Vol.4 (1), pp. 1-13, March 2016
ISSN 2354-4163
Article Number: DRJA15595935

Direct Research Journal of Chemistry and Material Science
http://directresearchpublisher.org/journal/drjcm

Research Paper

Mechanisms and modelling phosphate removal from textile wastewaters by chemical coagulation

AMOKO[2], J. S., FEHINTOLA[2] *E. O.*, OBIJOLE[2], O. A., BOLORUNDURO[3], K. A., and *[1]OKE, I. A.

[1]Department of Civil Engineering, Obafemi Awolowo University, Ile-Ife, Nigeria.
[2]Department of Chemistry, Adeyemi College of Education, Ondo; Obafemi Awolowo University, Ile-Ife,Ngeria.
[3]Post Graduate student, Department of Civil Engineering, Obafemi Awolowo University, Ile-Ife, Nigeria.

*Corresponding Author E-mail: okeia@hotmail.com

Received 8 December 2015; Accepted 22 January, 2016

This study presents a report on relationship between selected factors and phosphate removal from textile wastewaters using alum. Synthetic textile wastewaters were prepared from poly and ortho-phosphate using standard methods as stated in Standard Methods of Water and Wastewater Analysis. Synthetic and industrial wastewaters were subjected to chemical treatment (coagulation) using alum and combined treatment of biological and chemical treatment. Efficacies of the treatment were based on ability to remove phosphate from the wastewaters. Effects of pH, coagulant dose and initial concentration of phosphate on efficacies of the treatment processes were evaluated statistically. Models that relate alum concentration to phosphate removed were obtained from literature and was solve using least squared, Gaussian elimination and Microsoft excel solver techniques. The equations and methods were evaluated statistically. The study revealed that efficacies of chemical treatment ranges from 0.24 to 0.70, while combined biological and chemical had efficacies ranging from 0.92 to 1.00. Removal of phosphate from textile wastewaters by chemical coagulation followed hyperbola pattern with correlation coefficient of 0.9316. Parameters for model equation for the treatment processes were k_1 = 0.035 and 0.952; k_2 = 0.399 and 0.074; k_3 = 0.344 and 0.046; and k_4 = 0.033 and 0.025 for phosphate from industrial textile wastewater using chemical coagulation and combined biological and chemical coagulation processes respectively. Analysis of the variance of these efficacies revealed that there is significant difference between the treatment process (F = 3.624; p = 0.002) and between the efficacies (F = 37.339; p = 0.000) at 95 % confidence level. It was also revealed that pH, initial phosphate concentration and coagulant dose had effects on efficacies of the treatment processes. Initial phosphate concentration and coagulant dose were significant factors at 95 % confidence level for all the wastewaters and all the methods. It was concluded that initial concentration of the pollutant and pH have effects on effluent quality. Pre-treatment and coagulant dose were significant factors in the treatment of textile wastewaters.

Key words: Biological treatment, chemical treatment, concentration of phosphate, pH and textile wastewaters.

INTRODUCTION

Environmental issues have become serious social concerns at a global scale. Among these issues is the impact of water pollution, which is getting more serious because it is closely related to the health and lives of human beings. It is well documented that eutrophying substances in water (like organic matters, nitrogen and phosphorous) are the most common pollutants caused by human activities (Horan, 1993). These substances are discharged not only by domestic activities but also by agriculture such as livestock raising and industrial activities.Today, wastewater containing eutrophying substances is treated by the bio-treatment process, in which microbes decompose these substances. Bio-treatment is an economical wastewater treatment method, but it has some disadvantages (it takes a long treatment time, it requires large-scale treatment facilities, and the problem of how to get rid of sludge produced by treatment, Horan 1993). Another useful wastewater treatment method is chemical water treatment, which has been studied (Sawsan et al*.,* 2009). In the chemical treatment process, organic pollutants in wastewater are chemically oxidized, precipitated or reduced to non-hazardous inorganic substances. In this wastewater treatment method (chemical), coagulation and coagulant material are the important factors that affect treatment efficiency (Oke et al., 2006). In recent years, the application of various coagulants chemical for wastewater treatment with a particular attention to phosphate reduction or removal has been studied (Hala and Laila, 2014; Davarkhah et al*.,* 2012; Mahdi et al*.,* 2007; Klimiuk et al*.,* 1999, Leader et al*.,* 2005, George et al*.,* 2013; Arash et al*.,* 2011).

