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RESEARCH ARTICLE

Kinetic Studies of Wastewater Treatment from Pharmaceutical Industry, using Snail Shell Powder

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Abstract

The kinetics studies of the treatment of wastewater from Pharmaceutical industry, shows that the treatment fit the pseudo-second order kinetic model, as compared to the other two kinetic models (Pseudo-first order or Lagergrien kinetic and intraparticle diffusions model) studied, since the correlation coefficient (r^2) values of most parameters were $\geq$ 0.99. Moreover, the food composition (Nitrogen free extract, protein, fibre, fat and ash content), the mineral compositions (Fe, Mn, Zn and Cu) as well as the surface area and pH were analysed for the four species of snail shell (Archatina archatia, Archtina marginata, Achatina fulica and limucularia species). In addition, the physicochemical properties (pH, temperature, alkalinity, turbidity, total solids, suspended solids, dissolved solids, dissolved oxygen, biochemical oxygen demand, chemical oxygen demand, electrical conductivity, and phosphate, Nitrate-Nitrogen, Sulphate, Pb, Cd and Hg) were analysed for wastewater from pharmaceutical industry. The data derived from the physicochemical properties were treated with three kinetic models (Pseudo first order- Lagergrien, Pseudo second order and intraparticle diffusion). From the kinetic models, the results show that for the wastewater from pharmaceutical industry, the correlation coefficient (r^2) of the pseudo-second order was 0.999, indicating that the treatment fit the pseudo-second order kinetics.

Introduction

Many methods are available for the treatment of wastewater.

Biosorption, a process whereby certain types of inactive dead biomass (such as snail shell, peat, rice husk, fruit peels etc.) may bind and concentrate heavy metals from aqueous solution is considered as an alternative technology for the removal of these heavy metals and other pollutants from wastewater and industrial effluents, (Naja et al., 2003, Volesky 1990). Biosorption technology is advantageous due to the cost effectiveness of biosorbent (biomass) since they are derived from cheap sources.

A range of adsorbents had been examined, such as clay, charcoal, cassava waste etc.

In general, there are various technological methods existing for the treatment of wastewater, such methods include, chemical precipitation, ion exchange, adsorption, membrane processes, supercritical fluid extraction, bioremediation and oxidation with oxidizing agent (Asia and Oladoja., 2003). However, most of these technologies are either extremely expensive or too inefficient in the treatment of water and wastewater.

Efficient and environment friendly methods are thus needed to be developed. It is observed that adsorption among other methods is a cost effective technique and simple to operate.

Adsorption involves the accumulation of substances on the surface of a solid or liquid. The Surface area of the adsorbent plays an important role. The larger the surface area the greater the extent of adsorption.

Adsorption is of two types, which are physical, or van der waal's adsorption and chemical or activated adsorption or chemisorptions. (Negi and Anad., 2007).

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It is also important to study the rate at which this adsorption process can take place. This is possible by studying the kinetics at which there will be efficient treatment as regard adsorption.

KINETICS OF ADSORPTION: In adsorption, kinetic study is very important; this is to know the detail about the performance and mechanism of the adsorption. The solute uptake rate which determines the residence time required for the completion of adsorption can be obtained from kinetic analysis (Qiu., et al 2009).

Adsorption kinetics is the base to determine the performance of fixed bed or any flow-through systems. Several mathematical models have been proposed to describe adsorption data, these models can be classified as adsorption reaction models and adsorption diffusion models. Both models are used to describe the kinetic process of adsorption.

These models are however different naturally. Adsorption diffusion models are always constructed on the basis of the following three consecutive steps (Lazaridis and Asouhidou, 2003):

(1) Diffusion across the liquid film surrounding the adsorbent particles, i.e., external diffusion or film diffusion; (2) diffusion of the liquid contained in the pores and/or along the pore walls which is so-called internal diffusion or intra-particle diffusion; and (3) adsorption and desorption between the adsorbate and active sites, i.e., mass action.

Adsorption reaction models originating from chemical reaction kinetics are based on the whole process of adsorption without considering the steps mentioned above.

Presently adsorption reaction models have been widely developed to describe kinetic process of adsorption (Banart et al., 2005; Sun and Yang., 2003; Aksu and Kabasakal., 2003).

Three kinetic models, that is Lagergran first- order, pseudo-second order and intraparticle diffusion equations were considered to interpret the time dependent experimental data.

The Lagergren first- order equation is given as

$$\log\ (q_e - q_t) = \log q_e - \frac{k_{p1}}{2.303} t \text{ -----} \quad (1)$$

(Lagergren 1898). Where q_e and q_t (mg/g) are the adsorption capacity at equilibrium and time t (min), respectively. $k\ p^1$ (min^{-1}) is the pseudo-first order rate constant for the kinetic model.

