of heavy metals from wastewater. The disadvantages of various traditional water treatment technologies are high maintenance and operational costs, a difficult procedure for the treatment and production of toxic sludge [5,6]. Comparatively, the adsorption method is convenient, with simple design and ease of operation [7].

Sorption describes a group of processes, namely; adsorption and precipitation reactions [8]. Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, which are liquid-liquid, gas-liquid, gas-solid or liquid-solid interface [9]. The physisorption attraction interaction is Van der Waals forces. An adsorbent material must have some significant properties, such as high internal volume access to the different target components, a high surface area, particularly the internal surface area, pore size distribution and the nature of the pores that markedly influence the type of adsorption processes [10].

Adsorption kinetics explains the dynamics in the uptake of an adsorbate with time [11]. The most conveniently used kinetics models in sorption processes are Pseudo-first-order kinetics (Equations 1 and 2), Pseudo-second-order kinetics (Equations 3 and 4) and the Elovich model (Equations 5 and 6) [12].

$$q_t = q_e [1 - \exp(-K_1 t)] \qquad (1)$$

The linear form of Eqn. 1 for pseudo-first-order kinetic model is given as Eqn. 2 [12,13].

$$\ln(q_e - q_t) = \ln q_e - K_1 t \qquad (2)$$

$$q_t = K_2 q_e^2 \frac{t}{(1 + K_2 q_e t)} \qquad (3)$$

Eqn. 3 is rearranged to Eqn. 4 as linear form of Pseudo-Second-Order Kinetic Model.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e} \qquad (4)$$

$$\frac{dq_t}{d_t} = \alpha \exp(-\beta q_t) \qquad (5)$$

For pseudo-first-order kinetic (Eqn. 1), q_t and q_e (mg/g) are the amounts of adsorbate, adsorbed at time, t and at equilibrium respectively, t is the time (min) and K_1 is the rate constants (min-1) and can be determined by plotting $\ln(q_e - q_t)$ versus t [12]. Pseudo-Second-Order Kinetic model's K_2 is the rate constant (g mg-1 min-1). Elovich equation (Roginsky–Zeldovichmodel) is also used to describe the second order kinetics, assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate-adsorbent [14], α is the initial adsorption rate (mg/g/min), β is the disruption constant (g/mg). If the adsorption fits to the Elovich model, a plot of q_t versus $\ln(t)$ should give a linear relationship with a slope of $(1/\beta)$ and an intercept of $1/\beta \ln(\alpha\beta)$.

In adsorption processes, it is important to know the rate limiting step. Which might be intra-particle diffusion (Eqn. 7) [15] or film diffusion model (Eqn. 8)

$$q_t = K_{id} t^{1/2} + I \qquad (7)$$

$$\ln(1 - F) = -K_f d_t \qquad (8)$$

From Eqn. 7, The physical quantity, I is the intercept (mg/g). K_{id} and I values are obtained from the slope and intercept of the linear plot. Applicable postulated mechanism gives a linear plot passing through the origin. The slope depicts the rate constant of intra-particle diffusion. However, exhibition of multi-linear plots, implied two or more steps influence the sorption process. In general, a mass transfer process is diffusion controlled and its rate is dependent upon the rate at which components diffuse towards one another. Three forms of applying intra-particle diffusion model exist (i) a situation when a system is sufficiently agitated and mixed with high turbulence, the rate is not limited by mass transfer across the boundary layer giving a plot of q_t against $t^{1/2}$ as straight line passing through the origin. (ii) Existence of multi-linearity in q_t versus $t^{1/2}$ plot. This implied that two or three steps are involved in the process wherein the first step depicts external surface or instantaneous; the second step is where intra-particle diffusion occur as rate controlling step, and indicated by gradual adsorption while at the third step, the solute moves slowly from larger pores to micro pores resulting to a slow adsorption rate. This is the step of final equilibration. (iii) For slowly stirred batch adsorption process wherein q_t versus $t^{1/2}$ gives a straight line with an intercept [16], implying a rate that is limited by mass transfer across the boundary layer. Film diffusion is used to investigate the transport of adsorbate from the liquid to the solid phase boundary [17]. F is the fractional attainment of equilibrium (F = q_t/q_e), $K_f d$ is the model's constant. Linear plot of $\ln(1 - F)$ versus t without intercept suggest that film diffusion controls the kinetics of the process.

In order to meet regulatory standards, effluent decontamination via heavy metal removal is critical. This research is aimed at evaluating brewery effluent from Kaduna, Nigeria and studying the kinetics and mode of transport of toxic metals reduction from the brewery wastewater, using adsorbent derived from the spongy mesocarp of Borasssus aethiopum.

2. EXPERIMENTAL

2.1. Reagents

All reagents used were of analytical grade and were prepared in line with standard routine laboratory practices. Reagents used in this study, including ethyl alcohol (95 %), starch, methylene

blue and others were procured from FISONS Science, Wembley Middlesex England.

2.2. Sampling

(a) Effluent Sampling was carried out in accordance with published protocol [18,19]. Effluent samples were collected from effluent discharge point of the Nigerian breweries industrial layout Kakuri, Kaduna state and homogenized to obtain a representative sample; first by stirring, before lowering a pre-cleaned 4L glass bottle (previously washed with 0.1 M HNO_3 before it was rinsed with distilled water into different depths of the effluent, allowed to over flow before withdrawing. The bottle was sealed before storing at 4 ºC till required for further analysis. pH and conductivity were determined in situ. The effluent sample to be used for metal analysis was treated with concentrated HNO_3 in order to lower the pH of the sample to less than 2 before refrigeration.