Chemical treatment of textile wastewaters containing phosphate has some attractive properties such as high chemical stability and strong oxidization capability due to its high oxygen-over-potential in water. It has been documented that textile industry consumes large quantities of water and produces polluted wastewater (Balasubramanian et al*.,* 2006; Ozmihci and Kargi, 2006; Dhaouadi and M'Henni, 2008; Li et al*.,* 2005; Toledo et al*.,* 2005; Corella and Toledo, 2006; Taib et al*.,* 1999; Balogh and Nollet, 2008; Tang et al*.,* 2008; Karamalidis and Voudrias, 2007). The bio- processing units and chemical reagents used both in developing and washing processes to maintain the steady and effective operations of the textile materials have lead to large amounts of wastewater produced by this industry (Lubello et al*.,* 2009; Lin and Peng, 1996; Pala and Tokat, 2002; Zodi et al*.,* 2009; Manhong et al*.,* 2011). In addition, large quantities of organic waste, mixed sludge contain a large amount of iron and aluminum ions from added coagulants and flocculants lead to serious secondary pollution. Previous studies on textile wastewater treatment can be found in literature (Oke et al., 2006; Oke and Okuof, 2000; Rosa et al*.,*2007a, 2007b; Manhong et al*.,* 2011; Murakami et al*.,*2009; Balasubramanian et al*.,*2006; Ozmihci and Kargi, 2006; Dhaouadi and M'Henni, 2008; Li et al*.,*2005; Toledo et al*.,* 2005; Corella and Toledo, 2006; Taib et al*.,* 1999; Balogh and Nollet, 2008; Tang et al*.,* 2008; Karamalidis and Voudrias, 2007; Wong et al*.,*2000; Kikuchi, 2001; Zhang et al*.,* 2001; Autret et al*.,* 2007; Behbahani et al*.,* 2011). Literature on adequate amount of coagulant require for textile wastewater treatment are rare. This shows that there is a need to document models of factors for chemical coagulation of textile wastewater. In the present study, investigation on the chemical coagulation of textile wastewater was conducted with a particular attention to phosphate removal using alum (aluminium sulphate) through effects of selected factors.

MATERIALS AND METHOD

Phosphate removal from textile wastewaters was studied as a follow up on Oke and Okuofu (2000). Synthetic and industrial textile wastewaters were subjected to chemical treatment using alum (coagulant) only and combined treatment of biological and chemical treatments. Industrial textile wastewaters were collected from selected textile industries in Kano and Kaduna states, Nigeria. Synthetic wastewaters were prepared by dissolving known masses of potassium phosphates (poly and ortho phosphate) in distilled water using standard methods (APHA, 1998, Oke and Okuofu, 2000). Effects of selected factors (pH, doses of coagulant and concentration of phosphate) on efficacies of these treatment processes were evaluated statistically using Analysis of variance (ANOVA). Model $e = K_1 + K_2 \log\beta + K_3 \log P_i - K_4 pH)$ that relates alum concentration to phosphate removed was obtained from literature (Oke and Okuofu, 2000). The model equation was solve using least squared, Gaussian elimination and Microsoft excel solver techniques. The models from these techniques were evaluated using statistical methods (model of selection criterion, total errors, absolute error, mean error and root squared error).