Pseudo-second order kinetic model equations (Ho and Mckay 1998) is giving as

$$\frac{t}{q_t} = \frac{1}{v_o} + \frac{1}{q_e} t \text{ -----(2)}$$

and $v_o = kp^2 q_e^2$ where v_o (mg/g.min) means the initial adsorption rate and the constant can be determine experimentally by plotting $\frac{t}{q_t}$ against t.

The intraparticle diffusion model equations (Chien and Clayton, 1980) is given as $q_t = k_{\text{int}} t^{½}$ ----- (3), where k_{int} is the intraparticle diffusion rate constant.

According to the above equation a plot of qt vs $t^{½}$ should be a straight line with a slope k_{int} when the intraparticle diffusion is the rate limiting step.

Due to its particular significant in adsorbent evaluations and applications, adsorption kinetic studies still attract considerable interest today, more deliberate and complicated models will be proposed on the basis of adsorption mechanism and diffusion analysis.

Contrast to the study of adsorption using activated carbon and different agricultural and animal by products the study of snail shell as an adsorbent is scarce, and the kinetic and thermodynamic study of the treatment using this animal product is new. The only close information is on the use of chitosan in the treatment of wastewater (Zhinguang, et al 2011).

Snail shell is one of the most astonishing wonders of evolutions in all of the animal kingdom. The name snail though applies to all gastropods; it commonly means only those species with an external shell large enough that the soft part can withdraw into. This hard and fleshless shell protects the visceral hump that is, the soft and flexible body which is absent of skeleton both internal and external. The shell is not however permanently attached to the body of the snail.

The snail belongs to the phylum Mollusk and class Gastropods. The gastropods are the largest class of the phylum Mollusk (Brunt *et al.*, 1999), a group of animals commonly known as snails and slugs.

The snail's soft body consists of a head, a foot, and a visceral mass or lump, which remains permanently inside a hard protective shell (Poppe et al., 2006). Gastropods have worldwide distributions from near Arctic and Antarctic zone to the tropics. They are found predominately in West Africa.

The shell of the large land snail is brownish yellow in colour with dark markings and is up to 10cm or more in length, it is very hard. Snail shell has several important uses, which results from the hard nature of the shell. The shell protects the snail from physical damage, predators and dehydration. They are use also in the manufacture of buttons, jewels, and art collections.

Recent development involves its application in the treatment of water and wastewater resulting from its chemical composition and large surface area; this composition includes proteins, carbohydrates, fats, and minerals such as iron, zinc, copper, etc. (Botkin and Edward, 1988).

The snail shell cell wall is built in different layers each with a special purpose and each built by a different cell layers. There is transversal cell layer which secretes calcareous matter that solidifies into prism or plate crystals at the snails pallium (mantle) rim in the apertural (shell mouth) layer of the shell.

The prism stand tightly packed transversely to the shell wall, so a maximal firmness is achieved as the plate in contrary stand lengthwise and alternately, this prism layer is also called the ostracumn.

There is another layer in front of the ostracumn whose cell does not secrete the calcareous matter, but an organic skin (the shell skin or periostracum), this is placed over the ostracumn from the outside.

This organic skin is made up of protein known as the concholin which is related to keratin found in hair or tortoise and dentin found in teeth.

The main shell layer which consist of a hard mineral aragonite ($CaCO_3$) is mechanically very hard and is very susceptible to chemical corrosion, on the other hand the skin shell though mechanically weak is quite unsusceptible to chemical corrosion and hence protect the shell layer below.

In contrary to those two shell layers produced in the apertural layer of the shell, there is another which is made all over the pallium (mantle) on the inside of the shell. This shell matter is responsible for the thickening of the shell wall. This consists mainly of amorphous calcium carbonate materials.

Material and Methods

Collection of snail shell: Four different species of snail shell was collected from the environment within Ekpoma. The shells were washed with hot water to remove sand and dirt, it was then sun dried.

Analysis of snail shell: The snail shells were homogenized to fine powder, and sieved using a sieve of 0.5µm pore size to obtain a fine powder. Stability test was carried out on the snail shell powder to know the pH at which the snail shell will dissolve in acid or alkali medium; this was done by preparing acid solution using CH_3COOH and alkali solution using NaOH.

Analyses carried out on snail shell are:

Protein estimation which was done by the determination of total nitrogen using the micro Kjeldahl procedure.

Ash content was determined using the method described by Pearson (1976).

The crude fat was estimated by extraction with petroleum ether using soxhlet apparatus.

Nitrogen free extract was not determine directly but was obtained as difference between 100 percent and the sum of% ash, protein crude fat and crude fibre. N.F.E = 100- (%ash + %crude fibre + %crude fat + %crude protein).

