

ACTIVATED CARBON SYNTHESISED FROM BOTTOM ASH FROM COAL FIRED BOILERS BY KOH ACTIVATION FOR LIQUID PHASE ADSORPTION

MUSONZA, L. MANDIPA¹, DUBE, DONATUS¹, SIBALI, L. LINDA²,
TUMISANG SEODIGENG³ AND CHIRIRIWA, HARRY^{3*}

¹*Applied Chemistry, National University of Science and Technology, Bulawayo, Zimbabwe*

²*Department of Environmental Sciences, College of Agriculture and Environmental Sciences, University of South Africa, Florida, South Africa*

³*Department of Chemical Engineering, Vaal University of Technology, Private Bag X021, Vanderbijlpark, 1911, Andries Potgieter Blvd, South Africa*

(Received 13 October, 2020; accepted 14 December, 2020)

ABSTRACT

The potential use of bottom ash activated with potassium hydroxide in liquid phase adsorption was studied. Proximate analysis, iodine value and batch experiments were used to characterize activated carbon. In order to perceive the mechanism of adsorption, experimental data was fitted to Freundlich, Langmuir, Temkin and Dubinin-Radushkevich adsorption isotherm models, and the coefficients of correlation were calculated to be 0.8092, 0.5936, 0.8865 and 0.5031. The kinetic data is fitted with pseudo first, second order together with models involving intraparticle diffusion. The pseudo second order rate constant was calculated to be 0.0547g/g.min with correlation coefficient of 0.984. Based on Temkin isotherm model, heat of sorption was found to be -2 704.77J mol⁻¹ and the equilibrium binding constant comparable to the ultimate binding energy was 13.255Lg⁻¹. The mechanism showed that the process was a chemisorption type of adsorption. Activated carbon was established to be very efficient in adsorption of industrial effluents with percentage removal reaching up to 100%.

KEY WORDS : Bottom ash, KOH activation, Adsorption, Isotherms, Kinetics

INTRODUCTION

In Zimbabwe, about 50 million tons of bottom ash is produced per year from burning approximately 200 million tons of coal per year producing large landfills that occupy more than 10 000 acres of land (Rafieizonooz *et al.*, 2017). The quantity of bottom ash is increasing at an alarming rate per month. Landfills of bottom ash at thermal power stations are accumulating resulting in handling and storage problems (Youcai, 2017). These are also causing land pollution with regards to presence of alkaline heavy metals and their leaching problems. The community benefits from the reuse of bottom ash in that the activated carbon produced can be used for the purification of water at the wastewater

treatment plant and also be used for agricultural purposes (Mandal and Sinha, 2014). This also reduces the risk of land-slides and death of animals due to drinking of polluted water caused by leaching of heavy metals. Activated Carbon is used to remove the natural organic compounds (i.e. tannins) that produce carcinogenic chlorinated by-products during chlorine disinfection of water (Tak and Vellanki, 2018). It is also used for the removal of odours or colours, foaming compounds, oxidizing chemicals, and as metal ions that constitute invisible impurities that are invisible.

Activated carbon can be used to improve product stability and provide better crystalline. It is used to recover valuable materials, improve purity, improve product appearance and act as a barrier to prevent

color body migration. Activated carbon is a very effective adsorbent due to porosity which is advanced, a surface area which is very broad up to $3000\text{m}^2\text{g}^{-1}$, wavering properties of high degree of surface reactivity and chemistry. These exclusive features make activated carbon a very adaptable material. It has not only been studied as an adsorbent, but also used as a catalyst support and as a catalyst for a range of applications, such as the removal of pollutants liquid phase or gas or recovery and cleaning of chemical products (Ali *et al.*, 2012). These materials are more expensive than other adsorbents due to their exorbitant production costs. Coal based thermal power plants produce fly ash in huge quantities and it is either a waste or a by-product (Dwivedi *et al.*, 2014). Fly ash has been researched for the expulsion of dyes that are cationic, rosaniline hydrochloride and crystal violet (Albanis *et al.*, 2000; Elass *et al.*, 2010). Activated Carbon used commercially is desired for the removal of micro-pollutants in the aqueous phase. Non-conventional wastes like industrial activities can be used to prepare activated carbon that are utilised in a variety of processes that utilise aqueous treatment. When the activation processes are enhanced, the non-convective or convective wastes can similarly contend with the ones already available in the market (Diasa *et al.*, 2007).

The effluent from dye stuff manufacture and certain other industries, like textile, pulp and paper dyeing, printing and leather industries contain small amounts of dyes. They impart color to water whereby lowering its aesthetic value. Therefore, it is highly essential to remove the dyes from water and wastewater systems. Shrivastava (2012) investigated the removal of methylene blue dye using potato husk as an adsorbent by batch adsorption technique. Activated carbon prepared from elephant dung by acid treatment was used to remove acid yellow 17 dye by adsorption from the aqueous solution (Theivarasu and Chandra, 2013).

Activated carbon prepared from bottom ash from thermal power stations have been explored partially (Dinçer *et al.*, 2007). Recent studies show that very little work has been performed on eradication of heavy metals employing sludge based activated carbon and bottom ash from thermal power stations (Diasa *et al.*, 2007). In this research, Munyati Power Station waste in the form of bottom ash was used to develop activated carbon as a result of availability and cheap cost of material, which has low inorganic

but high carbon content.

Experimental Section

The study was carried out in batches. All other factors remain the same, but the factors discussed are different. For each set of constant factors, each problematic factor must be run three times, and all experiments are performed at room temperature.