(b) The drupes of *Borassus aethiopum* were collected from Achokpa, a village in Igalamela L.G.A of Kogi state, Nigeria. The samples were taken for proper identification in the Department of Taxonomy, Ahmadu Bello University, Kaduna State. The drupes were washed and rinsed with distilled water, sun dried, ground into powder, screened to obtain the target particle size, washed many times with distilled water to remove the surface impurities, then oven dried at 110ºC and stored at room temperature [20].
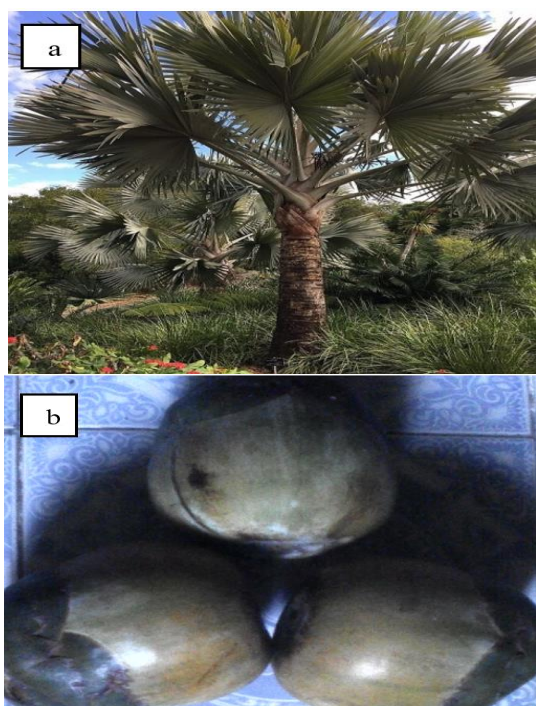

Fig. 1. Borassus aethiopum (a) plant and (b) drupes [21].

2.3. Characterization of brewery effluent

The sampled effluent was analyzed for physicochemical parameters as well as active functional groups following procedures outlined in the standard method for the examination of water and wastewater [22,23]. These parameters include pH, Conductivity, Turbidity, Biochemical Oxygen Demand, (BOD), Chemical Oxygen Demand (COD).

2.4. Preparation of adsorbents

Untreated adsorbent (UAD) was prepared by size modification, according to the stated design [24]. The spongy mesocarp from *Borassus aethiopum* were collected, washed and rinsed with distilled water, dried, ground into powder and screened into a target particle size of< 2 mm. The treated adsorbent, (TAD) was derived by chemical modification [25]. Part of the UAD was treated with alkali by a process known as chemical impregnation. This was done by allowing early prepared UAD to soak in 5% NaOH solution for 24 hours at room temperature (25 ± 2ºC), washed with distilled water and acetic acid, rinsed until filtrate attains neutral pH. The chemically treated adsorbents were oven dried at the 110 ºC to a constant weight, sieved to remove the unwanted particles and stored in an airtight container. Commercial activated carbon (CAC) was used as received for control experiment.

2.4.1. Characterization of adsorbents

Adsorbent characterization was based on the classical (bulk density, moisture content, ash content and iodine number test) and instrumental techniques, namely; Scanning Electron Microscope (SEM) and Fourier Transform Infra-red (FT-IR). SEM (Phenomenon Prix, MVE016477830) micrograph displays the surface structure or morphology of the adsorbent while the FTIR spectrum was recorded on an FT-IR (Agilent technologies Cary 630) for untreated and chemically treated Adsorbent. Procedures have been reported [26,27].

2.4.2. Physi-cochemical Characterization of Brewery Wastewater

The physicochemical parameters investigated for the brewery wastewater include the following: pH and conductivity using a multimeter (Jenway 4510), BOD [28], COD [12], turbidity [29], recorded in nephelometric turbidity units - NTUs and heavy metals analysis was conducted using Atomic adsorption Spectrophotometer (Varian AA240FS).

2.5. Batch Adsorption Experiments
2.5.1. Effect of Effluent concentration (% v/v) and other parametric factors
The effluent (10 mL) was taken and made up to a final volume of 50 mL. One-gram adsorbent was introduced into the flask and agitated for an hour at room temperature [30]. The same procedure was repeated using 20, 30, 40 and 50 mL volumes of effluent. The conical flask containing the adsorbent was placed on a shaker and agitated at 150 rpm, at room temperature for 1 hr to ensure equilibration. The suspension was then filtered using Whatman No. 2 filter paper. Other investigated parametric factors include the effect of pH [31], temperature [30], and the effect of contact time [30].

2.5.2. Digestion of Brewery Effluent for Metal Analyses
To 50 mL effluent sample, 9 mL of freshly prepared acid mixture (65 % HNO_3 was added and 37 % HCl) was added. The mixture was boiled gently over a water bath (95 °C) for 5 hrs (until the sample had completely dissolved) [32]. During the digestion, the inner walls of the beakers were washed with 2 mL of deionized water to prevent loss of the sample. Digestion continued until a clear solution (digest) was obtained and filtered with Whatman 42 (2.5-µm particle retention) filter paper. Digest filtrate was quantitatively transferred to a volumetric flask and made up to 50 mL volume with deionized water. Initial heavy metal quantitation was carried out using AAS.

