Benzene Uptake onto Modified Tea Waste: Perspective Applicability of Empirical Sorption Kinetic Models

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Abstract

The uptake of Benzene onto modified solid materials have been reported most commonly with abrupt peripheral application of the defining models based chiefly on regression parameter validation. This paper considered a perspective application of mainly the empirical kinetic models of predetermined applicability as well as their parent nature to contemporary kinetic models. Verification of the applicable kinetic mechanisms defined by the models were based mainly on interpretations of the model parameters other than the statistical regression parameters. The Tea waste used was modified by impregnation using iron salt and carbonized at 500^{o}C. The modified Tea waste (TW) of average particle diameter of 0.09mm was used in the batch sorption of benzene dissolved in methanol. The $Z_{(t)}$ plot predetermined the applicability of the Diffusion, Elovichian and Quasi first order models. The linearity change in the Elovich plot illustrated the energetic heterogeneity typical of heterogeneous sorbents. Though the PFO showed lower error and lesser deviation of the estimated and observed uptake, the authentication coefficient ($\alpha = 1.06$) indicates that the PFO may not really be applicable at the process time (60min). However, the PSO gave higher correlation (0.999), significantly low error and deviation, and a higher rate constant. Hence, based on time effect of rate constant and the equilibrium coefficient ($f_2 \rightarrow 1$), the Langmuirian uptake is better in the PSO domain. The transfer of benzene sorptive for uptake was complementarily controlled first by internal diffusion then by film diffusion.

Keywords: Sorption Kinetics, uptake, Diffusive Transfer, diffusion

Introduction

Over three decades, environmental concerns have been on its contamination with toxic and carcinogenic organic and inorganic pollutants and subsequent viable remediation. Sorption has remained the most popular technique studied. The reasons have been the high energy consumption, expensive synthetic resins and chemicals (Chatterjee et al., 2009), application difficulty, inefficiency especially at low concentration (Chakraborty et al., 2003; and Blackburn, 2004) relative to the effluent volume, non-eco-friendliness (Mondal 2008 and Gadd 2009) and the expertise associated with other remediation techniques. Sorbent uptake capacity is widely known as a function of the sorption process factors: time, sorbent dosage, sorptive concentration, pH, particle size, temperature, etc easily applicable in batch systems. As a result of its physical and superficial nature, unlike chemisorption, the entropy of physisorption is often negative which conform to the associative uptake that leaves sorbent intact during and after the sorption. Generally, physisorption in contaminant removal is an effective method of quick lowering of the contaminant concentration.

Benzene is a very potent class of environmental pollutant that occur both naturally and can be released via anthropogenic activities. Besides its prime carcinogenic (Rogers, et al., 1980) and mutagenic effects, it is culpable of other adverse health and environment effects making its presence in the environment of serious concern, even at low concentrations. As a major and popular member of petroleum hydrocarbons: Polycyclic aromatic hydrocarbons (PAHs) and Volatile organic compounds (VOCs), Benzene can naturally be released to the environment via natural and anthropogenic activities. Some common means include volcanic eruptions, crude oil and coal deposits, forest fires, residential wood burning, exhaust from auro-engines, automobiles and trucks; and components in industrial solvents and raw materials waste discharged in the environment. Being a recalcitrant VOC (Ritter et al., 1995) of numerous derivatives, its environmental ubiquity via wet and dry atmospheric deposition, hydrocarbon spillages and hydrocarbon/crude effluent discharge, have made its elimination from the environment practically infeasible. However, it is requisite to keep their terrestrial and aquatic concentrations as low as possible. Generally, sorption provides a simple but effective approach for organic pollutants removal from aquatic environments (Cabal et al., 2009 and Derylo-Marczewska et al., 2008).

Though literature has widely reported on non-conventional, low cost and locally available sorbents carbonized and non-carbonized Bio-wastes are continuously being applied in the extensive sorption studies. Various sorbents have been applied in the contaminant removal from fluids. Rasheed Khan et al, (2005) used Wool Fiber and Cotton Fiber while Chitosan was applied as sorbent for dye removal (Chatterjee et al., 2009). Neem (Azadirachta Indica) Husk has been used by Alau et al (2010), Kadirvelu et al (2003) studied adsorption with Coconut tree sawdust, and Singh and Srivastava (2001) and Guo et al (2003) studied Rice husk. Studies has also been reported on dye uptake on Rice husk (Singh and Srivastava, 2001; Guo et al, 2003), Tuberose Sticks (Ahsanhabib et al, 2006) and Tamarind Fruit Shell (Saha 2010). Studies have also been reported for hydrocarbon uptake; Brezovska et al. (2004) studied the sorption of benzene vapor onto bentonite, Akhtar et al. (2006) considered sorption potential of Moringa oleifera pods for aqueous Benzene. Also Aivalioti et al. (2010) have adsorbed Benzene and its derivatives onto raw and modified diatomite while Osagie and Owabor (2015) investigated Benzene uptake onto Clay and Sandy Soil.

Tea waste as used in this study, common littery of the contemporary Nigerian society, have not been reported for benzene uptake. Attributive to the medicinal value of its brew, Green tea consumption is recording exponential growth making for the abundance and availability of its waste.

Chemical and thermal reforms are the most common and frequent techniques applied on sorbents. Chemical treatment in sorbent modification is to enhance particle disaggregation, surface cleaning, removal of mineral impurities, partial dissolution of external layers and free silica generation (Gonzalez et al., 1989; Bhattacharyya and Gupta, 2009). Thermal reform of sorbent, that is, carbonization (biomass) or calcination (clay) improves it porosity hence the sorption capacity. Therefore, the application of chemical and thermal treatment on tea waste may alternate the over use of commercially activated carbon sorption processes. This work overviewed an insight on sorption kinetics using the uptake of aqueous benzene on modified Tea waste.

Theoretical Framework

Sorption Kinetics

Knowledge of sorption kinetics will continue to be major leitmotif in soil science and engineering (Sparks, 1998) owing to the persistent interest in predicting the fate of contaminants and controling their presence in the environment. It provides valuable insights into sorptive interaction pathways and the mechanism involved (Thajeel et al 2002**)** for predicting the rate parameters for treatment techniques and designs. Sorption kinetics explains the time dependence of the extent of sorptive transfer and interactions at the surface of the sorbent. As time progresses, sorbate increases, sorptive concentration decreases, and sorption rate slows down.