Materials

Bottom ash was obtained from Munyati Power Station and dried at $105\text{ }^{\circ}\text{C} - 110\text{ }^{\circ}\text{C}$ and crushed manually using a pestle and mortar before sieving the ash through a $200\text{ }\mu\text{m}$ test sieve making the samples suitable for the activation process. The pulverised ash was termed as fine and the ash $>200\mu\text{m}$ was termed as coarse (granular). Prepare working solutions from stock solutions by diluting to the required concentration.

Apparatus

Samples were tested for absorbance using a UV Visible Spectrophotometer (Perkin Elmer Lambda 2).

Preparation of adsorbent material

Two portions of 100 g bottom ash were weighed into beakers and 125 ml of 10% KOH was added to cover the bottom ash. Samples were pyrolysed in a furnace at $400\text{ }^{\circ}\text{C}$ for 1 hour 30 minutes. After activation the pyrolysed carbons were cooled to ambient temperature and samples leached for 2 hours with 2 % HCl followed by washing with distilled water before filtering using Whatman filter paper (No. 42). Samples were oven dried at $110\text{ }^{\circ}\text{C}$ overnight (Singh *et al.*, 2013).

Effect of adsorbent concentration (Dosage)

The effect of activated carbon on the adsorption capacity is achieved by mixing 50 mL of 0.05 g/L methylene blue solution with 1, 3, 5, 7 and 10g of activated carbon at room temperature. Absorbance was recorded at 664nm (Goswami *et al.*, 2013).

Effect of initial dye concentration

Dye (50 ml) was prepared in 5 different flasks with different concentrations of 0.05g/l, 0.025 g/l, 0.0125 g/l, 0.00625 g/l and 0.003125 g/l. To each of the flasks 1g of the activated carbon was added and agitated. This was allowed to settle for 15 minutes and absorbance was recorded at 664 nm.

Effect of acidity and alkalinity

Dye solution (100 ml) was formulated in a flask with final concentration 0.5g/l and adsorbent concentration (1g/50 ml) and initial pH of the conical flask is to be measured. Dilute HCl (0.05N) and KOH (0.05N) were used to adjust the pH of the dye solution. The flasks were placed on magnetic stirrer maintained at 27 °C and final concentration of dye was measured.

Effect of particle size

50 mL of 0.05g/l dye solution was prepared in 10 different conical flasks. To the first five conical flasks 1g of fine AC (<200 µm) was added and agitated. To the last five conical flasks 1g of coarse AC (>200 µm) was added and agitated at 120 rpm for 30minutes. This was allowed to settle for 15minutes and absorbance recorded.

Effect of contact time

Dye solution (100 ml) was prepared in 5 different flasks and 1g of AC added and agitated. The flasks were allowed to settle at different times before recording the absorbance. The contact times used were 5, 10, 15, 20 and 25 minutes.

RESULTS AND DISCUSSION

Effect of adsorbent concentration (Dosage) on dye removal

As adsorbent dosage increases, the percentage removal of the dye increased as well. The Q_e value decreased with increase in solid to solution ratio. There was no drastic increase in adsorption rate on increasing the dosage of adsorbent beyond 7.0016 g of activated carbon. This can be attributed to the increase in adsorbent sites for adsorption of the dye at the fixed 0.05 g/L. The adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption sites rises by amplifying adsorbent dosage (Amuda *et al.*, 2014). This is as a result of resistance to mass transfer of dye from bulk liquid to the solid surface, which is very crucial at high adsorbent loading when the experiment was performed. The percentage removal increased from 24.85% to 75.6%.

Effect of initial concentration on removal of dye

Percentage removal of methylene blue dye increased from 36% to 52% then decreased to 5.2%. A high affinity between the adsorbent and the

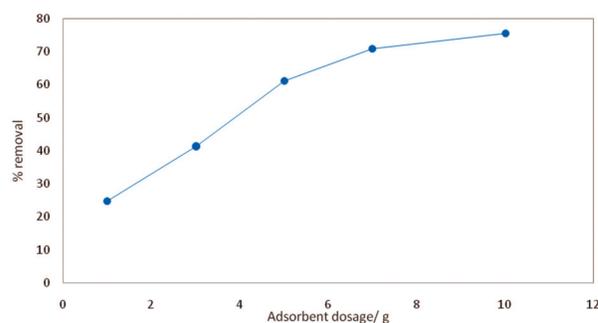


Fig. 1. Effect of adsorbent dosage on % removal

adsorbate reflected in good uptake values at low concentrations and thus percentage adsorption decreases as initial dye concentration increases. At reduced concentrations, the proportion of the first methylene blue dye molecules compared to the accessible surface area is reduced and consequently the adsorption will be fractionally independent to the original concentration of dye.

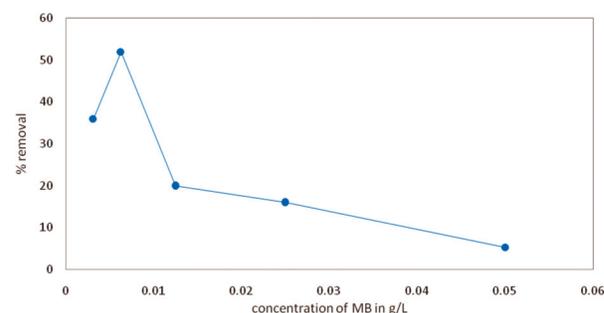


Fig. 2. Effect of initial concentration of Methylene Blue on % removal

The initial methylene blue concentration affords a critical driving force which overcomes all resistance caused by the mass transfer of the dye between solid and aqueous phases. The reduced uptake at increased concentration results from a higher ratio of initial adsorption number of molecules of dye to surface area that is available, hence adsorption that is fractional becomes dependent on the initial concentration (Amuda *et al.*, 2014). This was also because the number of ions competing for the available activated carbon surface sites was high hence resulting in lower dye adsorption capacity.