2.6. Adsorption Studies
The amount of metals adsorbed by the adsorbent was evaluated using equation 9 [33], for adsorption of metal ion at equilibrium:

$$q_e = \frac{(c_o - c_e)v}{M} \qquad (9)$$

Where q_e, C_o, are equilibrium metal uptake sorption capacity, initial metal concentration (mg/L) and C_e is final metal concentration (mg/L). v is the volume of effluent in dm^3 while M is the weight of adsorbent in grams. The percentage of metal removed was calculated using the Eqn 10 :

$$(\%)RE = \frac{(c_o - c_e) \times 100}{c_o} \qquad (10)$$

RE represents the metal adsorption efficiency, C_o, the initial metal concentration (mg/L) and C_f is the final metal concentration (mg/L).

3. RESULT AND DISCUSSION
3.1. Physical inspection of sample and Sampling Site
Physical examination showed that the effluent from both discharge point at Kakuri, Kauna state and receiving water body at Makera, Kaduna (Fig. 2) is polluted evidenced by the brownish colouration, with distinct foul odour and microbial activities in the surroundings. Similar report has been documented [34].

Fig. 2. Pictorial presentation of (a) Effluent discharge point and (b) Receiving point of impact.

3.2. Physicochemical Parameters
Reports of the physico-chemical parameters of brewery effluent and adsorbents were presented in Tables 1 and 2 respectively.

3.2.1. pH
pH value of the discharged brewery effluent falls within the acceptable discharge limits of NESREA and WHO regulatory Standards (6.0 to 9.0). If the pH value of the surface water drifts off the range of 6.5-7.5, lives of some sensitive aquatic organisms may be lost. Metals tend to stay insoluble or more inert, and hydrogen sulphide evolution is controlled. As pH increases, surface proton is removed, increasing the attraction metal and the surface. Sorption could be enhanced at increase pH [35].

3.2.2. Conductivity
The mean conductivity values of effluent in this research work are fairly high (12.68 µS/cm) as against the regulatory standards of the WHO. 12.00 µS/cm but are below the EPA standard of 15.00 µS/cm. The high conductivity values of brewery effluent could be as a result of the concentration of ions present in the wastewater.

3.2.3. Turbidity

Turbidity is the measure of clarity of a water body and its optical [29]. Turbidity value (39.3 NTUs) of the effluent is above the standard limit set by both NESREA and WHO (5NTUs). This may be due to the presence of suspended and colloidal matter sucked as clay, silt, finely divided organic and inorganic matter, plankton and other microscopic organism. This compares to the intensity of light scattered by a standard reference suspension with its records in neophelometric turbidity units (NTUs).

3.2.4. Chemical oxygen demand (COD)

The COD of the brewery effluent is 15.48 mg/L, which is below the regulatory standard limit of NESREA (60-90 mg/L) and WHO (250 mg/L). The semi-colloidal material in suspended solids of this effluent may be lesser in organic load of the waste water. This lower value of COD in this effluent is against the report of possibility of depletion of natural oxygen present in the effluent [32].

3.2.5. Biological oxygen demand (BOD)

The BOD is a measure of the oxygen demands of bacteria under controlled conditions, many effluents takes longer lag than the period of analysis to break down [31]. The BOD result of the analysis is 8.991 (mg/L) which is also below the regulatory standard of NESREA (30-50 mg/L) and WHO (30 mg/L). This is equally attributed to the low presence of colloidal suspended material in the waste water [29].

3.3. Classical Characterization of Adsorbent
3.3.1. Ash

This includes the bulk mineral matter after carbon, oxygen, sulphur, and volatility during combustion [36]. The ash content of untreated adsorbent (UAD) is 12.21 ± 0.370 %, which is higher than the value recorded for commercial activated carbon (7.10 ± 0.03), making it less attractive for adsorption, the ash content of treated activated carbon (TAD; 4.22 ± 0.60 %) is lower as against the CAC and that made it favorable for high sorption. The ash content of Commercial activated carbon (CAC) is mostly found to be 2% [29].

3.3.2. Bulk density

The density of granular activated carbon if loaded into its packaging with a lower limit on bulk density standard set by the American Water Works Association is 0.25g/mL. The result of the bulk density value of the adsorbents is shown in Table 2. The value, 0.02 ± 0.01 g/cm³ for treated Adsorbent (TAD) is in agreement with values reported in literatures [36].

3.3. Iodine number

Iodine number measures the level of activities and values are reported in mg/g. The iodine number test is used to determine the adsorption rate of iodine from an aqueous solution. It shows the extent of micro-pores and account for total surface area of adsorbents. Adsorbents with a high iodine number performs better in removing small size particle (contaminants), while those with low iodine number performs better in removing medium sized particles [37]. From the result (Table 2) untreated adsorbent (UAD) gave a fairly high iodine number of 94.14 mg/g, treated Adsorbent (TAD) indicated a higher value of the iodine number of 182.19 mg/g and the commercial activated carbon (CAC) showed the least value of iodine number of 73.36 mg/g compared to others, owing to its granular design.

3.3.4. Moisture content

This referred to be a measure of the amount of water in any form of a substance or adsorbent. Moisture content for UAD was valued at 7.08%, TAD at 3.12% and the CAC is 6.67%. Low moisture content is an indication of low microbial activities and high shelf life.