The crude fibre was determined by removing the fat from or defatting the sample by boiling the sample with tetraoxosulphate (VI) acid and sodium hydroxide repeatedly.

Heavy metals were determined using atomic absorption spectrophotometer (AAS).

Wastewater sample collection

The wastewater sample used for this study was collected from the discharge unit of pharmaceutical industry.

Sampling technique

Grab sampling method was the mode of collecting the wastewater for this study and all analysis were done in triplicate to ensure representative and reproducible results. The jerry can for the collection of wastewater was properly washed using distilled water, it was allowed to dry and some quantity of Manganeous sulphate salt was poured into the container for collection, this was to fix the dissolved oxygen, since its determination was not carried out on site during collection.

Analysis of wastewater

pH and temperature were determine on site and the wastewater was preserved at a temperature of 4^0C for more analysis.

Analysis of the sample was done immediately as describe in the standard methods for the examination of water and wastewater APHA (1998), and standard methods for water and effluent analysis (Ademoroti., 1996).

Where analysis was not immediately possible, the wastewater was preserved in a refrigerator maintained at 4^0C, at this temperature, bacteria are inactive and biodegradation is inhibited (Ademoroti., 1996).

Kinetic study experiment

Glass wool was placed at the bottom of a column and was packed with 50g of snail shell, 100ml of the wastewater was introduced into the column with the

aid of a dropping funnel, this was allowed to stay for a maximum of three months, sample was withdrawn for analysis at every 24 hrs for the first one week, every three days for the second week and third week and every week for three months. Physicochemical parameters of the treated wastewater were determined.

Result and Discussion

The pH value of snail shell in solution is 8.84, which shows that its solution is alkaline, which may results from the presence of Calcium carbonate and protein as some of the composition of the shell (Aboua., 1995).

It was easy to homogenise the snail shell into fine powder, hence giving a large surface area of 40.29, it serves as a good adsorbent for the removal of pollutants from wastewater.

The analysis of the various food compositions of different species of snail shell is presented in table 1 below.

Sample	%Protein	%Fiber	%Fat	%Ash	%N.F.E
Archatina archatina	0.12±0.4	4.06±0.1	0.79±0.2	2.00±0.4	93.04±0.3
Archatina maginata	0.42±0.5	3.37±1.0	0.75±0.3	10.00±0.4	85.46±0.6
Archatina fulica	0.30±0.1	3.96±0.4	0.38±0.2	10.00±0.4	82.36±0.4
Limucularia Species	0.23±0.4	4.14±0.2	0.48±0.3	13.00±0.1	82.15±0.5

Nitrogen free extract is also referred to as the soluble carbohydrate, analysis showed that *Archatina archatina* (Africa giant snail) had the highest carbohydrate value; hence it can be added to some food materials to enhance their carbohydrate content (Gaman and Sherington, 1977).

Since carbohydrate has oxygen and hydrogen elements as some of its chemical composition, there is the tendency of the formation of charges such as hydrogen and oxygen ions. The oxygen ion is negatively charge and can attract metallic ions and possibly remove them from solution (Harold., 1963).

The ash content is an indication of the presence of carbon compounds and inorganic components in the form of salts and oxides (Usman, 2006) in the snail shell, carbon plays a vital role in the adsorption of substances due to its porous nature, this is an indication that snail shell in its granular or ash form can play a vital role in the removal of metals and other particles from solution, it can remove colour and some other precursors of gaseous substances that generate odour and smell in wastewater, and as such can remove smell or odour from water and other solution.

The fibre content of each species enhanced the strength of the snail shell; hence gave the shell its toughness and hardness (Ihekoronye and Ngoddy, 1985).

Apart from its hardness and toughness, it was observed that the fibrous content of the snail shell contributed immensely to its ability of removing insoluble particles from solution, hence serving as a semi permeable medium; it can also remove some heavy particle from solution.

The analysis of the composition of metals or minerals of snail shell shows that all the species consist of manganese, Zinc, Copper and Iron in different amounts. However the amount of Iron is the highest in all the species. Sample A, *Archatina archatina* has the highest amount of iron; the value is 251.23 mg/l as unveiled in Table 2.

A similar study was carried out by Ogbonde Chukwu (cited by Ademoroti, 1996), shows a similar trend. Iron is one of the most abundant metals on earth. It ranked 9th most abundant metal (Ademoroti, 1996), and are used in a variety of ways, example, Iron (III) chloride is use as a coagulant in the treatment of water and wastewater especially in the removal of heavy metals and particles. The mechanism of this reaction is that when in solution that is in water, it forms hydroxide, example Fe $(OH)_3$; this is one of the possibilities of the relevance of snail shell as a coagulant in treatment of water and wastewater (Ademoroti, 1996).