Effect of particle size on removal of dye

A good adsorbent is one with a large surface area and which requires less time for adsorption equilibrium. The raw material endures primary stages before the actual preparation of

activated carbon, such as milling, crushing and sieving to the relevant particle size. Particle size is critical for the handling of the raw materials, such as in mixing with the catalyst. Nonetheless, sizes of the particles can also affect the properties of the activated carbon to be produced. Adsorption rate increases with the decrease in particle size and increase in mesopore volume (Alslaibi *et al.*, 2013). Finer particles also marginally increase the percentage of the resulting micro-porosity. Observations on the adsorption efficiency of bottom ash decreased as the particle size decreased from <75 to 300-600 μm (Nidheesh and Gandhimathi, 2012). This can be attributed to the fact that smaller adsorbent particles have shortened diffusion paths and increased total surface area and therefore the ability to penetrate all internal pore structures of adsorbent is very high.

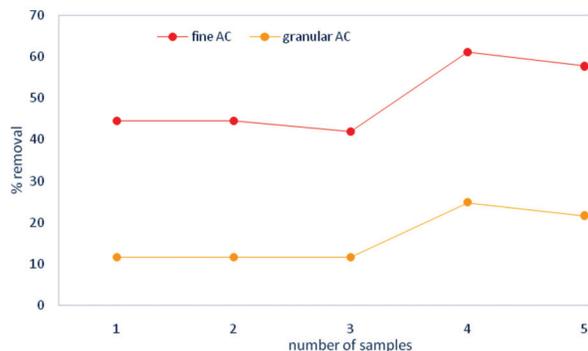


Fig. 3. Effect of Particle size on % removal

Fine activated carbon (<200 μm) percentage removal of dye was from 41.6% to 61.2%. This was high compared to the percentage removal of granular activated carbon which was from 11.6% to 21.6%. Fine activated carbon was more efficient. Dye removed increases as particle size decreases (Santhi and Manonmani, 2010). This is as a result of smaller particles having a large surface area than larger particles and hence adsorb more dye during the adsorption. For this reason, adsorbent particle size of <200 μm was selected for all the batch experiments.

Effect of contact time on dye removal

When contact time was increased from 5 to 25 minutes, the percentage removal of the dye increased from 24.8% to 57%. Adsorption increases with the increase in stirring time (Gumus, 2016). The removal of dye was rapid at the initial period of contact time and slowed with the increase of time. This is due to the strong attractive forces between

the dye molecules and the adsorbent. The change in removal rate over time may also be due to the fact that initially all adsorbent sites are empty and the solute concentration gradient is steep. This is as of the repulsion between molecules of solute in bulk and solid phases, thus making equilibrium to be reached after a long time.

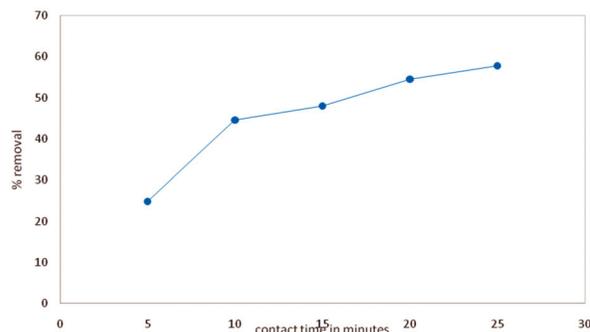


Fig. 4. Effect of contact time on % removal

Effect of pH on the removal of dye

pH of dye solution plays a critical role on capacity of adsorption. Efficiency of adsorption process is strongly dependent on pH, which affects the degree of ionization of the adsorbate as well as the surface properties of adsorbent. Methylene blue dye removal increased from 88.2% to 91.2% and then decreased to 44.6%. The optimum pH was found to be at 3.57 and the percentage removal was 91.2%. The minimum uptake of methylene blue dye was at pH 12.58. The shift in pH of solution causes development of distinctive species that are ionic and distinct surface charges of carbon whereas, the surface of the adsorbent was more protonated and competitive adsorption occurred between H^+ and free methylene blue ions and their OH^- ions towards the fixation sites at increased pH values. The same can be explained for acidic pH conditions.

At pH values greater than 7, the zwitterions from the methylene blue dye in water may cause an

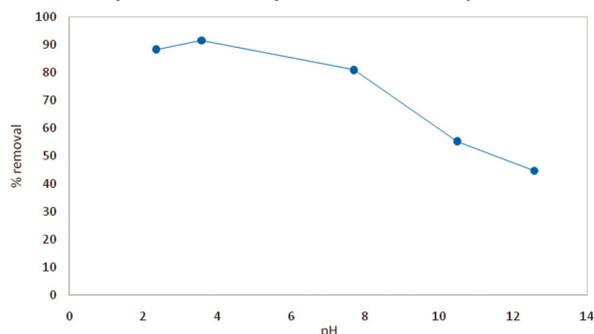


Fig. 5. Effect of pH on removal %

upsurge in the aggregation of methylene blue dye to construct a huge molecular form (dimer) which is not able to penetrate the structural pores on the surface of the carbon (Parthasarathy and Manju, 2010). This is as a result of attractive electrostatic interaction between groups that are ionic inside the monomer.