Several kinetic models have been proposed in the unending quest to describe the rate of sorbate transfer and interaction in sorbents. The kinetic models encompasses the ordered (zero, first and second) equations, Elovich model, Bangham or fractional-power equation, parabolic, particle or internal diffusion model and film diffusion model. The mechanisms of some of these models are not well understood and mechanistic conclusions, till date, have primarily been based on macroscopic and kinetic studies (Sparks, 1998). Yes, experimental data has always fitted to one empirical kinetic model or the other however, the significance and interpretation of the parameters obtained, especially as reported in most papers, have not really been clear. Some authors have not appropriately applied these models, resultant of inadequate understanding of the models' theory or principle (Ho, 2004). Owing that chemical kinetics like transport processes are rate mechanisms; solely time dependent, discription of holistic uptake process within completion time is an integral of rate models predominant at certain limited time ranges. The finding that diffusion accounts for the slow interactions at the sorption interface indicated that interaction mechanism alone cannot proffer complete description of sorption kinetics (Sparks, 1998). Therefore, only a simultaneous application of transport phenomena and interaction kinetics can give a holistic kinetic description and understanding of any sorption process. These complementary mechanisms describing sorption kinetics on solid surfaces can be categorized as physical non-equilibrium: film and particle diffusion models and chemical non-equilibrium: ordered and Elovichian kinetic equations typical of surface interactions. Because mass transfer in the mobile liquid phase is not rate limiting, physical non-equilibrium models focus on diffusion into the immediate vicinity of the solid phase of the system.

The fitness of the Pseudo first order (PFO), Elovich and parabolic models are restricted to certain time limit and range: consequent of their being approximations of a more general model expression (Pavlutou and Polyzopoulos, 1988; Aharoni et al., 1991; Sparks, 1998). That a particular kinetic model best describe the sorption mechanism denotes that, most likely, the experiment and data collection was done within the time limit where the model is predominantly operational.

Kinetic studies in the recent past revolves around the assumption that only two sorption sites exist. The instantaneous interaction site typical of fast sorption is described using isotherm models and time dependent interactions site, slow sorption is described using kinetic models. These models are characterized by two fitting parameters – fraction of site occupied at local equilibrium consistent with uptake (q_t) and rate constant k_{ad}. Due to the complex heterogeneous nature of most sorbents and their modified forms, there are still many unknowns as regards to sorption onto these solid materials (Sparks 1998). This accounts why simple kinetic models like the PFO equation may not appropriately describe the entire sorption mechanism.

As most commonly reported in sorption studies, fitness of the kinetic models have been based on the statistical parameters: plot linearity, coefficient of determination (R), correlation coefficient (R^2), normalized standard deviation (Δq) (Ölenera Şölener Şölener et al., 2008) and the estimated standard error (χ^2). However, due to the empirical nature of the simple kinetic models, statistical parameters alone cannot give complete authentication of the operational mechanism(s). It is worthy to note, despite the wide applicability of the kinetic models to various experimental results, there is no consistent correlation between the equation of best fit and the physicochemical and mineralogical properties of the sorption system (Aharoni et al. 1991). Therefore, Sparks (1989 and 1998), Aharoni and Suzin (1982a,b), Pavlatou and Polyzopoulos (1988) and Aharoni et al. (1991) criticized the use of statistical data fitness parameters as the sole tool for deducing the sorption mechanism. Critical examination of the inconsistencies and problems associated with the application of the simple kinetic equations and the ambiguity in the use of the statistical fitness parameters have revealed that the $Z_{(t)}$ plot is a better test tool that authenticates the applicability of the PFO, Elovich and Parabolic models. Statistics verifies how well the data fits the choice models, therefore, is better applied as the experimental data test tools after the findings of the $Z_{(t)}$ plot.

In recent studies, the empirical sorption models: Freundlich, Langmuir, PFO, Pseudo second order (PSO), and Elovich have been modified. Considering factors and conditions that describe the aggregative and combinative representation of the different features of the models, other models have been derived from them. The derived models include the Marczewski's Integrated Kinetic Langmuir equation (IKLE) (Marczewski 2010) from the Langmuir model, the Fractional power (two-constant rate) equation derived from Freundlich model. From the PFO and PSO equations comes the mixed 1,2-order rate equation (MOE) (Marczewski, 2010). The Ward et al. Statistical Rate Theory (SRT), one of the derived models describes interfacial sorption rate (Rudzinski et al. 2000, 2006; Panczyk et al., 2004; Azizian et al., 2008 and Plazinski et al., 2009). Other derived models comprise the Avrami's kinetic model of particle nucleation for sorption at solid/solution interface (Lopez et al., 2003), Brouers and Sotolongo-Costa's universal fraction, fractal kinetics for sorption kinetics at solid/solution interface using statistical concepts (Brouers and Sotolongo-Costa, 2006) and the Fractal-like forms (Haerifar and Azizian, 2012). A comparative critical survey of the above empirical sorption models' derivatives would show not more than a mirror of each other different only with the introduction of descriptive constants and special conditions. The reflection of the derived model in one another is evident in the obvious similarity in IKLE, MOE and their fractal-like forms and also with their common dependence on the parameters of their parent models. Accordingly, a derived model can authenticate the statistical definition of the parent and controlling empirical model. The empirical models, their modified forms and/or derivatives can proffer independent or concomitant description of sorption and its kinetic mechanisms.

In using the ordered equations, the implied general assumption holds that all the surface sites are potential reactants at any time and they have an opportunity of participating in the sorption process. The PFO equation proposed by Lagergren (1898) and the subsequent PSO equation proposed by Ho (1995) are often the bases of the contemporary proposed sorption kinetic models. Unlike the true (reaction) ordered rate equations which are based on solution concentration, sorption rate equations are based on the sorbent uptake. The rate equations applicable in sorption kinetics comprises of the PFO (Lagergren, 1898), the PSO (Sobkowsk and Czerwinski, 1974; Ritchie, 1977; Blanchard et al.,1984; Ho, 1995), the Elovich model (Zeldowitsch, 1934; Low, 1960 and Chien and Clayton, 1980), and other modified form. The Azizian theoretical analysis on Langmuir rate equation relative to the Marczewski's derivation of MOE has revealed that the Langmuir model can be a primo foci in the derivation of the PFO and PSO models (Haerifar and Azizian, 2012). Although satisfactory kinetic descriptions have been reported using one or a combination of these models, none has been proved universally valid (Pavlatou and Polyzopoulos, 1988). While Lagergren, Boyd et al, Blanchard et al and Ho considered liquid-solid systems; Zeldowitsch, Sobkowsk and Czerwinski, and Ritchie worked strictly on gas-solid systems. However, the gas-solid based equations like the liquid-solid based equations were also proposed based on reactive sorption and in recent studies, have been applicable in liquid-solid systems.

To verify the model that dominates at a considered time limit, the S-shaped $Z_{(t)}$ plot has been reported to illustrate different mechanism by interpreting the different portions of the plot. The plot shows convex within small time interval where the parabolic law is operational; linear inflation at intermediate time range where Elovichian kinetics is determinate; and at larger time, shows concave typical of first order model (Pavlatou and Polyzopoulos, 1988; Sparks, 1998; Aharoni et al. 1991):

$$Z_{(t)} = (\Delta q/\Delta t)^{-1} = (dq/dt)^{-1} \qquad (1)$$

The power function equation and the first order equation representing the initial and final portions of the $Z_{(t)}$ plot respectively are typical of homogeneous diffusive sorbate transfer. While intermediate linear portion, representing the Elovichian kinetics is typical of heterogeneous diffusion. Therefore, diffusional transfer to and through heterogeneous surface is operational when the Elovich model predominates. This is n by a larger linear part of the S-shaped curve. However, when either or both fractional power and/or first order model predominate the plot, homogeneous diffusion is operational (Pavlatou and Polyzopoulos, 1988; and Sparks, 1998).