Table 2: Heavy metal Composition of four Different Species of Snail Shell

Samples	Zinc mg/l	Manganese mg/l	Copper mg/l	Iron mg/l
Archatina archatina	9.85	4.31	6.47	251.23
Archatina maginata	2.50	6.71	5.33	57.45
Archatina fulica	8.02	16.98	5.51	37.04
Limucolaria species	6.30	1.99	4.46	208.58

From the result of the analysis, it is possible for snail shell to liberate or release Iron in the form of Iron (III) ion, to form Iron (III) hydroxide which is effective as a coagulant in water and wastewater treatment (Ademoroti, 1983). A study of the treatment of municipal sewage containing some heavy metals, when treated with Iron (III) chloride at pH 4.1 and optimum dosage of 300mg/l shows

effective treatment. Hence, there is a correlation between this and the above report.

Other metals present in snail shell from this analysis are also useful in various ways, though they could be toxic when in large amount or at high concentration.

Due to the high content of iron in the archatina archatina (giant snail), the large surface area and less absorption of water, it was chosen as a best species in the treatment study.

Physicochemical characterisation of wastewater from pharmaceutical industry:

Wastewater was obtained from a pharmaceutical industry in Benin; physicochemical characterization was carried out on the wastewater, it was then subjected to treatment at different time using snail shell powder. The result of the physicochemical characterization is presented in table 3 below:

Table 3: Results of physicochemical analysis of untreated wastewater from pharmaceutical industry

S/NO	PARAMETERS	UNIT	VALUES
1	pH		6.6±0.1
2	TEMPERATURE	^{0}C	27.6±0.6
3	ALKALINITY	mg/l	634.3±1.5
4	TURBIDITY	NTU	402.6
5	TS	mg/l	172±1
6	TSS	mg/l	20.6±1
7	TDS	mg/l	151.3±0.5
8	COD	mg/l	822±2
9	BOD	mg/l	31.4±0.1
10	DO	mg/l	3.43±0.15
11	EC	µS/cm	671.3±1.5
12	NO_3-N	mg/l	2.87±0.01
13	PHOSPHATE	mg/l	0.16±0.01
14	SULPHATE	mg/l	0.85±0.01
15	Pb	mg/l	0.0031±0.001
16	Cd	mg/l	BDL
17	Hg	mg/l	0.012±0.001

The wastewater was slightly acidic almost neutral as the pH value is 6.6, this is because some of the composition of the wastewater contain substances such as ethylene glycol, methanol, isopropanol and acetone which when in water will reduce the pH of the waste by producing hydrogen ions, some of this hydrogen ions combine with water to form hydroxonium ion hence the pH value.

However the wastewater is within the acceptable limit of 6-8 for safe discharge. The temperature of the wastewater is within the acceptable limit when discharge into the water body.

The alkalinity value was high; this is as a result of the waste generated during the production process. Though wastewater varies from different pharmaceutical company since they produce different drugs, generally the wastewater from most pharmaceutical companies contains volatile organic compounds (VOCs), which include organic solvent, nitrogen compounds, salts, catalysts, additives, reactants, intermediates, raw materials, Active pharmaceutical ingredients (APIs) and metals (Jones., 2006).

These compounds in the wastewater can contribute to the high value of alkalinity. The wastewater was quite turbid; this is reflected from the value of turbidity in the table. The reason for this turbidity is that large amount of waste which are in colloid form are generated, such compounds are the phythalates, vinyl acetate, xylene and many other compounds. The total solid was also high, though most of the solid are in the dissolved form, since wastewater from the pharmaceutical industry contains compounds of high molecular weight which are hardly biodegradable.

The metals have very low values, since metals are not used to produce most drugs, it is obvious that these metals may be generated from the washing of machines or equipment used for production; however their values are within the acceptable limit for the safe disposal of wastewater or reused.

The COD value was high because wastewater from the pharmaceutical industry contain high amount of pollutants that are susceptible to oxidation such compounds include chloromethane, cyanide, ethyl benzene and many others. This can be seen from the high value of electrical conductivity which indicates the high amount of substances or waste that are generated during the production process of these drugs.

Soap and detergent are used in the washing of production equipment; this can produce inorganic waste and surface active agents that are hardly biodegradable. The wastewater contains nitrogen in the form of NO_3-N, sulphate and phosphate which are generated during various chemical reactions such as nitration, amination, halogenations, sulphonation and alkylation during production process.