The results indicated that activated carbon adsorbent had good removal capacity in acidic medium than in basic medium. Therefore, H⁺ ions react with functional anionic groups on the adsorbent surface resulting in restriction of the number of binding sites favourable for the removal of methylene blue dye. However, a favourable increase in percentage removal for activated carbon was observed below pH 7.0.

Effect of pH_{zpc} on removal of dye

The variation of adsorption with pH can be explained by also considering the difference in the structure of the dye as well as the point of zero charge of the activated carbon. The zero point charge describes the condition when the electrical charge density on a surface is zero. The activated carbon had a zero point charge at pH 9.7. At pH < pH_{zpc} the adsorbent is positively charged and at pH > pH_{zpc} adsorbent is negatively charged. Cationic adsorption will be favourable at pH > pH_{zpc}. The surface will be negatively charged and favours the uptake of cationic dyes to increased electrostatic force of attraction. Thus methylene blue removal is favoured at higher pH (pH > 9.7). At lower pH (pH < 9.7), adsorbent surface is positively charged, concentrations of H⁺ were high and they compete with positively charged methylene blue cations for vacant adsorption sites causing a decrease in dye uptake from pH 3.57 to 12.48 according to figure 4.6. Similar trend was observed for adsorption of methylene blue onto rice husk and wheat shells (Rahman *et al.*, 2012).

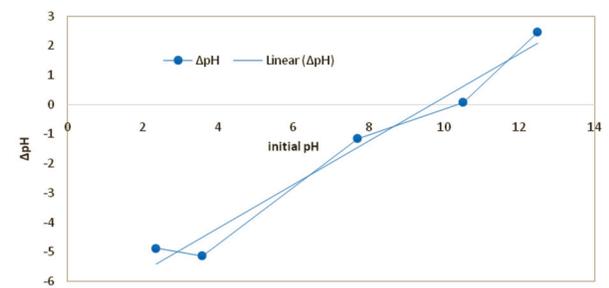


Fig. 6. Change in pH vs initial pH

Batch equilibrium study

Adsorption isotherm experiments were done in batches employing 250 mL flasks. Add a known mass of adsorbent (0.2-0.8g) to 100 mL of dye solution. The mixture was stirred for 30 minutes and after filtering, a spectrophotometer (UV/VIS) was used to calculate the equilibrium concentration of dye in each sample. Equilibrium (q_e) calculations of the amount of dye adsorbed by the adsorbent and the removal percentage are done according to equations (1) and (2).

$$q_e = \frac{V(C_i - C_e)}{M} \quad \dots (1)$$

$$\text{removal (\%)} = \frac{(C_i - C_e)}{C_i} \times 100 \quad \dots (2)$$

where C_i and C_e are initial and equilibrium concentrations of methylene blue, Volume of the solution is V in litres and mass of the adsorbent is given as M in grams.

Adsorption Isotherms

The adsorption isotherms were evaluated by fitting experimental data to four models, Freundlich, Langmuir, Temkin and Dubinin-Radushkevich and these models have widely been applied to describe the process of metal ion adsorption (Abdelhamid *et al.*, 2012; Johnson and Arnold, 1995; Kapoor *et al.*, 1989). Adsorption isotherms are the basic requirements for the analysis and design of the adsorption separation process. Table 1 shows the isotherm constants of the four adsorption isotherms which were studied.

Table 1. Adsorption Isotherms and their constants

Isotherm model	Constant	Methylene blue
Langmuir	Q _o (mg/g)	48.540
	b (L/mg)	1.347
	R ²	0.809
Freundlich	1/n	-1.617
	K _f (mg/g)	-974.316
	R ²	0.594
Temkin	a ₁ (L/g)	13.255
	b ₁ (J/mol)	-2 704.771
	R ²	0.887
	Dubinin-Radushkevich	Q _m (mg/g)
	K (mol ² /kJ ²)	0.2911
	E (kJ/mol)	1.311
	R ²	0.503

Langmuir

The development of the Langmuir isotherm is modelled according to the following premise: each site can hold only a single molecule of the adsorbate without molecular migration, and the energy of adsorption is consistent over the entire surface (Richardson *et al.*, 2002). Maximal adsorption happens when the adsorbate molecule monolayer becomes permeated adjacent to the surface of the adsorbent and along with consistent adsorption energy giving a model in linear (Equation 3):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_A q_m C} \quad \dots (3)$$

Where; C is concentration at equilibrium of adsorbate (mg/L), q_e is metal adsorption capacity per gram of adsorbent in equilibrium (mg/g), and q_m is the maximum single-layer covering capacity (mg/g), K_A represents the Langmuir isothermal constant (L/mg).

Using a quantity with no dimension, the separation factor R_L (Equation 4) we can then determine the associated advantage of the process of adsorption under the experimental conditions.

$$R_L = \frac{1}{[1+(1+K_A C_0)]} \quad \dots (4)$$

Where K_A is an adsorption energy constant, and C_0 is the initial concentration

The maximum capacity for adsorption correlates to the monolayer of adsorbate molecules which is saturated on the surface of adsorbent with energy which is constant and of adsorbate not transmitting in the adsorbent surface plane (Parthasarathy and Manju, 2010). The adsorbent prefers to bind acidic ions as observed from obtained values and speciation dominates on sorbent properties, when ion exchange which is the predominant mechanism occurs in the adsorption of methylene blue dye. For determining the advantages of the procedure of adsorption, the dimensionless separation factor (R_L) was calculated. The value was found to be 0.0146 and confirmed that the ongoing adsorption process was favourable since $0 < R_L < 1$ hence showing a monolayer coverage (Gumus, 2016). In general a good adsorbent is one with a high adsorption efficiency, Q_o , a steep initial adsorption isotherm slope and low Langmuir constant values.