The $Z_{(t)}$ plot's remedial inclination to the criticisms of statistical deduction of kinetic mechanism and its embodiment of the Elovichian mechanism made it the best tool to examine the applicability of the simple kinetic equations. From the characteristic models of the $Z_{(t)}$ plot, physically meaningful parameters appropriate for the prediction of the sorption phenomena can be calculated (Aharoni et al. 1991). Therefore, though various models may appear to describe sorption, the simple kinetic models that gives description of the overall sorption process are those characterized by the $Z_{(t)}$ plot.

First order equation

Lagergren (1898) described rate in terms of the amount of the entity adsorbed on the surface of the sorbent rather than the amount in the bulk fluid. This predicated his rate equation being termed quasi and reported as Pseudo. The model considered sorption of sorptive on the mathematical principle of the first order rate equation. Though driven by the sorbent affinitive capacity at the process time, it is given by the difference in the reference capacity (maximum/equilibrium) of the sorbent and the amount adsorbed at any time, t $(q_\infty - q_t)$. Most often than not, in actual experimental runs, large time: in hours may be needed in sorption process to attain true equilibrium. Therefore, in the time considered in most studies, sorption actually tends to equilibrate and the equilibrium plot likely gives a pseudo equilibrium uptake. Also, worthy to reckon is the dynamics of equilibrium especially in a prolonged sorption that is susceptible to noise effect of fluctuating factors like temperature, pressure and concentration. More so, most studies have used low process time limits that may not really be enough to attain the true equilibrium uptake of the sorbent as requisite for application in the PFO model. Thus, the $Z_{(t)}$ plot is pertinent; to help support the applicability of the PFO model for the time range. Though data for low time limit may conform, with or without extrapolation and/or manipulation, the model may not give useful uptake result and information. This follows from the possible qausi equilibrium uptake typical for low process time range. Due to the adsorption-desorption nature of physisorption, the state of equilibrium uptake (q_e), must often than not, is dynamic and can be best reported experimentally as tending/approximate value. These limitations often disallow the attainment of sustainable true equilibrium; making the PFO model, in contemporary, best useful as basic model for sorption analysis rather than applicable model for useful design results and information. Therefore, in accordance with notations of Boyd et al (1947) this uptake is better reported as uptake (q_∞) as time tends to infinity ($t \to \infty$). Otherwise, for the equation to fit the experimental data, the equilibrium uptake, q_e must be known:

$$\frac{dq_t}{dt} = k_1(q_\infty - q_t) \quad (2)$$

To use the actual uptake at equilibrium, which may not be attainable within the experimental time considered, there is need to extrapolate the data or treat q_e as an adjustable parameter determinable by trial and error. The parameter $\ln q_e$ is an adjustable parameter; often, contrary to a true first order process, it is found not equal to the intercept of the $\ln(q_\infty - q_t)\, vs\ t$ plot. This informs the introduction of an authentication coefficient, α which corresponds to a time constant, t_o considered for a pseudo-first order process to make up for the time sufficiency for equilibrium attainment. Generally, at applicable time regime, $\alpha = 1$ and $\alpha \succ\succ 1$ when the time regime is sufficiently small for the first order equation to be valid (Aharoni et al., 1991). Integration of equation (2) at boundary conditions $q_t = 0$ at $t = 0$; $q_t = q_\infty$ at $t = \infty$ gives the integrated form:

$$\frac{q_t}{q_\infty} = 1 - \alpha \exp(-k_1 t) \quad (3)$$

Linearizing to get:

$$\ln(q_\infty - q_t) = \ln \alpha q_\infty - k_1 t \quad (4)$$

Where q_t is uptake at time t (mg/g); k_1 is the first order rate constant (min^{-1}), q_∞ is the equilibrium uptake as time tends to infinity, and $q_e = \alpha q_\infty$.

Elovich

This model, primly proposed by Roginsky-Zeldowitsch (1934) for chemisorption on an energetically heterogeneous solid surface has widely been applied and in several contemporary works has been peripherally applied or just mentioned as a model. Basically, the model proposed that as the sorption progresses, surface coverage increases, rate of sorption decreases and the energy requirement at sorbent surface varies leading to sorption heat varying inversely with the sorbent surface coverage. Sorption heat is usually high at low surface monolayer coverage and decreases steadily with an increase in uptake (Saha and Chowdhury, 2011). This is usual with film diffusion controlled sorption. It follows therefore that the sorbent surface during uptake is energetically heterogeneous, giving an implicit character of giving information on the degree of sorbent heterogeneity and capacity. Though proposed on the basis of a gas-solid system, the Elovich model has widely been applied in liquid-solid systems: Sparks and Jardine (1984), Pavlatou and Polyzopoulos (1988), Ho (2006) and is expressed as (Low, 1960):

$$\frac{dq}{dt} = \alpha e^{-\beta q} \quad (5)$$

Integrating equation (5) for $q_t = 0$ at $t = 0$ gives (Sparks and Jardine, 1984)

$$q_t = \frac{1}{\beta}\ln(1+\alpha\beta t) \quad (6)$$

Where α [mg/g.min] is initial sorption rate and β [g/mg] is desorption coefficient for any one experiment. Sparks and Jardine assumed that before actual uptake that started at a certain time, *τ* there was an instantaneous uptake (q_o) at a rate α just before equation (5) begins to apply. The time from zero to the instantaneous time *τ,* is given as *t₀* where $t_o = \frac{1}{\alpha\beta}$ and $\tau = t_o e^{\beta q_o}$ making equation (6) becomes

$$q_t = \frac{1}{\beta}\ln(t+t_o) - \frac{1}{\beta}\ln t_o \quad (7)$$

Considering the instantaneous uptake, q_o at time, *τ* and at a rate α,

$$q_t = \frac{1}{\beta}\ln(t+\tau) - \frac{1}{\beta}\ln t_o \quad (8)$$

Assuming the boundary conditions of $q_t = 0$ at $t = 0$, $q_t = q_t$ at $t = t$ and that *τ* is negligible in comparison with *t* gives:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) - \frac{1}{\beta}\ln t \quad (9)$$

The constants α and β are obtainable from $q_t\ vs\ lnt$ plots. If $\alpha\beta t \gg 1$ (Chein and Clayton, 1980 and Sparks and Jardine, 1984), then $(1+\alpha\beta t) \approx \alpha\beta t$ and equation…becomes:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) \quad (10)$$

Although attempt has been made to find q_e from the Elovich equation, the value obtained is an approaching value; arbitrarily identified, not the real, q_e.