Table 1. Physico-chemical Parameters of Brewery Effluent and Discharge Limit.

Parameters	Values		
	Current Study	NESREA	WHO
pH	6.512	6.0 - 9.0	6.5 – 85
Conductivity (µS/cm)	12.68	-	12
Turbidity (mg/L)	39.3	5	5
COD (mg/L)	15.48	60 – 90	250
BOD (mg/L)	8.991	30 – 50	30

Table 2. Physicochemical Parameter of Adsorbents.

Parameters	Derived adsorbents		
	UAD	TAD	CAC
Ash (%)	12.21± 0.370	4.22 ± 0.600	7.10 ± 0.030
Bulk Density (g/cm³)	0.09 ± 0.020	0.02 ± 0.010	0.10 ± 0.020
Iodine Number (mg/g)	124.14 ± 0.05	89.19 ± 0.06	250.36 ± 0.30
Moisture (%)	7.08 ± 0.040	3.12 ± 0.050	6.67 ± 0.070

3.4. SEM Characterization

The surface morphology of the adsorbents, by SEM micrographs is shown as Figure 3 for untreated (UAD) and treated adsorbent (TAD). The pore size development in untreated adsorbents (UAD) is not pronounced and evidenced by a cemented or smooth surface, whereas, the SEM image of treated adsorbent (TAD) and CAC shows some level of

resemblance with rough surfaces which are indicative of pore size development. This implied more adsorption sites for adsorbate occupancy [28]. Comparatively, UAD indicates smooth external surface depicting less reactive sites.
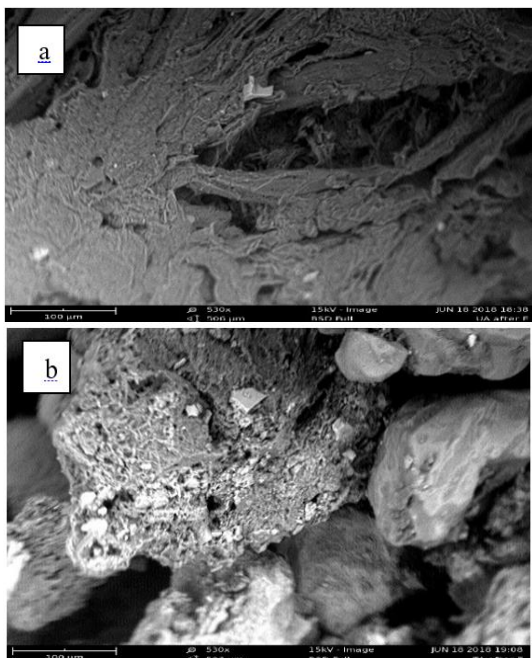

Fig. 3. SEM Micrograph of (a) UAD and (b) TAD.

3.5. FTIR Characterization
Difference in functional groups like hydroxyl (-OH), amine (-NH), carboxulate anions (-COO-) and others (-C-C), (-C=C), (-C≡C), (-C-N), (-C-H), (-C=O) have been said to be responsible for metal binding [38]. Other factors include; quantity of sites, site accessibility, chemical state or affinity between the site and metal, pores and oxygen availability, among others [38]. The FTIR spectra of adsorbent given in Figure 4 with interpretation in Table 3 for UAD, TAD and CAC (Adsorbents) in The displayed peaks at 3634.2cm^{-1} and 3693.8 cm^{-1} fall within the frequency range of stretching vibration for OH groups (Mohammed *et al.,* 2010). The band at 3272.6 cm^{-1}, 3201.8 cm^{-1} and 3287.5cm^{-1} in the range of 3499-3000 cm^{-1} for UAD, TAD and CAC indicates the presence of the NH group [39]. The band noticed at 2918.5 cm^{-1} and 2914.8 cm^{-1} for UAD and CAC in the range of 2999-2500 cm^{-1} is assigned to asymmetric stretches of –CH group from alkanes [40]. Frequency range of 2499-2000 cm^{-1} due to C=O stretch from esters/carboxylic acids, C≡N, C≡C and SP^2 C-H stretches from Nitriles, Alkynes and Aromatic compounds, respectively observed in the derived adsorbents are among those reported to support adsorption [27].
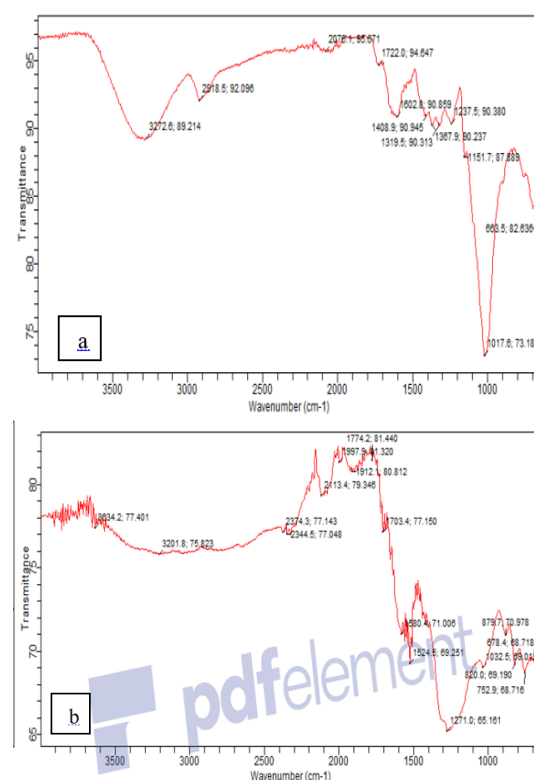

Fig. 4. FTIR Spectrum of (a) UAD and (b)TAD.