Freundlich

The Freundlich isotherm was established on

heterogeneous surfaces to simulate multilayer adsorption and the linear form of the model is given in equation 5 (Freundlich, 1906):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \dots (5)$$

Where q_e is amount of metal ions adsorbed in equilibrium (mg/g), C_e is concentration (ppm) adsorbed at equilibrium, K_f is the Freundlich constant related to adsorption capacity, and n is the dimensionless heterogeneity coefficient.

According to Freundlich isotherm model, the adsorption intensity of the dye onto the activated carbon is heterogeneous, developing into homogenous as the value approaches zero. Values of $1/n < 1$ indicate normality in the Langmuir isotherm thus the results agree to a monolayer coverage. The correlation coefficient was 0.5936 which showed that it could not be comparable with the Langmuir model. The adsorption intensity, n , is an indicative of bond energies between adsorbent and dye and the probability of slight chemisorption instead of physisorption. The favourability of the sorption process gave n as -0.6184 hence the isotherm model is not favourable. The factors limiting or increasing the possibility of methylene blue dye adsorption onto the adsorbent include molecular weight, size and radii. The adsorption of methylene blue dye which appears to be multilayer is however possible through percolation.

Temkin

This isotherm contains a factor that distinctly considers the interaction between adsorbent and the adsorbate. By ignoring the acutely low and high values of the concentration, the model assumes that the heat of adsorption (change with temperature) of all molecules in the layer will decrease linearly, rather than the logarithm of the coverage (Temkin and Pyzhev, 1940; Aharoni and Ungarish, 1977). As shown in the equation, the characteristic of its derivation is to draw a distribution of binding energy which is uniform (up to the maximum binding energy) by plotting the adsorption amount of q_e relative to $\ln C_e$, and to determine the constant from the slope and intercept. The model is given by the equation. (6):

$$q_e = B \log A_t + B \log C_e \quad \dots (6)$$

Where A_t is the Temkin isotherm equilibrium binding constant (L/g), B_t is the Temkin isotherm constant, R is the gas constant (8.314 J mol⁻¹K⁻¹), T is

temperature at 298 K, and B is heat of adsorption and is a constant (J/mol).

Study of the data demonstrates that Temkin isotherm model fitted well for dye adsorption. Due to adsorbent/adsorbent interaction, adsorption heat of all molecules in the layer will decrease linearly with the coverage (Gumus 2016). This was found to be -2704.77 J/mol while the equilibrium constant for binding corresponding to the maximal energy for binding was 13.255 L/g and the coefficient of determination was 0.8865 . The coefficient of determination was proportionate to that obtained for Langmuir equations which explains the suitability of Temkin model to the methylene blue dye adsorption (Santhi and Manonmani, 2010). This indicates chemical adsorption and assumes that the bonding energy is evenly distributed until a certain maximum bonding energy is reached.

Dubinin-Radushkevich

These isotherms are usually used for expressing the mechanism of adsorption, have Gaussian energy distribution on heterogeneous surfaces (Gunay *et al.*, 2007; Dabrowski, 2001). This model usually successfully fits the middle range of high solute activity and concentration data. This method is usually used to differentiate the chemical and physical adsorption of metal ions and their free average energy. The adsorbate E of each molecule (used to move the molecule from its position in the adsorption space to infinity) can be determined by the following relationship Formula to calculate (Dubinin) (1960; Hobson, 1969)

$$\text{Log } q_s = \text{Log } q_e - K_{ad} \left[RT \left(\text{Log } 1 + \frac{1}{c_e} \right) \right]^2 \quad \dots (7)$$

where; q_e is quantity of adsorbate in the adsorbent at equilibrium (mg g^{-1}), q_s is theoretical isotherm saturation capacity (mg g^{-1}); K_{ad} is Dubinin-Radushkevich isotherm constant ($\text{mol}^2 /$

Kj^2) and E is $\frac{1}{\sqrt{2BDR}}$.

One of the unique characteristics of the Dubinin-Radushkevich isotherm model is that it is temperature-dependent. When the adsorption data at different temperatures is plotted as the adsorption capacity $\log q_e$ vs $\left[RT \left(\text{Log } 1 + \frac{1}{c_e} \right) \right]^2$ the square of the potential energy, all suitable data will be on the same curve, called the characteristic curve (Foo and Hameed, 2010).

The energy of activation as proposed by Dubinin-Radushkevich model shows that the adsorption process in this study is chemisorption since the activation energy is 1.311 kJ/mol. Reports found in literature (Gumus, 2016) revealed that mean sorption energy less than 8 kJ/mol indicates physical sorption, $8-16$ kJ/mol indicates chemical ion exchange and above 40 kJ/mol favours chemisorption mechanism. The physico-sorption process plays the significant role in the adsorption of methylene blue dye as indicated by $E < 1$ kJ/mol.

Adsorption Kinetics

The kinetic models studied include pseudo first and second order kinetics alongside intra-particle diffusion models.