Model of selection criterion

The model of selection criterion (MSC) is interpreted as the proportion of expected data variation that can be explained by the obtained data. High MSC indicates high accuracy, validity and the good fitness of the method. MSC can be computed using equation (1) as follows (Oke, 2007):

$$MSC = \ln \frac{\sum_{i=1}^{n} \left(Y_{obsi} - \overline{Y}_{obsi}\right)^2}{\sum_{i=1}^{n} \left(Y_{obsi} - Y_{cali}\right)^2} - \frac{2p}{n} \quad (1)$$

Where, $\overline{Y}_{obsi}$ is the average of observed concentration of phosphate and $\overline{Y}_{cali}$ is the average of calculated concentration of phosphate; p is the number of parameters and n is the number of selected parameters (n= 3).

Total error

The lower the value of total error the higher the accuracy, validity and good fitness of the method. Total error (Err^2) can be computed using equation (2):

$$Err^2 = \sum_{i=1}^{n} \left(Y_{obsi} - Y_{cali}\right)^2 \quad (2)$$

Absolute error

The lower the value of absolute error the higher the accuracy, validity and good fitness of the method. Absolute error (AbErr) can be computed using equation (3):

$$AbErr = \sum_{i=1}^{n} \left|\left(Y_{obsi} - Y_{cali}\right)\right| \quad (3)$$

Mean error

The lower the value of mean error the higher the accuracy, validity and good fitness of the method. Mean error (MnErr) can be computed using equation (4):

$$MnErr = \frac{\sum_{i=1}^{n} \left|\left(Y_{obsi} - Y_{cali}\right)\right|}{n} \quad (4)$$

Error

The lower the value of error the higher the accuracy, validity and good fitness of the method. Error (Err) can be computed using equation (5):

$$Err = \sqrt{\sum_{i=1}^{n} \left(Y_{obsi} - Y_{cali}\right)^2} \quad (5)$$

The selected factors were evaluated using ANOVA technique. Equation that relate factors that influence phosphate removal from textile wastewaters was derived from adsorption using Freudlich isotherm equation, which can be written as follows (Oke and Okuofu, 2000):

$$e = c + b\left(\log k' + \log \beta + q_1 \log P_i - q_2 pH\right) \quad (6)$$

Where; e is the relative phosphorus removal ; c is the intercept., b is the slope of the approximating straight line; β is the ratio of alum dose to phosphate concentration; P_i is the phosphate concentration (mg/l); q_1; q_2 and k' are constants (Oke and Okuofu, 2000).

Setting $K_1 = c + b \log k'$; $K_2 = b$; $K_3 = bq_1$ and $K_4 = bq_2$ (7)

then

$$e = K_1 + K_2 \log \beta + K_3 \log P_i - K_4 pH \quad (8)$$

RESULTS AND DISCUSSION

Results of the study were divided into the following categories: quality of textile wastewaters; phosphate removal and analysis of variance of the phosphate removal, relationship between alum concentration and phosphate removed, solving model equations and statistical evaluation of the models; effects of the selected factors and analysis of variance of the selected factors.

Quality of textile wastewaters

Literature such as Leader et al. (2005); Behbahani et al. (2011) presents quality of textile wastewater in respect to phosphate; Arash et al. (2011); Kyzas et al. (2013), reported the quality of textile wastewater with respect to colour and dye. Stanistaw and Monika (1999); Ahmet et al. (2003); Arslan. and Isil (2002); Arslan et al. (2002); Azbar (2004); Georgiou et al. (2002); Mehmet and Hasan (2002); Olcay et al. (1996); Sheng and Chi (1993) ; Hala et al. (2014) characterised textile wastewater using more parameters other than colour, dye and phosphorous. Oke et al. (2006) provided detailed characterization of textile wastewater in Nigeria as follows:

Physical Characterization

The physical characterization of wastewater involves temperature, colour, odour, turbidity, solids, density, flow rate and conductivity. Colour in water may be resulted from the presence of natural metallic ions such as iron and manganese, humus, peat materials, plankton weeds and industrial wastes. Colour in the wastewater under investigation was classified into two (true and apparent colours). Apparent colours are the total colour due to both turbidity and the colour of the wastewater. True colour is the colour after filtration of the wastewater (after removal of suspended solids). The true colour has a mean of 60, a minimum value of 40 and maximum of 80 colour units. The apparent colour has 310, 200 and 230 colour units for maximum, minimum and the mean respectively. This result may be attributed to the dyes used in the production of textile materials. With the result of apparent colour higher than true colour indicates that floating materials or suspended solids contribute to the colour of the wastewater more than dissolved materials (Oke et al*.,* 2006).

Temperature is basically important for its effects on other properties of wastewater. Average temperature of wastewater under investigation is 41.07 °C. This result indicates that some reactions could be speeded up by the discharge of this wastewater in to the stream. It will also reduce solubility of oxygen and amplify odour due to anaerobic reaction (less dissolved oxygen). Solid in wastewater was developed according to the relative size and condition of solids particles. Literature characterized raw wastewater into four categories, based on the settling properties of the constituent material. The total solid material can be characterized into non-filterable and filterable solids fraction. The non-filterable fraction consists of settleable and non-settleable fraction, and the filterable fraction consists of total dissolved solids (TDS) and colloidal fraction. Each of these fractions consists of volatile (organic) and fixed (inert) fraction (Oke et al*.,* 2006).

Evaluation of the suspended solid includes the settleable solid in the liquid streams and the total solid. Settled sludge are used to determine solids removal by any biological treatment system. Solids in wastewater may be present in suspension or in solution. They may be divided into organic matter and inorganic matter (Rossle and Pretorius, 2005; Oke et al*.,* 2006). Total dissolved solid (TDS) are due to soluble materials whereas suspended solid (SS) are discrete particles, which can be measured by filtering the wastewater. Suspended solids (SS) concentration is the measure of amount of floating matter in the wastewater, because of its relationship with sedimentation tank; sludge formation and biological treatment suspended solids of the wastewater under investigation were measured. The suspended solids concentration was in the range of 580.6 mg/l to 854.2 mg/l with a mean of 725.9 mg/l with volatile suspended solids fraction of total solid varying from 0.861 to 0.914 and non-volatile fraction of total solid ranges from 0.086 to 0.139. Literatures classified wastewaters with SS as follows: SS less than 100 mg/l as weak, SS greater than 100 mg/l as but less than 220 mg/l as medium and SS greater than 220 mg/l as strong wastewater. Results of the study show that wastewaters from textile mills can be classified as strong wastewater and cannot be discharged in to the stream, as it will encourage sludge formation the stream, which will in turn encourage anaerobic reaction that will affect self-purification of the stream. Similarly, dissolved solid concentration was in the range of 2080.50 to 3100.6 mg/l with the mean of 2702.26 mg/l with a fraction range of 0.717 to 0.831 of total solids indicating that textile wastewaters contain soluble solid as well as floating solids which must be taken care of in wastewater treatment process design and sludge removal (Oke et al*.,* 2006).

Results for solids in textile fall in the range stated in literature. The flow rate characteristics measurement reflects a mean of flow rate of 352.8 m^3/d, maximum flow rate value of 500 m^3/d and minimum flow rate of 212.5 m^3/d there is no FEPA (1991) limit for quantity of wastewater to be discharged into the environment, and therefore it is a free access of assessment. It can be said that textile industries discharge a large volume of wastewater.