Treatment of wastewater from pharmaceutical industry at different time (days):

The wastewater from pharmaceutical industry was treated at different time using snail shell as the adsorbent. The results obtained from the treatment were presented in table 4

Table 4 : Result of the analysis of treatment of wastewater from Pharmaceutical industry ,using snail shell powder at different time (DAYS):

S/NO	PARAMETERS	UNITS	DAYS					
			1	10	20	40	60	120
1	pH		8.46	8.4	8.31	8.49	8.56	8.42
2	TEMPERATURE	^{0}C	28	27	28	29	28	27
3	ALKALINITY	mg/$CaCO_3$	532±3.1	500±2.4	400±3.4	400±4.1	386±3.4	372±4.1
4	TURBIDITY	NTU	276±2.4	265±2.1	254±3.1	243±2.5	217±2.4	204±2.5
5	EC	µs/cm	240±4.2	225±4.3	234±3.6	219±3.4	207±3.2	202±3.5
6	TS	mg/l	156.2±1.4	138.5±1.2	120.2±1.3	109.3±1.5	102.1±1.2	61.8±1.2
7	TSS	mg/l	0.42±2.1	0.21±2.3	0.16±2.1	0.14±2.4	0.01±2.2	0.01±2.3
8	TDS	mg/l	155.8±0.5	138.3±0.4	120.1±0.3	109.26±0.5	102.5±0.4	61.75±0.5
9	BOD	mg/l	28.95±2.2	27.86±2.1	27.02±2.3	26.78±2.3	25.92±2.4	25.23±2.2
10	COD	mg/l	480±2.4	473±2.6	469±2.5	465±2.3	461±2.5	460±2.4
11	DO	mg/l	4.20±0.2	4.40±0.1	4.90±0.2	4.92±0.1	4.94±0.3	4.94±0.2
12	NO_3-N	mg/l	0.26±1	0.16±1.4	0.13±1.3	0.06±1.5	0.03±1.4	0.01±1.3
13	PHOSPHATE	mg/l	0.021±0.4	0.014±0.4	0.003±0.2	0.00	0.00	0.00
14	SULPHATE	mg/l	0.280±2.4	0.146±2.2	0.143±2.5	0.081±2.3	0.024±2.4	0.020±2.3
15	Pb	mg/l	BDL	BDL	BDL	BDL	BDL	BDL
16	Cd	mg/l	BDL	BDL	BDL	BDL	BDL	BDL
17	Hg	mg/l	BDL	BDL	BDL	BDL	BDL	BDL

BDL= below detectable Limit

From the table, there was increase in the pH of the wastewater after treatment; this increase could results from the adsorbent used during the treatment. Since snail shell contains calcium carbonate, there is the possibility that some of the carbonate went into solution to form calcium hydroxide hence increasing the pH value of the treated wastewater which was a bit alkaline.

However its value is within the acceptable limit for safe disposal. There was slight variation of temperature at different days of treatment; however the values were within the acceptable limit for wastewater disposal. This slight temperature increase could be as a result of the exothermic nature of the treatment process.

There was reduction of alkalinity value at different days of treatment as can be observed from the table. This reduction could result from the adsorption capacity of the snail shell, since most of the waste contain solids such as starch used in the coating of the tablets, phthalates and waste drugs (solids and hazardous waste) (Jones., 2006). There is the possibility that most of these substances were adsorbed from the wastewater during treatment.

The turbidity value was reduced at the different days of treatment, the water obtained at 120 days was almost clear this can be seen from the turbidity value. The reason for this reduction is that most of the wastes in the colloid form have been removed from wastewater by the snail shell, since the snail shell has a large surface area for adsorption; it is possible that the shell was able to adsorbed most of this colloid substances.

The values of electrical conductivity at different days of treatment shows that there was reductions in the electrical conductivity, this do not eliminate the fact of the existence of some substances in the treated wastewater which could be in the liquid form, such substances as the volatile organic compounds (VOCs), solvents from solvent extractions and some other organic compounds which are generated during the production of active ingredients of the drugs. There is the possibility that these substances could not be removed because treatment was done at room temperature.

There was reduction in the total solid of the treated wastewater at the different days of treatment. This results from the adsorption of most of the solid waste which are either in the dissolved or suspended form. A similar result was reported by (Csefalvay et al., 2007) in the treatment of pharmaceutical wastewater by hybrid separation process.

This same reduction was also reflected in the values of total suspended solids and dissolved solid, the value of TSS was 0.01mg/l at 120 days of treatment, and this means that the total suspended solid was almost removed during treatment.

The BOD values of the treated wastewater were reduced at the first day of treatment, which reduced further during the other days of treatment. Wastewater from pharmaceutical industry contain waste that are toxic or recalcitrant substances which

are hardly biodegradable hence the slight reductions of the BOD values (Kanu et al., 2011).