Table 3. Comparative FTIR Spectra Characteristics of UAD, TAD and CAC.

Group Freq.(cm^{-1})	Functional group	Observed freq.			Assignment
		UAD	TAD	CAC	
4000-3500	Alcohols	---	3634.2	3693.8	O-H stretch
3499-3000	Amines	3272.6	3201.8	2387.5	N-H stretch
2999-2500	Alkanes	2918.5	---	2914.8	SP^3 C-H stretch
1999-1500	Aromatic compounds	---	1997.9	---	Aromatic overtones of ring bends
	Ketones/Esters	---	1774.2	---	C=O stretch
	Aldehydes	1722.0	---	---	
	Alkenes	---	---	1636.3	C=C stretch
	Aromatic compounds	1602.8	---	---	
1499-1000	Aromatic compounds	1408.9	---	---	C=C stretch
	Amines	1319.5	---	---	C-N stretch

3.6. Effect of Parametric Factors

3.6.1. Effect of pH

Figure 5 shows the effect of pH on equilibrium phase or un-adsorbed metal concentration, C_e (mg/L). B_{eff}-UAD showed highest unadsorbed Cd at pH 10, B_{eff} – TAD at pH 8 and B_{eff} – CAC at pH 6 while, B_{eff} – UAD showed highest equilibrium phase Cr at pH 2, B_{eff} – TAD at pH 2 and B_{eff} – CAC at pH 10. The removal of Cd ion was more for TAD and CAC because, the surfaces of activated carbons are negatively charged as a result of excessive OH^- ions present in the solution [41]. Consequently, the electrostatic attraction

n between cationic metal ions and anionic surfaces of adsorbents increases the quantity of Cd adsorbed [42].
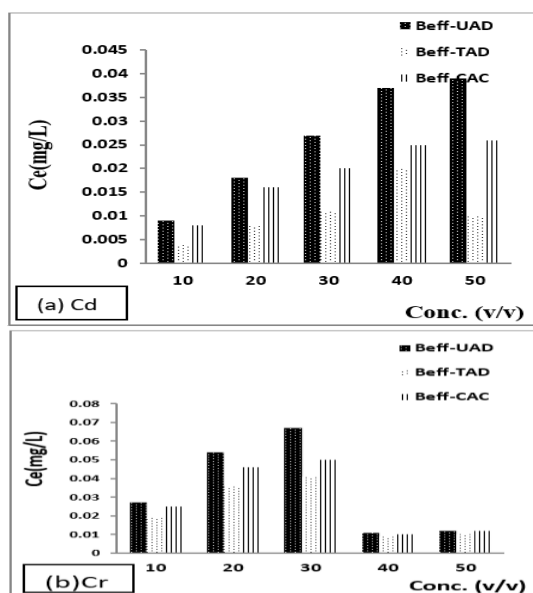

Fig. 5. Effect of Effluent Concentration on (a) Cd and (b) Cr Uptake.

From Fig. 6 (a) and (b), while the increase in pH favors Cd sorption efficiency, reverse scenario was observed for Cr uptake. The %RE for Cr by the treated adsorbent (TAD) decrease steadily with an increase in pH except for a rapid increase at pH 10. Effect of pH on Cr- B_{eff} – CAC is irregular.

3.6.2. Effect of time

Variations in removal efficiency of metal ions with elapsed time are shown in Figure 6 c & d. The removal efficiency for UAD is least compared to those of TAD and CAC. Highest in the series is Cd-B_{eff} –TAD followed by Cd-B_{eff} – CAC. The removal efficiency increases with increase in time. A similar trend was observed for Cr uptake. The percentage removal using TAD

was higher compared to CAC due to its pore size development and high iodine number. Metal-B_{eff} –TAD recorded the highest value of the iodine number compared to UAD and CAC [26].

3.6.3. Effect of temperature

The experiments were carried out at temperatures varying from 313 to 393k (Figure 6 e & f). It was found that the effect of temperature is not pronounced on Cd uptake. The %RE trend follows; Cd-B_{eff}–UAD< Cd-B_{eff} –CAC < Cd-B_{eff} –TAD. On the contrary, the Cr removal efficiency increases with temperature up to 373 K before desorption sets in at 393 K. The efficient removal of metals due to increasing temperature causes more interaction between adsorbate and adsorbent [43]. The highest removal percentages were recorded at 373K for the metal ions. The increase in temperature increases the mobility of the ions of the effluent and yielded a swelling impact with the interior structure of adsorbent, thus allowing the larger molecules to move deeper [30].