Pseudo first-order kinetics

Integrated linear form of the first order kinetic model is given by Eqn (8):

$$\log (q_e - q_t) = \log q_e - [k_1/2.303]t \quad \dots (8)$$

Where:

k_1 is first order kinetic constant, min^{-1} , t is time, minutes, q_e is amount adsorbed at equilibrium and this was found to be 2.5925 mg/g, q_t is amount adsorbed at equilibrium time.

Lagergren (pseudo-first order) model describes adsorption rate and depends on the available sites in the adsorbent for physisorption process (Mercado-Borrayo *et al.*, 2014; Lagergren, 1898).

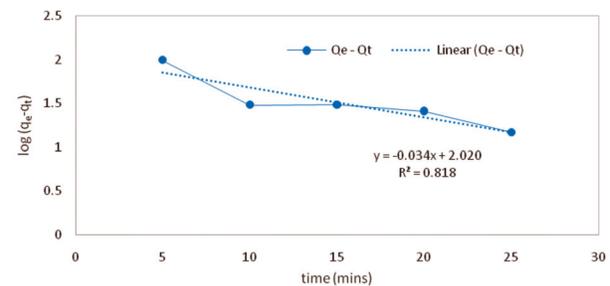


Fig. 7. Pseudo-first order kinetics

Pseudo second-order kinetics

This was determined using the linear Eqn (9):

$$(t/q_t) = (1/k_2 q_e^2) + (1/q_e)t \quad \dots (9)$$

where q_t and q_e are the amounts of adsorption at time t and at equilibrium (g/kg), respectively, and k_2 is the PSO rate constant ($\text{kg}/(\text{g min})$). It is noticed that k_2 and q_e in Eq. (9) could be calculated from the intercept and slope in the plot (t/q_t) vs. t shown in

Fig 8, q_e is 1.8896 mg/g and the rate constant k_2 is 0.0547 g/mg min.

The initial adsorption rate h (mg/g min) is given in Eqn 10 as:

$$h = k_2 q_e^2 \quad \dots (10)$$

and h for the second order kinetic model is 0.1958 mg/g min.

The Pseudo-second order kinetics describes adsorption processes better with coefficient of *det* as 0.938 compared to the pseudo first order model which is 0.818.

Intra particle diffusion model

According to recent literature, the initial adsorption occurs on the surface of the adsorbent (Gumus 2016). The methylene blue dye had a possibility of diffusing into the interior pores of the activated carbon and the kinetic model to investigate if the adsorption is intra particle diffusion is described by linearization of Eqn (10) (Weber and Morris, 1963):

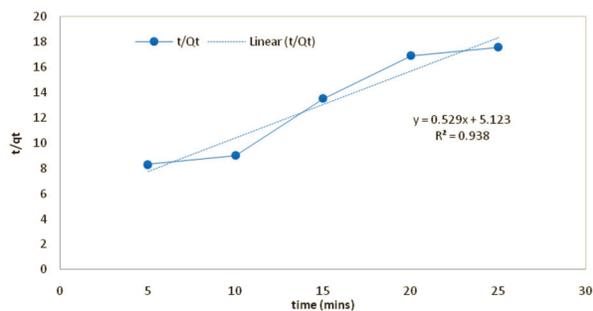


Fig. 8. Pseudo-second order kinetics

$$q_t = k_d t^{0.5} + C \quad \dots (10)$$

Where:

k_d - diffusion constant and t – contact time in minutes

However, this formula was introduced originally for pure diffusion and does not account explicitly for the effect of adsorption except in the limit of very low adsorbate concentration (Simonin and Boute, 2016).

In agreement with this model, the relationship between uptake (q_t) and the root square of time ($t^{1/2}$) must be of linear fashion if intra-particle diffusion participates in the adsorption process. The intra-particle diffusion is the rate control step if the lines pass through the origin but when the line does not pass through the origin, as shown in Figure 9, a certain degree of boundary layer control, indicating that intra-particle diffusion is not the only rate-

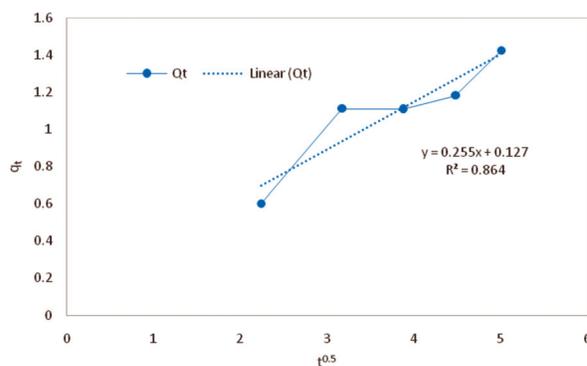


Fig. 9. Plot of intra particle diffusion

limiting step can be postulated. Other kinetic models may also control the adsorption rate which can run simultaneously (Yakout and Elsherif, 2010).

Adsorption of industrial effluents

Table 2 shows how the activated carbon adsorbed the dye from the effluent thus removing the brightly coloured water soluble reactive since these dyes show resistance to many chemicals, oxidizing agents and light.

The industrial effluent pursued the anticipated design of higher percentage adsorption as there was an increment in dosage. Higher adsorption percentages were observed at lower concentrations of the dye. Fig. 10 shows the removal of industrial dyes using activated carbon and the percentage removal ranged from 96.32% to 100% and this shows that activated carbon prepared from bottom ash was very effective and efficient in the removal of dye from industrial effluent.