There was also reduction of the COD values at the different days of treatment; this is an indication that most of the wastes in the pharmaceutical wastewater have been reduced through adsorption by snail shell.

The value of the dissolved oxygen increases with increase in the treatment days; because most of the waste that are susceptible to oxidation have been removed hence the wastewater is safe for discharge.

NO_3-N, phosphate and sulphate were reduced during treatment; phosphate was completely removed at 120 days of treatment

The metals in the wastewater were below the detectable limit after treatment of the wastewater at the different days.

Fig 1: Plot of log ($q_e - q_t$) against Time of treated wastewater from Pharmaceutical industry.

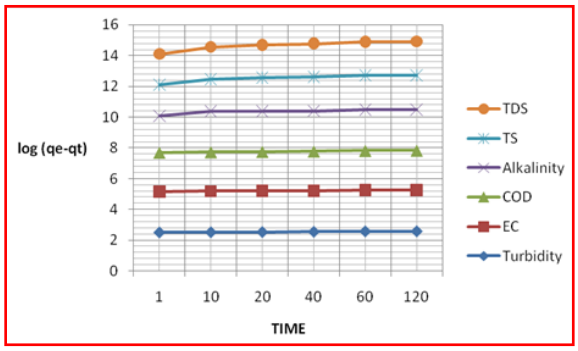


Fig 2: Plot of log ($q_e - q_t$) against Time of treated wastewater from Pharmaceutical industry

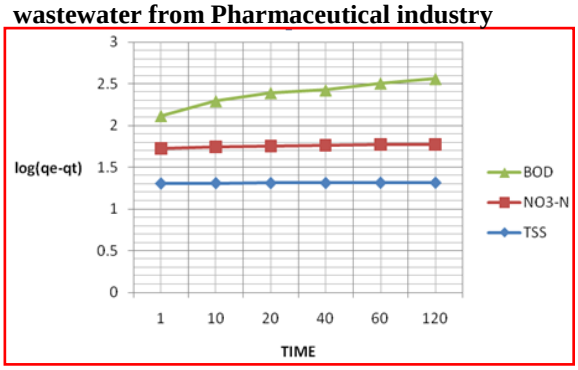
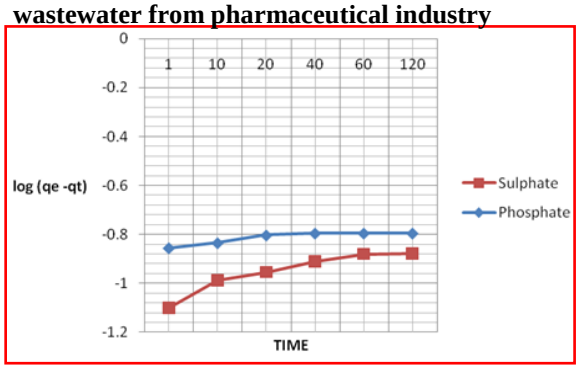


Fig 3: Plot of log ($q_e - q_t$) against Time of treated wastewater from pharmaceutical industry



Kinetic studies of the treatment of wastewater from pharmaceutical industry:

The results of the treatment of wastewater from pharmaceutical industry were subjected to kinetic studies using the Lagergrien (pseudo-first rate order) kinetics model, pseudo-second order kinetic model and the intraparticle diffusion model.

The values of K_1 and r^2 were obtained from the plot of log ($q_e - q_t$) against time as the slope and correlation value respectively, the values of K_2 and r^2 were obtained as the intercept and correlation coefficient of a plot of t/q_t against time and the values of K_{int} and r^2 were obtained as the slope and correlation coefficient of a plot of q_t against $t^{½}$ as shown in figures 1-9

Fig 4: Plot of t/q_t against Time of Treated wastewater from pharmaceutical industry.

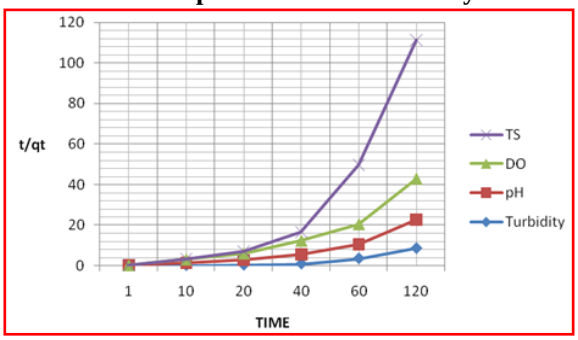


Fig 5: Plot of t/q_t against Time of treated wastewater from pharmaceutical industry