3.6. Adsorption Kinetics

It was adduced [44] that kinetics, modeled the rate process and could predict information about adsorbent- adsorbate interaction. The R^2 values for pseudo first-order equation (Figure 7 a& b; Table 4) for Cd-UAD (0.8295), Cd-TAD (0.8502), Cd-CAC(0.8387) and for Cr-UAD(0.5699), Cr-TAD(0.9791) and Cr-CAC (0.8257) were considerably lower than their corresponding values of the pseudo second order model (Figure 8 c & d; Table 4). The high coefficient of regression suggested the applicability of second-order kinetic model for Cd-UAD (0.9735), TAD (0.9977) and CAC (0.9992); Cr-UAD (0.9549), TAD (0.9977) and Cr-CAC (0.9864). This shows the overall rate of the adsorption process was controlled by chemisorption and could involve valence forces, via exchange of electrons between the adsorbents and adsorbate [13]. A model applicability test based on precision (high degree of agreement between calculated and experimented q_e values) and error analysis (least statistical sum of error square) all supported the adoption of the pseudo second order model as most applicable. Least in the series is the coefficient of applicability values in the elovich model (Figures 9), indicating; Cd-UAD (0.7538), TAD (0.8625) and CAC (0.8051); Cr-UAD (0.528), TAD (0.3575) and CAC (0.4649). In other words, rate of adsorption could not be interpreted based on the Elovich model, owing to poor correlation coefficient values. Unlike the R^2 values, the adsorption rate (Table 4) reported for the Elovich model is higher than

those estimated for the pseudo first order (K_1 = 0.0143- 0.0226 for Cd and 0.0097-0.0237 min^{-1} for Cr uptake). The lowest rate constant were the

results of pseudo second order (k_2 range of 0.0004- 0.0015 g.mg^{-1}min for Cd), which best represented the process rate in this study.
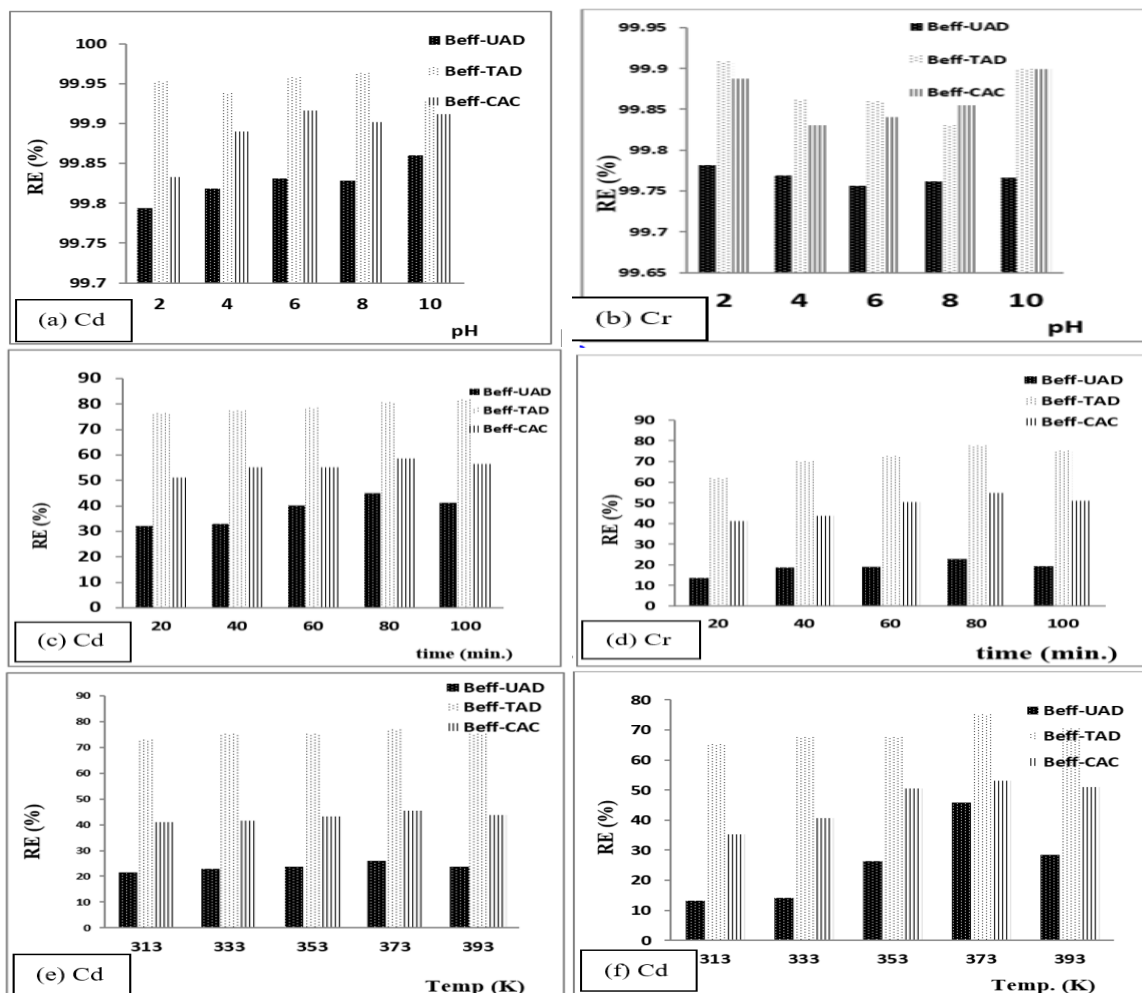