Chemical characteristics

In addition to physical characteristic, chemical characteristics tend to be more specific in nature than some physical parameters. Chemical properties are more useful in assessing the properties of wastewater samples. It includes oxygen demand, acidity and alkalinity, nitrogen, chloride, toxic metals, cyanides, phenols, oils and greases. Oxygen demand is important because organic compounds are generally unstable and may be oxidized biologically and chemically to a stable relatively inert end product. An indication of organic oxygen demand content of wastewater can be obtained by measuring the amount of oxygen required for its stabilization either as BOD, COD or PV. Biological Oxygen demand (BOD_5) is the measure of the oxygen required by microorganisms whilst breaking down organic matter at 5 days and at 20^{o}C. Permanganate value (PV) is the amount of oxygen used by chemical (Potassium permanganate) to breakdown organic and inorganic matter while Chemical Oxygen Demand (COD) is the measure of amount of oxygen required by both potassium dichromate and concentrated sulphuric acid to breakdown both organic and inorganic matters. BOD_5 and COD concentrations of the wastewater were measured, as the two were important in unit process design. The wastewater has an average COD concentration of 6477.57 mg/l of which non-biodegradable fraction has the range of 0.21 to 0.391

fractions. Biodegradable fraction of COD (slowly and readily) has the range of 0.609 (slow 0.446 against 0.153 for readily) to 0.790 (0.547 for slow and 0.243 for readily). This indicates that about 60.9 % to 79.0 % of the influent COD will be degraded biologically. BOD_5 concentration of the wastewater has a maximum value of 2010.60 mg/l, a minimum of 1260.4 mg/l, an average of 1593.42 mg/l with a standard deviation of 229.80. BOD_5 concentration has a mean of 4858.64 mg/l. High COD and BOD_5 concentration observed in the wastewater might be due to the use of chemicals, which are organic or inorganic that are oxygen demand in nature or variation in the process or method of production (Oke et al*.,* 2006).

Rossle and Pretorius (2005) reported that the carbonaceous materials content of the wastewater is estimated by the chemical oxygen demand. The typical chemical oxygen demand is subdivision into three main fractions, biodegradable (organic) chemical oxygen demand, non-biodegradable (inert) chemical oxygen demand and heterotrophic active biomass. The heterotrophic active biomass fraction is approximated as zero, as the influent is considered to be anaerobic, not seeded with recirculated-activated sludge or stabilization pond, and the wastewater is not supporting active biomass generation. The non-biodegradable (inert) chemical oxygen demand is further subdivided into particulate chemical oxygen demand and soluble chemical oxygen demand fractions, based on physical settling properties. The biodegradable (organic) chemical oxygen demand is further subdivided into slowly chemical oxygen demand and readily biodegradable chemical oxygen demand fractions, based on bio-kinetic responses. The readily biodegradable chemical oxygen demand can be further subdivided into short-chain volatile fatty acids (SCVFA) and non- short-chain volatile fatty acids (non-SCVFA or fermentable). These two divisions are normally represented by volatile fatty acids and fermentable readily biodegradable chemical oxygen demand. Alternatively, chemical oxygen demand is subdivision into two physical fractions, contains total soluble and total particulate chemical oxygen demand component. The non-biodegradable (inert) chemical oxygen demand fractions (Rossle and Pretorius, 2005) can behave as conservative substances that cannot be removed by the sedimentation process. The particulate material (particulate chemical oxygen demand) is mainly removed with the waste sludge and the soluble material (soluble chemical oxygen demand) passes through biological treatment processes largely unchanged (Oke et al*.,* 2006).