Using the Elovich equation to describe kinetics was criticized by Parravano and Boudant (1955) on the grounds that it does not describe a specific process, rather it is applied in a number of different processes such as bulk or surface diffusion, activation and deactivation of catalytic surfaces. Fitting experimental data, the Elovich model can reveal irregularities that ordinarily, other models would not notice or consider. Although the improved Elovich model (Ungarish and Aharoni, 1983) does account for the generally observed sigmoid plots, it does not usefully suggest the nature of the rate determining step in sorption (Pavlatou and Polyzopoulos, 1988). What seems more important about this model is that its conformity to sorption kinetics might be taken as evidence that the rate determining step is diffusional in nature (Pavlatou and Polyzopoulos, 1988). It also points that the diffusion is heterogeneous and the diffusional transfer is through a heterogeneous sorption surface. Any break in the linearity of the Elovich plot could indicate a changeover not in the kinetic consideration rather from one type of binding site and/or energy to another (Low 1960; Atkinson, et al. 1970; and Chein and Clayton, 1980). Due to heterogeneity in sorbent surfaces, the Elovich model is fervently applicable in situations of wide variation in activation energy and surface complexity.

Though the $Z_{(t)}$ plot and the Elovichian *q vs lnt* plot are characteristic of producing S-shaped (sigmoid) plots their curvatures are reversed (Aharoni et al., 1991). Besides the characteristic portions of the sigmoid $Z_{(t)}$ plot corresponding to the various equations, the applicability of the equation can also be verified by the differential slopes of the Elovich equation; *dq/dInt*. In the plot, the region corresponding to the parabolic law gives increasing slope, the regions conforming to Elovich model giving a constant slope while the region consistent with the quasi first-order equation shows decreasing slope (Aharoni et al 1991). The region where the slope d[q/qe]/dlnt < 0.24, Elovichian mechanism is obeyed and it reflects sorption in a heterogeneous medium (Aharoni et al 1991).

Second order equation

Considering the pitfalls of the Lagergren first order equation, Ho (1995) pitched on the works of Sobkowsk and Czerwinski (1974), Ritchie (1977), Blanchard et al. (1984), hence proposed the pseudo second order rate equation using liquid-solid systems. In many studies, this equation has always been applied even when the pseudo first order showed a good statistical fitness. It may have been predicated on the basis that the first order equation uses observed equilibrium uptake. More so, in most studies, the time considered may not have been enough to attain true equilibrium. On the other hand, the second order uses the uptake at time, t to determine the estimated equilibrium uptake. Consequently, verifying the rate model fitness based on statistical fitness parameters has been criticized and considered inappropriate (Aharoni and Suzin, 1982a,b and Pavlatou and Polyzopoulos, 1988). Though the validity of the second order equation cannot be verified with $Z_{(t)}$ plot, studies have shown that the closeness of observed and calculated uptake values ($q_{\infty} = q_{\exp}$ and $q_c = q_{cal}$) is a good validation for the statistical fitness. The second order equation has been expresses by Ho (1995) or Haerifar and Azizian (2012) respectively as:

$$\frac{dq_t}{dt} = k_2 (q_c - q_t)^2 \quad \text{or} \quad \frac{dF}{dt} = k_2 q_c (1 - F)^2 \quad (11)$$

At boundary conditions of conditions $t = 0$, $t = t$; $q_t = 0$, $q = q_t$ integration yields

$$q_t = \frac{k_2 q_c^2 t}{1 + k_2 q_c t} \quad \text{or} \quad F = \frac{k_2 q_c t}{1 + k_2 q_c t} \qquad (12a)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_c^2} + \frac{t}{q_c} \quad \text{or} \quad \frac{t}{F} = \frac{1}{k_2 q_c} + t$$

(12b)

The $\frac{t}{q_t}$ *vs t* plot, independent of q_c gives a slope from where q_c can be calculated and an intercept where k_2 can be estimated. Contrary to the first-order equation that has been verified to be applicable mainly at large time range, the second order model predicts the sorption behavior over the whole sorption time (Ho, 2006).

Marczewski used the Taylor's series to expand the Pseudo second order equation introducing equilibrium coefficients f_1 and f_2 which express the contributions of the pseudo ordered models; describing the extent of the dominant mechanism. The coefficient f_2 tends to zero when the uptake mechanism is less of PSO and more of PFO and vice visa giving that $f_1 + f_2 = 1$ (Marczewski 2010):

$$\frac{dF}{dt} = \frac{k_1}{1-f_2}(1-F)(1-f_2F) = \frac{k_1}{f_1}(1-F)(1-f_2F) \quad (13)$$

Integrated to give

$$\ln\left(\frac{1-F}{1-f_2F}\right) = -k_1 t \quad \text{or} \quad q = q_e\left(\frac{1-\exp(-k_1 t)}{1-f_2\exp(-k_1 t)}\right) \quad (14)$$

Where k_1 is rate constant accounting for PFO, q and q_e are the uptakes (mg/g) at time t and at equilibrium, $f_2 = \frac{k_2 q_e}{(k_1 + k_2 q_e)}$, $f_1 = \frac{k_1}{(k_1 + k_2 q_e)}$, k_2 is the PSO rate constant F is the equilibrium coefficient describing the fractional attainment of equilibrium. Linearizing the above equation gives:

$$\ln(1-F) = -k_1 t + \ln(1-f_2F) \quad (15)$$

Marczewski further considered uptake solely at equilibrium using the Langmuir model that measured sorbent capacity, q_m hence replacing f_2 with f_{eq} in the MOE above giving:

$$\frac{dF}{dt} = \frac{k_1}{1-f_{eq}}(1-F)(1-f_{eq}F) \quad (16)$$

Thus giving the integrated and linearized form:

$$\ln(1-F) = -k_1 t + \ln(1-f_{eq}F) \quad (17)$$

Where $f_e = \upsilon_e \theta_e$ is the Langmuir batch equilibrium coefficient, $\upsilon_e = \frac{C_a}{C_o} = (1 - \frac{C_e}{C_o})$ is the relative equilibrium uptake, $\theta_e = \frac{q_e}{q_m}$ is the surface coverage at equilibrium. In the Fractal-like form as postulated in Haerifar and Azizian (2012), the IKLE and MOE are given respectively as:

Diffusive Transfer

Aharoni et al (1991) have assumed that sorbent constituents (minerals) are mainly responsible for uptake and that rate controlling mechanism is often diffusion of sorptive into the sorbent and its vicinity. In the interpretation of kinetic data from a mechanistic point of view, prediction of the mass transfer rate-limiting step is an important factor to be considered (Vadivelan and Kumar, 2005). The overall mass transfer in solid/liquid system, apart from that influenced by the moving liquid, revolves around diffusive mass transfer, intra-particle transfer, interaction at the sorbent surfaces/sites, and desorption from surfaces/sites/vicinities into bulk solution. The diffusive mass transfer entails transfer through a thin liquid film to the sorbent immediate vicinity while the intra-particle transfer defines diffusive transfer in and through openings between sorbent particles. The transfer can best be governed by slowest of the above steps. However, interaction has rarely been reported as rate limiting in uptake processes (Michelson et al. 1975) because it is highly dependent on the transfer of sorptive to the sites. Depending on the concentration existing in the aqueous phase, the rate of sorptive uptake can be controlled either by diffusional transport across a thin liquid film enveloping the sorbent particles or by internal diffusion. The film diffusion controls the mass transfer of the sorptive from bulk phase to external sorbent surface while the internal diffusion, on porous solids, controls transfer in and through the sorbent particle. It is possible however, that both film and particle diffusion can play contributory roles with neither of them having sole control of the transfer. In a rapidly stirred batch sorption, the diffusive mass transfer can be related by an apparent diffusion coefficient, which will fit the experimental sorption-rate data.