CONCLUSION

Activated Carbon prepared had a relatively high iodine number, 588.136 mg/g, which indicated a high micro-porosity comparable to most

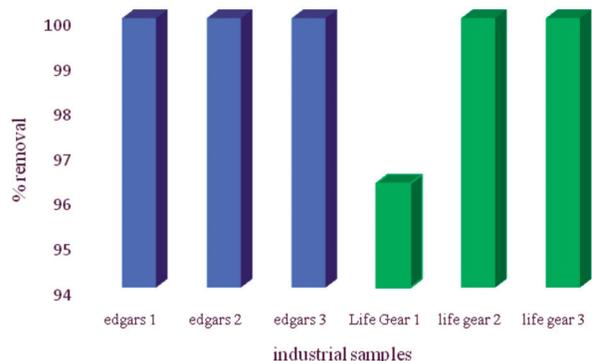


Fig. 10. % removal of dye industrial effluent

Table 2. Analysis of industrial effluent

Sample		AC(g)	A _o	C _o	A	C _e	% removal
Edgars	1	10.0173	0.143	0.0027	0.009	0	100.00
	2	10.0046	0.139	0.0026	0.03	0	100.00
	3	10.0458	0.138	0.0026	0.11	0	100.00
Life Gear	1	10.0548	0.968	0.0299	0.092	0.0011	96.32
	2	10.0475	0.968	0.0299	0.055	0	100.00
	3	10.0039	0.968	0.0299	0.037	0	100.00

commercial activated carbon of 600-1450 mg/g. High fixed carbon content of 62.11% suggested a positive adsorption of pollutants. According to Langmuir isotherm model, the activated carbon showed a monolayer coverage with a high adsorption efficiency, Q_o of 48.540 mg/g and a low Langmuir constant value of 1.347 L/mg.

The Temkin isotherm model shows that the adsorption heat of all molecules in this layer is -2704.77 J/mol, and the equilibrium binding constant corresponding to the maximal binding energy is 13.255 L/g. This indicates chemical adsorption and assumes that the binding energy reaches a distribution which is uniform up to some maximal binding energy. The adsorption followed the pseudo second-order kinetics with a rate constant of 0.0547 g/mg.min. The pore diffusion played a major role in the adsorption process with intra particle-diffusion rate at 0.2556 mg/g.min^{0.5}. The activated carbon adsorbed dye effluent from Edgars Industry and Life Gear Trading Pvt Ltd in the range of 96.32% and 100%. This showed that activated carbon prepared from bottom ash is a very effective and good adsorbent with large surface area for adsorption processes.

Conflict of interest The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

- Abdelhamid, B. Ourari, A. and Ouali, M.S. 2012. Copper (II) Ions Removal from Aqueous Solution Using Bentonite Treated with Ammonium Chloride. *Am. J. Phys. Chem.* 1 : 1-10.
- Aharoni, C. and Ungarish, M. 1977. Kinetics of activated chemisorption. Part 2.—Theoretical models. *J. Chem. Soc., Faraday Trans.* 1(73) : 456-464.
- Albanis, T.A, Hela, D.G., Sakellrides, T.M. and Danis, T.G. 2000. Removal of dyes from aqueous solutions by adsorption on mixtures of fly ash and soil in batch and column techniques. *Global Nest: the Int. J.* 2 : 237-244.
- Ali, I., Asim, M. and Khan, T.A. 2012. Low cost adsorbents for the removal of organic pollutants from wastewater. *J. Environ. Manag.* 113 : 170-183.
- Alslaibi, T.M., Abustan, I., Ahmad, M.A. and Foul, A.A. 2013. A review: production of activated carbon from agricultural byproducts via conventional and microwave heating. *J Chem Technol Biotechnol.* 88: 1183-1190.
- Amuda, O.S., Olayiwola, A.O. and Alade, A.O. 2014. Adsorption of Methylene Blue from Aqueous Solution Using Steam-Activated Carbon Produced from Lantana camara Stem. *Journal of Environmental Protection.* 5(13) : 1352-1363.
- Dabrowski, A. 2001. Adsorption-from theory to practise. *Advances in colloid and interface. Science.* 93: 135-224.
- De Gisi, S.Lofrano, G. Grassi, M. and Notarnicola, M. 2016. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. *Sustainable Materials and Technologies.* 9: 10-40.
- Dias, J.M., Alvim-Ferraz, M.C.M., Almeida, M.F., Rivera-Utrilla, J. and Sánchez-Polo, M. 2007. Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review. *Journal of Environmental Management.* 85(4) : 833-846.
- Dinçer, A.R., Güneş, Y. Karakaya, N. and Güneş, E. 2007. Comparison of activated carbon and bottom ash for removal of reactive dye from aqueous solution. *Bioresource Technology.* 98 (4) : 834-839.
- Dubinin, M.M. 1960. The potential theory of adsorption of gases and vapours for adsorbents with energetically non-uniform surface. *Chemistry Reviews.* 60 (96) : 235-266.
- Dwivedi, A. and Jain, M.K. 2014. Fly ash - waste management and overview: A Review-Recent Research in Science and Technology. 6(1): 30-35.
- Elass, K., Laachach, A., Alaoui, A. and Azzi, M. 2010. Removal of methylene blue from aqueous solution using ghassoul, a low-cost adsorbent. *Applied Ecology and Environmental Research.* 8(2) : 153-163.
- Foo, K.Y. and Hameed, B.H. 2010. Insights into the modelling of adsorption isotherm systems. *Chemical Engineering Journal.* 15(6) : 2-10.
- Freundlich, H.M.F. 1906. Über Die Adsorption in Lösungen, *Z. Phys. Chem.* 57 : 385-470.