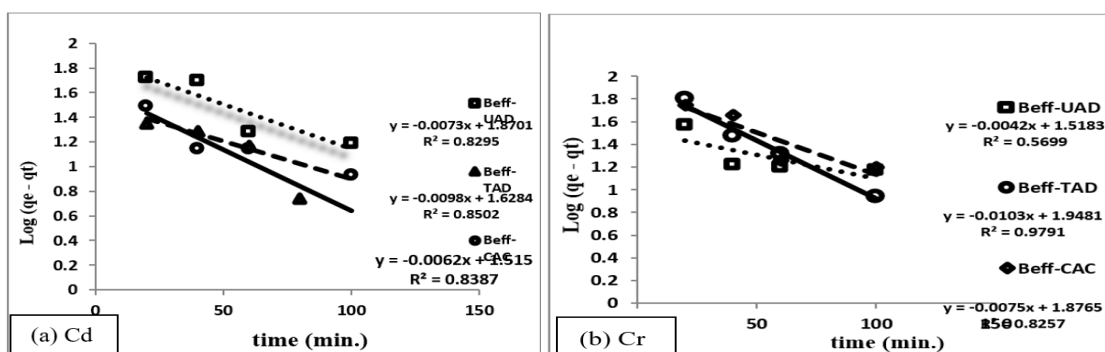**Fig. 6.** Effect of Parametric Factors on Adsorption of (a) Cd and (b) Cr.

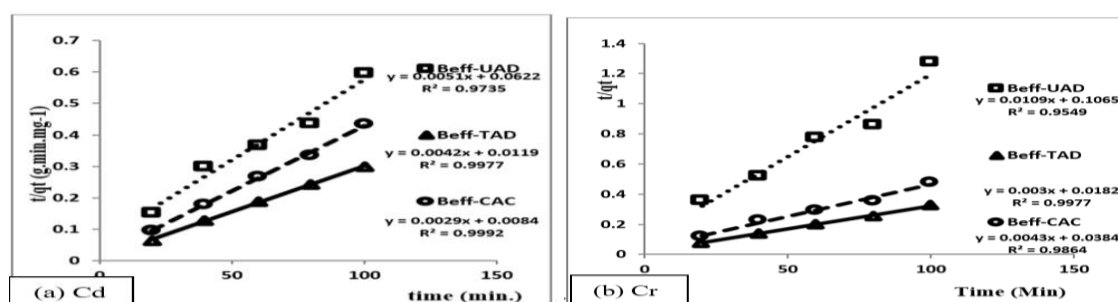**Fig. 7.** First-Order Kinetic Model for (a) Cd and (b) Cr Adsorption.

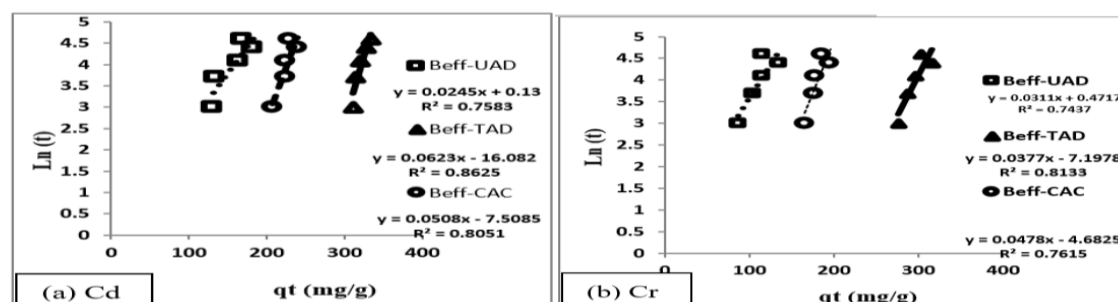**Fig. 8.** Second-Order Kinetic for (a) Cd and (b) Cr Adsorption.

Fig. 9. Elovich Kinetic Model for (a) Cd and (b) Cr Adsorption.

Table 4. Kinetic Study Experimental Constants for Metals onto Adsorbents.

Kinetic model	Experiment	Constants			
Pseudo First Oder		R^2	qt Cal.(mg.g^{-1})	qt Exp.(mg.g^{-1})	K_1(min^{-1})
	Cd-B$_{eff}$-UAD	0.8295	0.2719	183.05	0.0168
	Cd-B$_{eff}$-TAD	0.8502	0.2118	334.20	0.0226
	Cd-B$_{eff}$-CAC	0.8387	0.181	239.80	0.0143
	Cr-B$_{eff}$-UAD	0.5699	0.1814	093.00	0.0097
	Cr-B$_{eff}$-TAD	0.9791	0.2896	315.79	0.0237
	Cr-B$_{eff}$-CAC	0.8257	0.2733	223.60	0.0173
Pseudo Second Order		R^2	qt Cal.(mg.g^{-1})	qt Exp.(mg.g^{-1})	K_2(g.mg^{-1}min)
	Cd-B$_{eff}$-UAD	0.9735	196.0784	183.05	0.0004
	Cd-B$_{eff}$-TAD	0.8625	238.0952	334.20	0.0015
	Cd-B$_{eff}$-CAC	0.9992	344.8276	238.80	0.0010
	Cr-B$_{eff}$-UAD	0.9549	091.7431	093.00	0.0011
	Cr-B$_{eff}$-TAD	0.9977	333.3333	315.79	0.0005
	Cr-B$_{eff}$-CAC	0.9864	232.5581	223.60	0.0417
Elovich		R^2	α (mg/g^{-1} mg^{-1})	β (mg.g^{-1})	
	Cd-B$_{eff}$-UAD	0.7583	0.3577	0.0245	
	Cd-B$_{eff}$-TAD	0.8625	4.5327	0.0623	
	Cd-B$_{eff}$-CAC	0.8051	3.9039	0.0508	
	Cr-B$_{eff}$-UAD	0.5280	5.9044	0.8350	
	Cr-B$_{eff}$-TAD	0.3575	5.5878	0.3691	
	Cr-B$_{eff}$-CAC	0.4649	5.4169	0.4562	

Cd-B$_{eff}$-UAD: Adsorption of Cd from Brewery efflyent onto UAD.