Film diffusion

To ensure constant sorbate concentration at the solid/liquid interface, vigorous mixing has always been employed, mainly for powdery sorbents. However, it is presumed a concentration gradient is maintained at the thin liquid film surrounding the sorbent particles forming the boundary and resistance to diffusive transfer. At equilibrium, the distribution of sorptive between the solid and liquid phases can be estimated. This distribution is constant within experimental error on the assumption that the sorptive is a micro-component of the system i.e., infinitely dilute sorptive solution (Boyd et al., 1947). The magnitude of the distribution coefficient (κ) indicates a measure of the efficiency of the sorbent for the uptake.

$$\kappa = \frac{c_s^e}{c_l^e} \quad (18)$$

c_e^s and c_e^l are the equilibrium sorbate and sorptive concentrations. Following that equilibrium at the surface of the sorbent particle is assumed at all times as constant (Boyd et al., 1947):

$$c^l = \frac{c^s}{\kappa} \quad (19)$$

If film diffusion is rate limiting, then the rate of transfer from the Fickian theory: permeation (quantity transferred/unit time/unit area of unit thickness under a standard concentration difference) holds that (Boyd et al. 1947):

$$p = V\frac{dc}{dt} = -D^l \frac{\delta c}{\delta r} \quad (20)$$

Where D^l is the diffusion constant in the liquid phase, r is the radius of sorbent particle. Particles of porous sorbent are often considered spherical (Boyd et al. 1947) hence;

$$q = \frac{4}{3}\pi r^3 c^s \quad (21)$$

For mass transfer to the sorbent external surface through a bounding liquid film, total rate of transfer of sorptive across the film:

$$\frac{dq}{dt} = -4\pi r^2 p = 4\pi r^2 D^l \frac{\delta c}{\delta r} \quad (22)$$

The above equation for linear gradient where radial effect is constant is given as:

$$\frac{dq}{dt} = 4\pi r\, D^l (c^l - c^f) \quad (23)$$

c^f, the concentration within the film around sorbent; hence with $c = 3q/4\pi r^3$ we have

$$\frac{dq}{dt} = (3\,D^l/\kappa r^2)(q_e - q) \quad (24)$$

$K_f = 3\,D^l/\kappa r^2$ being the film transfer rate constant, integration at $t = 0$ and $q_t = 0$ gives

$$q = q_e(1 - e^{K_f t}) \quad (25)$$

Taking natural log and considering the fractional attainment of equilibrium, $F = \frac{q}{q_\infty}$

$$\ln(1 - F) = -K_f t \quad (26)$$

Equation (1.33) is similar to the integral form of PFO equation: this verifies that the empirical sorption models play complimentary and *validative* rule in sorption kinetics.

Internal/Particle diffusion

Earlier works that reported transfer kinetics in the internal vicinity of sorbents include Bingham and Burt (1924), Barred, (1941) and Boyd et al., (1947), and Weber and Morris (1963). For Fickian diffusion: the diffusion in and through solid (Boyd et al., 1947) and the Two-constant equation or Parabolic law (Spark, 1989; Spark and Jardine, 1991). In recent works, these models are reported as Internal diffusion model and Intra-particle diffusion equation (Weber and Morris, 1963) or Particle diffusion model, the parabolic law where the power of *t* tends to 0.5. The Weber and Morris model has been the most applied, though superficially in most works. Internal transfer as presented by Barrer, (1941) and Boyd et al., (1947) considered constant sorbate concentration in a liquid-solid system where the fractional attainment of equilibrium, *F* for internal diffusion is given as:

$$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-n^2 K_{in} t} \quad (27)$$

It follows that for sorption governed by diffusion, the estimated slope ($\frac{d(-\ln(1-F))}{dt}$) varies between infinity initially and $-K_{in}$: $\frac{d(-\ln(1-F))}{dt} = -K_{in}\frac{\sum_{n=1}^{\infty} e^{-n^2 K_{in} t}}{\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-n^2 K_{in} t}}$ otherwise, it is constant for sorption controlled by Chemical reaction (Boyd et al., 1947). Numerically, the series in (27) converges slowly for small values of $K_{in}t$ suggesting the use of an approximate equation. Thus, for small values of $K_{in}t$ which corresponds to small fractional equilibrium attainment ($F \leq 0.7$), uptake is low. The low uptake is applicable only on the external surface of the sorbent, relating mainly, the parabolic rate law valid in small time range of the $Z_{(t)}$ plot postulate. Boyd et al (1947) expressed this situation as:

$$F = \frac{6}{r}\sqrt{\frac{D^i t}{\pi}} = 1.08\sqrt{K_{in}t} \quad (28)$$

Where, $K_{in} = \frac{D^i \pi^2}{r^2}$ (mg/gmin$^{0.5}$) is the diffusion rate constant; D^i is the internal diffusion coefficient, equation (28) can be related to the Parabolic law:

$$q = K_i t^{0.5} \quad (29)$$

Where $K_i = 1.08 q_\infty K_{in}^{0.5}$, hence it follows that for $F > 0.05$, (29) may not be suitable to describe diffusion determining uptake. However, particle diffusion have often been described using the expression that considered the effect of boundary layer (film thickness, *I*):

$$q_t = K_i t^{0.5} + I \quad (30)$$

The Boyd curve obtainable from the *F vs* $K_{in}t$ plot of table 2 below can be applied for graphical estimation of $K_{in}t$ conforming to any observed value of *F*, enabling the calculation of K_{in} for the corresponding contact time.