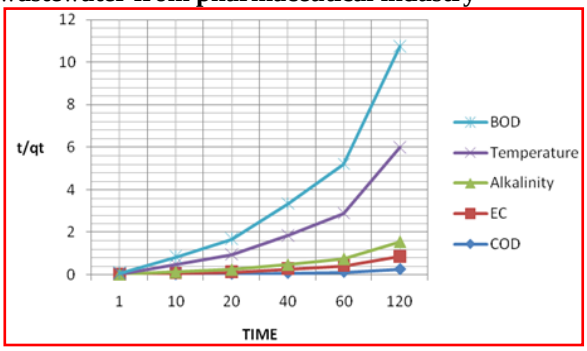


Fig 6: Plot of t/q_t against Time of treated wastewater from pharmaceutical industry

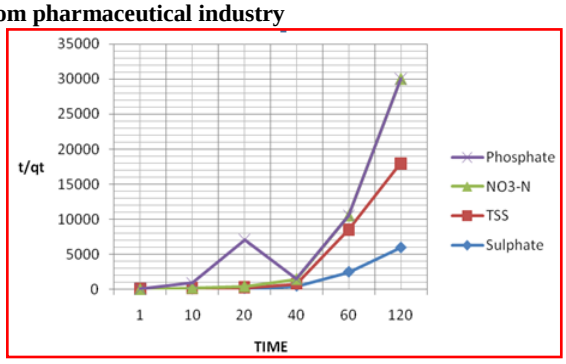


Fig 7: Plot of q_t against t½ of treated wastewater from Pharmaceutical industry

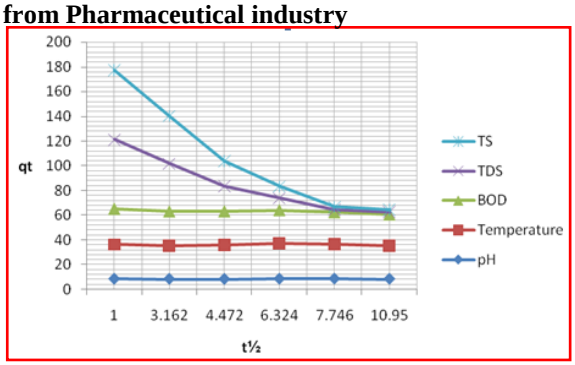


Fig 8: Plot of q_t against t½ of treated wastewater from pharmaceutical industry

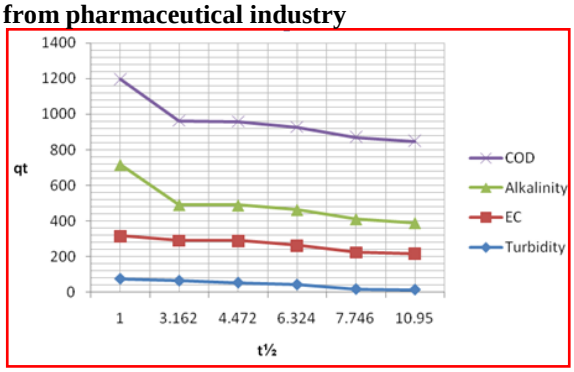
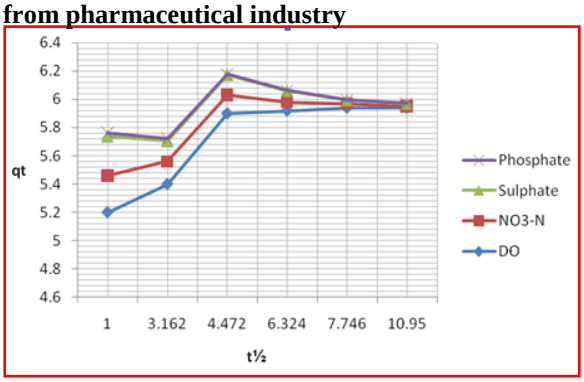


Fig 9: Plot of q_t against t½ of treated wastewater from pharmaceutical industry



The results obtained from the kinetic studies are presented in the Table 5.

Table5: kinetic studies of wastewater from pharmaceutical industry

PARAMETERS	PSUEDO-FIRST ORDER		PSUEDO SECOND ORDER		INTRAPATICLES DIFUSSIONS	
	K_1	r^2	K_2	r^2	K_{int}	r^2
pH	-	-	0.118	0.999	0.00545	0.0508
TEMPERATURE	-	-	0.037	0.999	-0.035	0.027
ALKALINITY	$1.3x10^{-3}$	0.285	0.0059	0.997	-17.7	0.530
TURBIDITY	0.0006	0.814	0.075	0.939	-6.90	0.928
EC	0.0003	0.829	0.00499	0.999	-3.94	0.873
TS	0.0012	0.596	0.606	0.939	-5.726	0.845
TSS	3.5x10-5	0.117	108.54	0.917	-0.039	0.840
TDS	0.00128	0.566	0.609	0.940	-5.686	0.845
BOD	0.0019	0.864	0.0398	0.999	-0.311	0.966
COD	$1.87x10^{-5}$	0.736	0.00218	0.999	-2.07	0.910
DO	-	-	0.167	0.999	0.0766	0.673
NO_3-N	$2.79x10^{-5}$	0.700	100.78	0.874	-0.025	0.904
PHOSPHATE	0.00042	0.480			-0.021	0.718
SULPHATE	0.0011	0.618	52.95	0.947	-0.025	0.853
Pb	-	-	-	0.926	-0.011	0.957