3.8. Transport (Diffusion) studies

The coefficient regression values of the intra-particle diffusion model (Figure 10; Table 5) include; Cd-UAD (0.7321), TAD (0.9734) and CAC (0.6752); Cr-UAD (0.5348), TAD (0.8057), and CAC (0.7513). This is very obvious from the high coefficient of regression that the boundary layer has a significant effect on the diffusion mechanism of metal uptake on the derived adsorbents and commercial activated carbon. This implies that diffusion is among determining parameter in the adsorption process. This model explains the movement of adsorbate across the external surface sites of the adsorbent particle [45]. The linear plot of qe vs t$^{0.5}$ with, intercept greater than zero but close to the origin indicates that inter-particles diffusion alone does determine the overall rate of adsorption [17].

The liquid film diffusion model plots of ln(1-F) vs t(min) gave low coefficient regression values for

Cd-UAD (0.1475), TAD (0.8502) and CAC (0.1443); Cr-UAD (0.1376), TAD (0.1576) and CAC (0.1474) It is obvious from the very low regression value above that the boundary layer has a less significant effect, indicating that film diffusion does not determine the rate of adsorption and does not show good fit and non-applicable to the sorption phenomenon [46]. The intercept values for the model is lower and close to origin, confirming liquid film diffusion as a non- rate determinant for the adsorption process [26,41].
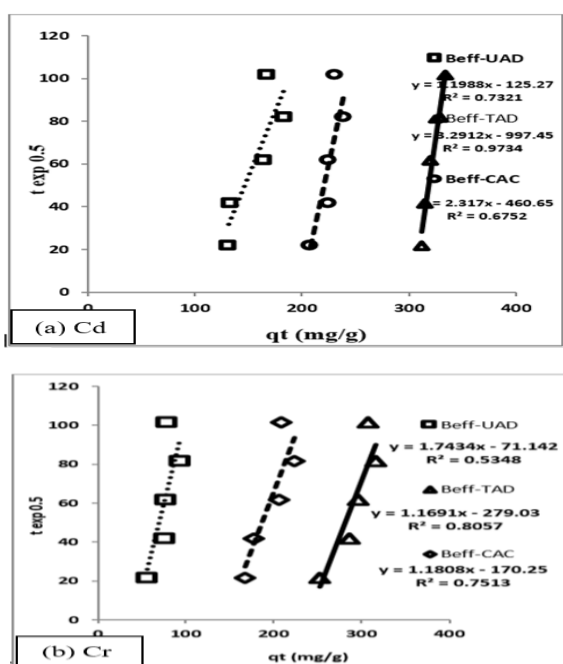

Fig. 10. Intra-particle Diffusion Model for (a) Cd and (b) Cr Adsorption.

Table 5. Transport model Experimental Constants for Metals onto Adsorbents.

Transport model	Experiment	Constants	
Intra-particle diffusion		R^2	K_{Id} (mg/g min$^{1/2}$)
	Cd-B$_{eff}$-UAD	0.7321	1.1988
	Cd-B$_{eff}$-TAD	0.9734	3.2912
	Cd-B$_{eff}$-CAC	0.6752	2.3170
	Cr-B$_{eff}$-UAD	0.5348	1.7434
	Cr-B$_{eff}$-TAD	0.8057	1.1691
	Cr-B$_{eff}$-CAC	0.7513	1.1808
Film diffusion		R^2	$K_{fd}(L^2T^{-1})$
	Cd-B$_{eff}$-UAD	0.1475	0.1837
	Cd-B$_{eff}$-TAD	0.8502	0.0227
	Cd-B$_{eff}$-CAC	0.1443	0.1788
	Cr-B$_{eff}$-UAD	0.1376	0.1788
	Cr-B$_{eff}$-TAD	0.1576	0.1881
	Cr-B$_{eff}$-CAC	0.1474	0.1885

Cd-B$_{eff}$-UAD: Adsorption of Cd from Brewery effluent onto UAD.

4. CONCLUSION

This study has successfully investigated brewery wastewater and found the values of some water quality parameters to be higher than those values set as threshold limits by existing legislations. The work also demonstrated the use of green adsorbents prepared from Borassus palm for the remediation of brewery spent water in Cd and Cr removal, with the removal efficiencies varying with conditions such as altering the effluent concentration (adsorbate loading), pH time and temperature. The comparable level of percentage removal using the adsorbents and CAC is an indication of their economic viability in the adsorptive treatment of brewery effluents. The kinetic study shows that adsorption of metals from brewery effluent is best modeled using the pseudo-second-order-model, an indication of chemisorption. Transport or diffusion of metals through the adsorbent studied implicate film diffusion model as odd and intra-particle diffusion as one, among other rate limiting processes.

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