Otherwise, Tsibranska, and Hristova, (2011) have applied Fourier transform on (27) forming expressions for $K_{in}t$ where K_{in} can be arithmetically estimated for agreeing contact time:

$$0.05 < F < 0.85 : K_{in} t = (\sqrt{\pi} - [\pi - (\pi^2 F / 3)]^{0.5})^2 \quad (31)$$

$$F > 0.85 : K_{in} t = -0.498 - \ln(1 - F) \quad (32)$$

When K_{in} is constant within the same time range where K_f varies, then internal diffusion controls the rate of sorptive uptake, else permeation through a thin, enveloping liquid film determines the rate of uptake. However, if film diffusion is rate controlling, the slope ($K_f = \frac{-\ln(1-F}{t}$) will vary inversely with the particle size, the film thickness and/or the distribution coefficient, κ. More so, if the data highly obeyed the internal diffusion, K_f would vary directly with particle size (r), film thickness (Δr) and/or distribution coefficient (κ) (Boyd et al. 1947) otherwise film diffusion is significantly involved. Where internal diffusion is rate determining, average D^i can be calculated from $K_{in} = \frac{D^i \pi^2}{r^2}$ knowing the particle size, r. Also, the film diffusion coefficient D^l can be determined from the diffusion rate constants ($K_f = \frac{3D^l}{r\kappa\Delta r}$). Film coefficient, D^l falls between 10^{-6} - 10^{-8} cm^2/sec while D^i falls between 10^{-11} – 10^{-13} cm^2/sec (Michelson et al. 1975; and Bhattacharya and Venkobacher, 1984). Semi-quantitatively, the ratio $\frac{K_{in}}{K_f} = \frac{D^i \kappa \pi^2 \Delta r}{3 D^l r}$ would give value < unity for internal diffusion controlling sorption rate, otherwise film diffusion would be the determining mechanism (Boyd et al. 1947).

Table 1: Solutions to Equation 27: The values in the first three columns were obtained from the approximate equation (28). The values of F are given to three significant figures, but the last figure may be in error (Boyd et al., 1947)

F	*Kt*	F	*Kt*	F	*Kt*	F	*Kt*	F	*Kt*
0.035	0.00	0.225	0.06	0.555	0.40	0.720	0.80	0.970	3.00
0.090	0.01	0.265	0.08	0.605	0.50	0.775	1.00	0.980	3.50
0.125	0.02	0.300	0.10	0.650	0.60	0.818	1.20		
0.155	0.03	0.365	0.15	0.690	0.70	0.865	1.50		
0.180	0.04	0.462	0.25			0.915	2.00		
0.205	0.05	0.497	0.30			0.950	2.50		

Materials and Method

Adsorbent preparation

About 100 grams of the Tea waste (TW) was soaked in distilled water for 2 hours to purify it of fine dusty particles and other adhered impurities. The TW was dried in the oven at 100°C after mesh-drained and partially air-dried. The oven-dried sample was cooled in a desiccator. 30 grams of TW was mixed with 2 grams of iron (III) nitrate dissolved in 200 ml of ethanol solution to prepare a 10 wt. % impregnated TW. The impregnation mixture was heated in an oven at 80 - 100°C for 12 hours and the dry impregnated TW was carbonized at 500°C for 3 hours. The carbonized TW was sieved with 140-200 ASTM sieve to ascertain the average particle size of the TW sorbent. Having a uniformity coefficient of 50/80 the 140-200 ASTM gave an average TW particle diameter of 0.09mm.

Preparation of Sorptive

To prepare the Benzene stock, 22.74µL of Benzene was discharged below the surface (to prevent volatilization) of about 80mL of the methanol in a 100mL flask and the solution was made up to 100mL. The flask was caped and inverted 3times to mix. The stock stored in the refrigerator in septum vials was brought to room temperature then diluted to 0.5mg/L solution. 0.25mL of stock was discharged below the surface of 90mL of distilled water in a 100mL flask and made up to mark with distilled water then inverted 3 times to mix and allowed to stabilize for 5 minutes.

Batch sorption

The solution in the neck of the flask was discarded and 10 mL of the diluted solution was transferred immediately to four (4) test tubes containing 0.5g TW each. The test tubes were capped airtight with a stopper after stocking the headspace above the liquid with cotton wool wrapped in a foil. The test tubes were placed on the test tube rag in the thermostatic shaker water bath for the uptake at room temperature (≈25^{o}C) and time interval of 15 to 65 mins. At the elapse of time, mixtures were centrifuged (~15 000 rpm) for 10min. and the supernatant solutions were drawn for chromatographic analysis.

Amount adsorbed

Amounts adsorbed (mg/g) were calculated using the mass balance equation:

$$q_t = \frac{(C_o - C_t)V}{m} = \frac{VC_a}{m} \quad (33)$$

Where q is the amount adsorbed (mg/g), C_o, C_e and C_{ae}: initial, equilibrium and adsorbed Benzene concentration (mg/L); V is solution volume (L), and m is dry Benzene weight (g).

Error Analysis for the adsorption models

The Correlation coefficient (R), Coefficient of Determination (R^2), standard error of the estimate (SE), and Normalized standard deviation (Δq) were determined applyin g the respective expressions below using Microsoft Excel.

Standard error of estimate (Spiegel and Stephens 2008)

$$\chi^2 = \left(\frac{\sum (q_{\infty,\exp} - q_{\infty,cal})^2}{n} \right)^{0.5} \quad (34)$$

The deviation of the calculated uptake from the experimentally observed can be estimated by the Normalized standard deviation (Sölener, et al, 2008; Nagashanmugam and Srinivasan, 2011) or the Hybrid fractional error (Gulipalli et al, 2011) given respectively:

$$\Delta q = 100\left(\frac{\sum\left(q_{\infty,\exp} - q_{\infty,cal}\right)^{2}}{q_{\infty,\exp}}\right)^{0.5} \quad (35)$$

Where $q_{\infty,\exp}$ and $q_{\infty,cal}$ are measured and calculated equilibrium uptakes, and *n* is the number of data points.

Result and Discussion

Generally, analysis of the sorption data helps in the development of equations which considerably describe the interactive behavior between sorbent and sorbate. From the uptake curve, (Fig. 1a), the uptake did not equilibrate at the max. time limit considered: 60min hence giving not the equilibrium value, rather the uptake at max. time (q_∞ as $t \to \infty$).

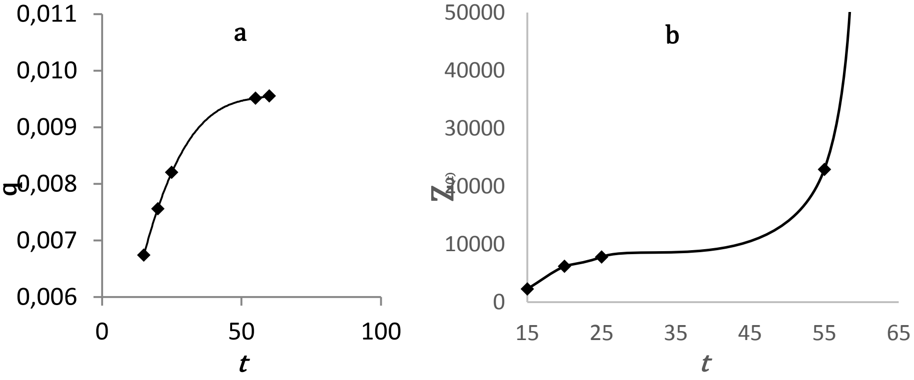

Figure 1: (a) The equilibrium uptake curve; (b) The $Z_{(t)}$ plot for the Benzene uptake

The application of the $Z_{(t)}$ plot ascertains the valid empirical model that is best applicable. Even when the first or second order gives better statistical fit to the data while the $Z_{(t)}$ plot showed otherwise, the $Z_{(t)}$ plot is considered (Pavlatou and Polyzopoulos, 1988). The $Z_{(t)}$ plot, (Fig.1b), showed an S-shaped curve that conformed to the postulate of Pavlatou and Polyzopoulos (1988), Sparks, (1998) and Aharoni et al. (1991). The plot showed convex within small time interval (15-20min) where the parabolic law is operational. Within the intermediate time range (20-45min), the linear portion of the plot described the Elovichian kinetics. The concave portion marked by the time regime (45-60min) portrayed when the PFO mechanism is supposedly expected. By this dictate, the kinetics of the Benzene uptake was verified within the ambits of the reaction order mechanism, the energy related Elovich model and the influence of diffusion in the uptake process.