The biodegradable (organic) chemical oxygen demand fractions are used by organisms in the biological process with the soluble material (readily biodegradable chemical oxygen demand) being used more rapidly than the slowly biodegradable chemical oxygen demand material, as measured by oxygen or nitrate utilization rate tests. The short-chain volatile fatty acids fraction is increased in a wastewater with the solubilisation of slow biodegradable chemical oxygen demand to readily biodegradable chemical oxygen demand, and the fermentation of fermentable readily biodegradable chemical oxygen demand to short-chain volatile fatty acids. pH value of wastewater is the intensity of acidity or alkalinity of the wastewater, which is actually the measure of hydrogen ion concentration in the wastewater. pH value of wastewater has no health implication but many chemical reactions are controlled by the pH value (Horan , 1993; Rossle and Pretorius, 2005; Oke et al*.,* 2006). Biological activities and some chemical treatment processes are usually restricted by pH. Wastewater for biological process is fairly narrowed in the pH range of 6-8 as highly acidic or highly alkaline wastewaters are undesirable because of corrosion hazard to sewers and possible difficulties in the treatment. pH value of the wastewater ranges from 8.3 to 11.50 with a mean of 9.79. FEPA (1991) recommends pH value of range 6.0 – 9.0 for effluent to be discharged into stream, with this range of 8.3 to 11.50 for textile wastewaters, the wastewaters are alkaline, cannot be discharged into stream based on FEPA (1991) limit because it will be harmful to man, aquatic animals and will disturb biological activity (self purification) of the stream if discharged untreated. Textile wastewater studied contains 22.0 mg/l of TKN (as maximum) and 7.49 mg/l as minimum with 13.87 mg/l as the mean. The presence of TKN can be attributed to the use of animal gum as adhesive in the production line of textile materials.. Nitrogenous compounds, termed total nitrogen, are in the form of organic (proteinaceous) nitrogen and inorganic total ammonia (NH_3 –N plus NH_4 –N) and oxidized nitrogen compounds, such as nitrate (NO_3 -N) and nitrite (NO_2 -N) represented together by the total Kjeldahl nitrogen (TKN). The oxidised nitrogen compounds are usually present in low quantities in typical wastewaters. The inorganic total ammonia nitrogen exists in solution as ammonia (NH_3 -N) and ammonium (NH_4 -N). These fractions depend on the pH, with NH_4 -N being predominant at conditions with a pH below 7, as found in the wastewater sludge. It is difficult to fractionate organically bound nitrogen (e.g. protein, urea) into biodegradable and nonbiodegradable soluble and particulate fractions of nitrogenous compounds. Bacterial decomposition and hydrolysis convert organically bound nitrogen to ammonia and ammonium. The non-biodegradable particulate and soluble nitrogen fractions are handled in a similar fashion as the conservative non-biodegradable (inert) chemical oxygen demand. The evaluation of the total Kjeldahl nitrogen and the NH_3 – N plus NH_4 –N fractions in wastewater is used to determine the changes in total Kjeldahl nitrogen to chemical oxygen demand nutrient ratio and the concurrent ammonia fraction changes across the treatment plant. This result of TKN seems lower than expected for value for wastewater to be treated biologically, but there is a way of inducing TKN in nitrogen deficient wastewaters (Rossle and Pretorius, 2005; Oke et al*.,* 2006).

The wastewater under investigation has total phosphorus of a maximum value of 15.30 mg/l, minimum value of 1.29 mg/l and a mean of 7.79 mg/l of TP as phosphorus. The presence of this pollutant can be attributed to washing activities (through the use of detergent and other phosphate products). Like nitrogenous compounds phosphorus compounds are also found in wastewaters, predominantly as phosphates and can be categorized by physical means (dissolved and particulate fractions) and by chemical means as phosphate compounds. The chemical fractions consist of dissolved inorganic orthophosphate (O-PO_4), polyphosphate or condensed phosphate, and organically bound phosphate. The orthophosphates $(PO_4)^{-3}$; $(HPO_4)^{-2}$, $(H_2PO_4)^-$, and H_3PO_4), usually the predominant fraction in wastewater, are available for biological metabolism without further breakdown. The polyphosphates include two or more P atoms ($P_3O_{10}{}^{-5}$, $P_2O_7{}^{-2}$) in a complex molecule, and revert together with the organic phosphates through a slow-rate hydrolysis process to the soluble dissolved inorganic orthophosphate forms. The organic phosphorus fraction refers to phosphate in organic chemicals (cells, pesticides and detergents) for which typical soluble and particulate constituent percentages are not available. Evaluation of biological treatment plant is based on the total phosphorous and inorganic orthophosphate fractions of liquid and sludge streams to determine the changes in the total phosphorous to chemical oxygen demand ratio and the concurrent inorganic orthophosphate fraction change across the biological treatment plant(Rossle and Pretorius, 2005; Oke et al*.,* 2006). This concentration of TP seems to be low to support biological treatment of textile wastewater, but the way out is to increase TP source through seeding and chemical nutrient addition.