From the table it could be observed that the results obtained from the analysis did not fit the pseudo-first order rate law, because the coefficient correlation (r^2) values for all the parameters is lower than 0.999. In this pseudo-first order, the rate of adsorption was assumed to be proportional to the difference between the maximum adsorption capacity at equilibrium (q_e)

and adsorption at any time (q_t) of the adsorption in a first order at the initial reaction stage.

When the results were subjected to the pseudo-second order rate kinetics it was observed that the correlation coefficient value (r^2) for most of the parameters studied was higher than 0.9, this is an indication that the treatment fit the pseudo-second order rate kinetics.

This suggest that the adsorption system is not a first order reaction and that the pseudo-second order model, is based on the assumption that the rate limiting step may be chemical adsorption or chemisorptions involving covalence forces through the sharing of electrons between the adsorbent and the adsorbate (Ho and Mckay.,1999).

The correlation coefficient (r^2) value of NO_3-N, was less than 0.9, this may results from the decomposition of nitrogenous waste by the action of bacterial into nitrates which will eventually break down into gases that will either escape from the wastewater as the various form of Nitrogenous gases or dissolve in wastewater to form acids.

Conclusion and Recommendation

The results of these studies show that snail shell can be used effectively in the treatment of wastewater from different industries. The shell is common in Nigeria, is cheap to obtain since it is waste generated from the consumption of the snail.

The proximate analysis of the different species of snail shell reveals that the shells of the giant African snail (Achatina achatina) is more effective in the treatment of wastewater, since the shell is easy to homogenised into fine powder giving it a large surface area for adsorption. It has the highest iron content which equally makes it to have a high coagulating property; hence the shell can function as good adsorbent and a coagulant or coagulant aid.

The snail shell has calcium carbonate as its chemical compositions which is in the form of aragonite, this can also makes the snail shell to have a good ion exchange capacity, also the calcium ions can combine with negative charged colloids in the wastewater and remove them as settle able flocs that can easily be removed by filtration.

The high iron content of the snail shell has also contributes to the coagulating ability of the snail shell. Iron exist in two oxidation states namely Iron (ll) and Iron (lll). The Iron (lll) ion is used for coagulation, and this contributes to the high coagulating property of the snail shell, since the higher the oxidation state of an ion the better the coagulating property.

Snail shell is very stable in both acidic and alkaline medium as observed from the stability study.

This is an indication that the shell can be used to treat wastewater at any medium; however it is possible to adjust the pH of the wastewater to the required pH during treatment.

From these studies it was observed that the treatment of wastewater using snail shell is more effective as the time of treatment increases, this is evidenced from the decrease in the physicochemical parameters and the increase in the values of dissolved oxygen as the treatment time increases.

However, the longer the wastewater spent with the adsorbent the better the treatment.

There is the need to change adsorbent by either regeneration or replacing it with fresh one, since at a longer time all the active sites of the adsorbent have been occupied by water and possibly be saturated with the adsorbent and water.

The kinetic studies of the treatment of the wastewater revealed that most of the parameters fitted the pseudo-second order kinetics, since their correlation coefficient values (r^2) is greater than (0.9).

In comparison to that reported by Ho and Mckay (1999), shows that the kinetic of sorption of Victorian blue, Aromatic compounds, p-nitro-phenol, o-nitro-phenol, a chrome dye, Omega Chrome Red ME (OCRME) on fly ash, copper (II) on peat and bottom ash, bicarbonate- treated peanut hull (PHC) and activated carbon, the kinetic of sorption of Cadmium (II) on wollastonite, of chromium (VI) on Bi_2O_3, of Cadmium on beech and reed leaves, of Lead (II) on cypress leaves and bottom ash and phosphate on tamarind nut shell activated carbon (TNSAC) were analysed on the basis of the pseudo-second order rate mechanism.

They reported that the pseudo- second order chemical reaction kinetics provide the best correlation of the experimental data.

The pseudo-first order model proposed fits the experimental date well for an initial period of the first reaction step only. However, over a long period of treatment the pseudo-second order provides the best correlations for all the system studied.

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