Table 2: Sorption kinetics and statistical parameters: Initial concentration (C_o) = 0.5mg/L. Benzene adsorbed, $q_t(mg/g)$; Equilibrium uptake: observed, $q_{\infty,\exp}(=0.0096 mg/g)$ and estimated, $q_{\infty,cal}(mg/g)$;PFO and PSO rate constants: $k_1(\min^{-1})$ and $k_2(g/mg.\min)$; the dimensionless Marczewski MOE equilibrium coefficients: f_1 and f_2. Elovich coefficients: α (*g.min*^{2}/m*g*) and β (m*g*/min.g). Regression coefficient (R^2), Normalized standard deviation, Δq (%) and Standard error (χ^2).

Pseudo First Order		Pseudo Second Order	
$q_{e,cal}$	0.0102	$q_{e,cal}$	0.011
k_1	0.085	k_2	9.76
f_1	0.47	f_1	0.44
f_2	0.53	f_2	0.56
f_e	1.08	f_e	1.28
R^2	0.9956	R^2	0.9997
Δq	0.61	Δq	1.43
χ^2	0.0006	χ^2	0.0014

From Tab. 2, though the PFO equation gave a significant coefficient for good correlation of benzene uptake, the PSO equation showed a better correlation coefficient. On the other hand, the normalized deviation and the standard error showed that the value of the observed uptake is more approximate to the value calculated from the PFO than the value of the PSO equation. The $q_{e,cal}$ for both the first and second order are greater than $q_{\infty,\exp}$ confirming the quasi state of q_∞ being considered as equilibrium uptake. From the PFO plot, α obtained from the intercept gave $\alpha = 1.06$ indicating that q_∞ is close to the true equilibrium uptake q_e. Also, it points that the time regime of 60min is not enough to attain the true equilibrium of benzene uptake onto the modified TW.

Clearly, the actual rate is dependent on the uptake capacity of the sorbent at the given time (t) and is qualified by the orders. It is however potential to get an idea about the rate by just observing the rate constant. At constant temperature, the higher the rate constant, k, the faster the interaction. Therefore, from Tab. 2, the rate constants showed that the uptake is faster in the second order than in the first order hence equilibrium may be attainable with the process time for a second order uptake.

In all cases, f_1 is lesser than its corresponding f_2 and the values of f_1 estimated from PFO and PSO are less than 0.5 hence tends towards zero while the values of f_2 are greater than 0.5 hence tends towards unity. It follows therefore that the uptake mechanism is less of PFO and predominantly PSO (Marczewski 2010). The higher values of f_e for both PFO and PSO compared to f_1 and f_2 showed that uptake at the entire process was predominantly Langmuirian that is, more of monolayer uptake, thus indicating physisorption.

The Elovich plot of Fig. 2a, showed a non-linear plot with the changes at 25min and at 55min indicating the likely changeovers from one type of binding site and/or energy to another (Low 1960; Atkinson, et al. 1970; and Chein and Clayton, 1980). This changeover illustrated energetic heterogeneity typical of heterogeneous sorbents. The regression plot of Fig. 2b gave a significant coefficient (0.9798) showing good correlation of the uptake data and fitness of the model to describe the uptake.

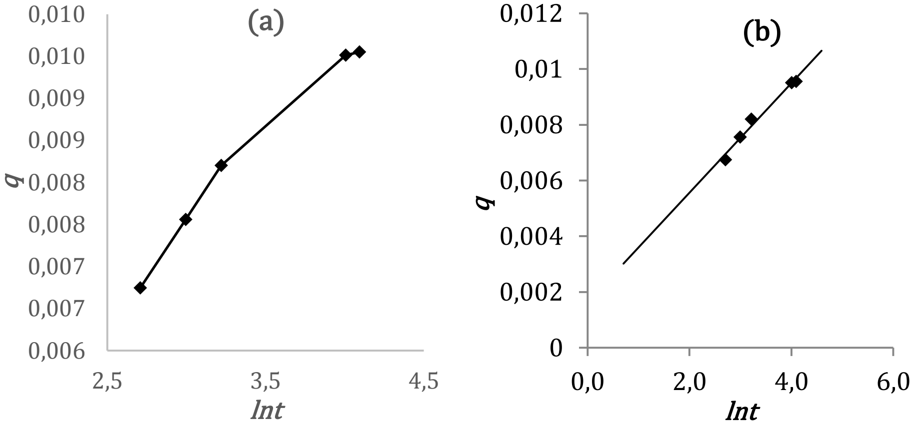

Figure 2: (a) The Elovich plot indicating the multilinear lines of the plot. (b) The Elovich regresion plot.

The $Z_{(t)}$ plot (Fig.1b) showing a linear intermediate portion, the constant slope, dq/dlnt within the Elovichian time regime of the $Z_{(t)}$ plot and the significant R^2 (Tab.3) of the q vs lnt plot are evident of an Elovichian mechanism typical of Fickian diffusion. This illustrates that the rate determining step of the uptake kinetics is diffusional in nature (Pavlatou and Polyzopoulos, 1988) and on a heterogeneous sorption surface, that is, heterogeneous diffusion.

Table 3: Elovich Model parameters -

Elovich	
A	0.004
B	500
R^2	0.9798

The slope, $\frac{dq}{d\ln t}$ (Tab. 4), supported the kinetic postulates: increased slope define low time regime of the Parabolic law, constant slope typifies the Elovichian time regime, and the decreasing slope at higher time regime for the PFO (Aharoni et al 1991). The slope as shown increased at $t \leq 20$min, maintained constancy at time, $20 < t < 55$min and decreased at time, ≥ 55min.