- Goswami, A.K., Kurlkarni, S.J., Dharmadhikari, S.K. and Patil, P.E. 2013. Fly Ash as Low Cost Adsorbent to Remove Dyes. *International Journal of Scientific Research and Management (IJSRM)*. 2(5) : 842-845.
- Gumus, R.H. 2016. Kinetic Studies of Methylene Blue Adsorption on to Activated Carbon Prepared from Plantain Pod (*Musa paradisiac*). *British Journal of Applied Science & Technology*. 15 (3) : 1-14.
- Gunay, A., Arslankaya, E. and Tosun, I. 2007. Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics. *Journal of Hazardous. Materials*. 6 (7) : 362-371.
- Hobson, J.P. 1969. Physical adsorption isotherms extending from ultra-high vacuum to vapour pressure. *J. Phys. Chem.* 7(3) : 2720-2727.
- Johnson, R.D. and Arnold, F.H. 1995. The Temkin Isotherm Describes Heterogeneous Protein Adsorption, *Biochim. Biophys. Acta*. 1247 : 293-297.
- Kapoor, A. Ritter, J.A. and Yang, R.T. 1989. On the Dubinin-Radushkevich equation for adsorption in microporous solids in the Henry's law region. *Langmuir*. 5 (4) : 1118-1121.
- Lagergren, S. 1898. About the Theory of so Called Adsorption of Soluble Substances. *Kungliga Svenska Vetenskapsakademiens Handlingar*. 24 : 1-39.
- Mandal, A.K. and Sinha, O.P. 2014. Review on Current Research Status on Bottom Ash: An Indian Prospective. *Journal of the Institution of Engineers (India): Agricultural Engineering Division*. 95(4) : 277-297.
- Mercado-Borraro, B.M., Schouwenaars, R. Litter, M.I., Montoya-Bautista, C.V. and Ramirez-Zamora, R.M. 2014. Metallurgical Slag as an Efficient and Economical Adsorbent of Arsenic. *Water Reclamation and Sustainability*. 95-114.
- Nidheesh, P.V. and Gandhimathi, R. 2012. Kinetic analysis of crystal violet adsorption on to bottom ash. *Turkish J. Eng. Env. Sci.* 36 : 249-262.
- Parthasarathy, S. and Manju, N. 2010. Adsorption dynamics of methylene blue by acid activated carbon. *J. Chem. Pharm. Res.* 2 : 626-641.
- Rafieizonooz, M.Salim M.R.Mirza, J. Hussin, M.W. Salmiati, Khan, R. and Khankhaje, E. 2017. Toxicity characteristics and durability of concrete containing coal ash as substitute for cement and river sand. *Construction and Building Materials*. 143 : 234-246.
- Rahman, M.A., Amin, S.M.R. and Alam, A.M.S. 2012. Removal of Methylene Blue from Waste Water Using Activated Carbon Prepared from Rice Husk. *Dhaka Univ. J. Sci.* 60(2): 185-189.
- Richardson, J.F. Harker, J.H. and Backhurst, J.R. 2002. (eds.), "Coulson and Richardson's *Chemical Engineering, Particle Technology and Separation Processes*", vol. 2, 5th ed., Butterworth-Heinemann, Oxford, UK.
- Santhi, T., Manonmani, S. and Smitha, T. 2010. Kinetics And Isotherm Studies on Cationic Dyes Adsorption Onto Annona Squamosa Seed Activated Carbon, *International Journal of Engineering Science and Technology*. 2(3) : 287-295.
- Shrivastav, P.V. 2012. Study on color removal of basic dye by potato husk as an Adsorbent. *J. Chem. Biolog. and Phys. Science*. 2(2) : 597-600.
- Simonin, J.P. and Boute, J. 2016. Intraparticle diffusion - adsorption model to describe liquid/solid adsorption kinetics. *Revista Mexicana de Ingeniería Química*. 15(1) : 161-173.
- Singh, R.K., Gupta, D.K., Kumar, S. and Kumar, S. 2013. Utilization of fly ash as biologically activated carbon on microbial consortium for the removal of pollutants from waste water. *International Journal of Advanced Biotechnology and Research*. 4(1) : 20-28.
- Tak, S. and Vellanki, B.P. 2018. Natural organic matter as precursor to disinfection byproducts and its removal using conventional and advanced processes: state of the art review. *J Water Health*. 16 (5): 681-703.
- Temkin, M. and Pyzhev, V. 1940. Kinetics of Ammonia Synthesis on Promoted Iron Catalysts. *Acta Physicochimica URSS*. 12 : 217-222.
- Theivarasu, C. and Chandra, S. 2013. Adsorption performance of activated carbon prepared from elephant (*Elephas maximus*) dung for the removal of Reactive Yellow 15 from aqueous solution. *Desalination and Water Treatment*. 51(40-42) : 7639-7654.
- Weber, W.J. Jr. and Morris, J.C. 1963. Sanit. *J. Eng. Div. ASCE* 18 : 31-42.
- Yakout, S.M. and Elsherif, E. 2010. Batch kinetics, isotherm and thermodynamic studies of adsorption of strontium from aqueous solutions onto low cost rice-straw based carbons. *Carbon - Sci. Tech.* 1 : 144-153.
- Youcai, Z. 2017. Pollution Control and Resource Recovery: Municipal Solid Wastes Incineration, Butterworth-Heinemann.
-