Chlorides in wastewater indicate the contact with human excreta (urine, or with common salt). Effect of chloride on biological treatment process has been discussed in standard environmental literature. Chloride concentration was in the range of 112.89 to 442.5 mg/l with the mean of 312.35 mg/l indicating that textile wastewaters under investigation was in contact with chloride source, FEPA (1991) limits for chloride in wastewater is 600 mg/l with lower concentration of chloride in textile wastewater it will not be harmful to man, aquatic animals and biological treatment process.

It is well known that day-to-day wastewater constituent concentrations usually exhibit considerable variations, but the ratios of constituents accommodate such fluctuations to some extent, the constituent ratios can be used as fairly representative benchmarks to characterise the wastewater for biological treatment evaluations. Wastewater with high nutrient ratios will not produce adequate denitrification for certain biological process configurations, which is a prerequisite for tertiary treatment. The strength of the settled sewage must also be considered, together with the total Kjeldahl nitrogen to chemical oxygen demand ratio, as the chemical oxygen demand content in the settled sewage contributes to the establishment of anaerobic conditions in the anaerobic zone of the biological treatment reactor. Substantial chemical oxygen demand consumption takes place during the biological process and about 8.6 mg/l chemical oxygen demand is needed to reduce 1 mg/l nitrate nitrogen to nitrogen gas during denitrification, and about 50 mg/l chemical oxygen demand, is required per 1 mg/l total phosphorous removed. The most efficient type of chemical oxygen demand fraction utilised during de-nitrification and phosphate removal is volatile fatty acid, which can be increased in the sedimentation process. A low strength biological process feed (chemical oxygen demand less than 250 mg/l; Rossle and Pretorius, 2005; Oke et al*.,* 2006) can therefore reduce the biological process performance. At a total phosphorus to total chemical oxygen demand ratio of greater than 0.02 chemical treatment will be necessary to precipitate phosphorus. When the total Kjeldahl nitrogen to chemical oxygen demand ratio is higher than 0.11 and the volatile fatty acid content is low (volatile fatty acid less than 50 mg/l), an external carbon source should be used (such as methanol), the anaerobic zone of biological reactor must be enlarged or sedimentation must be implemented (Rossle and Pretorius, 2005; Oke et al*.,* 2006).