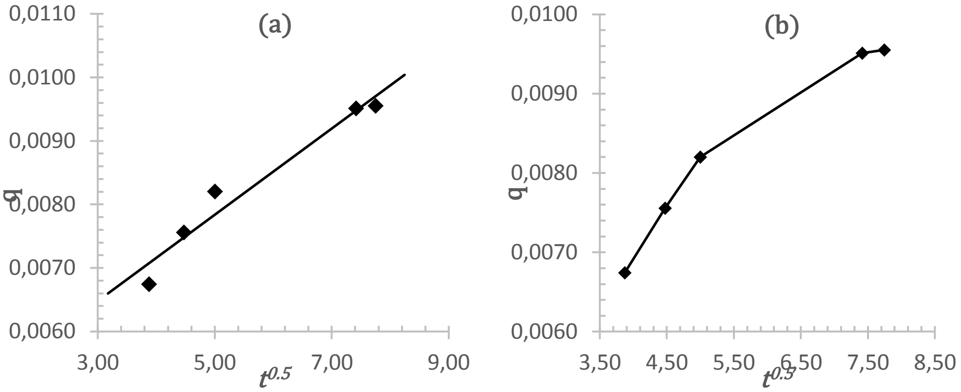

Figure 3: (a) The Regression plot of the Parabolic law. (b) The Multilinear plot of the Parabolic law

The diffusion based models were tested to verify the diffusion mechanism that best approximated the transportation of benzene sorptive to the sorbent surface sites. The regression line of Fig. 4.5a did not pass through the origin implying that the diffusion is not describe by the Weber and Morris Model. Moreover, uptake is not solely governed by particle diffusion. Fig. 3b showed a multilinear q vs $t^{0.5}$ plot which portrayed that diffusional transfer in the process is not solely particle diffusion. The first inclined portion represents the time regime of rapid uptake when the parabolic law (Weber and Morris particle diffusion) is applicable. The second inclined portion which prolong into the brief qausi horizontal portion corresponds to the regime of highest uptake characteristic of the film diffusion controlled uptake. Hence the diffusion mechanism that influenced the benzene transfer to the external and internal surface of TW is co-controlled (Sarici-Ozdemir, 2012; Gulipalli, et al., 2011). The intercept of the linear plot representing the film thickness (I) gave a value, $4.4 \, x \, 10^{-3}$ conforming to theoretical assumed value of 10^{-3} and significant enough to drive film resistance.

For sorptive transport from the solution phase to the sorbent surface sites, one or combination of the following steps would regulate the transfer process: transport of sorptive through liquid film to the sorbent exterior surface (film diffusion) and/or transport from the exterior surface to the interior surface, in and through the particles (particle/internal diffusion).

The film diffusion rate coefficient have values within the range 10^{-6} – 10^{-8} indicating film diffusion controled uptake however, the magnitude of its negative power reduces as time and uptake increases. This illustrates that the film diffusion was more profound at higher time regime and at increased uptake conforming to increased uptake chararteristic for film diffution controlled mechanism. The higher negative power at low time regime potray that diffusion in and through particles could be the controller at the earlier stage of the uptake. This dominant difusion may have continued as potrayed with the more close constancy in the K_{in} values within time inteval of 15 to 25 min., and the $\frac{K_{in}}{K_f}$ ratio of less than unity. The $\frac{K_{in}}{K_f}$ ratio was less than unity at the low time regime where internal diffusion is more predominant and tends to unity at higher time regime: 55 – 60 min. indicating the predominance of the film diffusion. While the negative slope, $\frac{d(\ln(1-F))}{dt}$ ascertained that uptake is diffusion controlled, the power of D^l that fall within 10^{-6} - 10^{-8} cm^2/sec conform to the Michelson et al postulate for film diffusion controlling uptake. The film thickness was assumed as 10^{-3} cm (Helffrich, 1962). More so, the inverse variation of K_f with κ potrayed film diffusion controlled uptake.

Table 4: Kinetic data for Diffusion models – Particle diffusion: $q_t = K_i t^{0.5} + I$, Internal diffusion and film diffusion: $\ln(1-F) = -K_f t$: - C_t: Benzene concentration in residual solution at time (*t*, min.) , C_a: Concentration of Benzene adsorbed at time (*t*, min.), κ: distribution coefficient, $q_t(mg/g)$: uptake at time (*t*, min.), K_{in} : internal diffusion rate constant (average $K_{in} = 0.031 \min^{-1}$), K_f : film diffusion rate constant (average $K_f = 0.049 \min^{-1}$), D^i : internal diffusion coefficient, D^l : film diffusion coefficient, $K_i = 0.0007 mg/g.\min^{0.5}$ **:** Particle diffusion rate constant, $I = 4.4x10^{-3} cm$: film thickness, $q_\infty = 0.0096$: uptake as $t \to \infty$ (equilibrium uptake), Average particle size (ASTM mesh): $diameter; d = 0.009 cm$ ($r = 0.0045 cm$). Initial concentration (C_o) = 0.5mg/L.

t	$t^{0.5}$	lnt	C_t	C_a	κ	q	$\frac{dq}{d\ln t}$	$\frac{d(\ln(1-F))}{dt}$	K_{in}	K_f	D^i	D^l	$\frac{K_{in}}{K_f}$
15	3.87	2.71	0.163	0.337	2.07	0.0067	0.0025	-0.063	0.033	0.063	2.1E-05	4.9E-07	0.53
20	4.47	3.00	0.122	0.378	3.10	0.0076	0.0028	-0.058	0.034	0.058	2.2E-05	6.8E-07	0.59
25	5.00	3.22	0.090	0.410	4.56	0.0082	0.0029	-0.055	0.034	0.055	2.2E-05	9.4E-07	0.64
55	7.42	4.01	0.024	0.476	19.48	0.0095	0.0017	-0.036	0.030	0.036	1.8E-05	2.7E-06	0.75
60	7.75	4.09	0.023	0.478	21.22	0.0096	0.0004	-0.034	0.025	0.034	1.6E-05	2.7E-06	0.74

However, the constant K_{in} at varied K_f values and the ratio of $\frac{K_{in}}{K_f}$ < unity depicts the control of internal diffusion. It follows therfore, within the time intervals of 15 to 25min, particle diffusion drives the gradient between the bulk and the sorbent making internal diffusion the uptake controller. However, at the bounds of 55 to 60min. showing highest uptake and weighty increase in κ, the diffusion to the sorbent surface is governed more likely by sorptive tranfer through the thin boundary layer. The thin boundary transfer is consiquent of the drastic reduction of the gradient within the film and between the internal/immidiate external sorbent surfaces. It can therefore be infered that the entire uptake mechanism is complementorily governed by both diffusion mechanisms: at low time regime, predominatly internal diffusion; and at higher time and uptake, the film diffusion governs.

Conclusion

The $Z_{(t)}$ plot, showed that the kinetic mechanism of the Benzene uptake can be described within the ambits of the reaction order mechanism, the energy related Elovich model and the influence of diffusion; illustrated by the empirical models: the Parabolic law, Elovichian kinetics and the Pseudo First Order equation. The uptake of the Benzene sorptive onto the impregnated TW was complementarily governed by the film and internal diffusion. However, the sorption followed second order rate mechanism predominantly driven by diffusional transfer within the internal surface of the heterogeneous TW sorbent.

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