Sedimentation is currently incorporated as a standard practice worldwide at many biological treatment processes, even for industrial wastewater treatment plant with feed total Kjeldahl nitrogen to chemical oxygen demand ratios of lower than 0.11(Rossle and Pretorius, 2005; Oke et al*.,* 2006). With TP to COD ratio of the wastewater been 0.0016 less than 0.02 chemical treatments would not be needed. Also, with TKN to COD ratio been 0.0024, which is less than 0.11 indicates that carbon source will not be required. .BOD_5: TKN: P ratios are important in process design. Horan (1993) highlights that BOD_5: TKN: P greater than 100; 5;1 is for anaerobic system and less than the value is for aerobic. The maximum COD: TKN: P ratio of the wastewater is 3690:5.8: 1, mean ratio of 832:2:1 and minimum ratio of 624: 1.5: 1 with BOD_5 : TKN: P ratio as 973 : 6:1 for maximum; 204:2:1 for mean and 134:2:1 minimum (Rossle and Pretorius, 2005; Oke et al*.,* 2006) . These are clear indication that carbon and phosphorus are available in textile wastewater but nitrogen content is deficit for effective biological treatment process. Therefore biological treatment of textile wastewater is possible but efficiency can be improved upon if nitrogen source can be added or if sedimentation tanks can be provided. Refractory in wastewaters include heavy metals, which are zinc, aluminium, lead, manganese, iron, copper and cadmium. The accumulation of metals in an aquatic environment has direct consequences to man and to the ecosystem. Zinc (Zn) is required for metabolic activity in organisms, its interest lies in the narrow "window" between their essentiality and toxicity. Others like cadmium (Cd) and lead (Pb) exhibit extreme toxicity even at trace levels. Zinc is present in wastewater streams from steelworks, rayon yarn, fibre manufacture, ground wood pulp production and recirculating cooling water systems employing cathodic treatment the plating and metal –processing industry. Nickel originates from the metal processing industries, steel foundries, motor vehicles and aircraft industries, printing and in some cases the chemical and food processing industry. Zn, Pb and Cd are common pollutants, which are widely distributed, in the aquatic environment. Their sources are mainly from weathering of minerals and soils; atmospheric deposition; industrial effluents, domestic effluents, urban storm water runoff and spoil heaps. Extensive literature on the aquatic toxicity of Zn and especially its toxicity to fishes has been reported in literature. Zinc is unusual in that it has low toxicity to man, but relatively high toxicity to fish (Rossle and Pretorius, 2005; Oke et al*.,* 2006)

Lead is present in wastewater mainly from storage battery manufacturing, petroleum refinery and run-off. Lead is defined by the United States Environmental Protection Agency (USEPA) as potentially hazardous to most forms of life, and is considered toxic and relatively accessible to aquatic organisms (FEPA, 1991). Low Pb concentrations affect fish by causing the formation of coagulated mucous over the gills and subsequently over the entire body and thus cause the death of fish due to suffocation. Lead is bio-accumulated by benthic bacteria, freshwater plants, invertebrates and fish. The chronic effect of Pb on man includes neurological disorders, especially in the foetus and in children. This can lead to behavioural changes and impaired performance in IQ tests (Fatoki and Ogunfowokan, 2002; Greben et al., 2005). Cadmium (Cd) is from metallurgical alloying, ceramics, electroplating, photography, pigment works, textile printing, chemical industries and lead mine drainage. Cadmium has been found to be toxic to fish and other aquatic organisms. The effect of Cd toxicity in man includes kidney damage and pains in bones (Itai-itai disease). Cd also has mutagenic, carcinogenic and teratogenic effects These heavy metal concentrations were determined because of their importance as nutrient and as toxic substance at a certain concentration. The results indicate that these heavy metals are not in concentrations that are harmful to humans, but their removal is essential to prevent accumulation in aquatic animals. Sulphate rich effluents can be treated biologically when sulphates reducing bacterial (SRB) and organic matter are present. The products of the biological sulphate removal technology are sulphide and alkalinity, which contribute to the pH increase of the treated wastewater. It has been reported that sulphides are fatally toxic to humans at gaseous concentration of 800 to 1000mg/l (Rossle and Pretorius, 2005; Oke et al*.,* 2006). Sulphate concentration of the wastewater under investigation is less than 800 mg/l which indicates that the wastewater can not cause serious damage to human and cannot cause corrosion in sewerage system.

Mechanism of Phosphate Removal and analysis of variance of the phosphate removal,

Davarkhah et al*.* (2012) reported that phosphorous compounds (orthophosphate, polyphosphate and organically bounded phosphorous) can get into the water bodies by many ways such as, domestic and industrial wastewater also precipitation, natural storm water and application of manufactured fertilizers. High levels of polyphosphate can be found in some industrial wastewater especially in fertilizer mills. Phosphorous compounds along with nitrogen can be led to alga bloom in water bodies which it will result in eutrophication. Phosphorous must be reduced below standard levels (usually 0.5-1.00 mg/l of P) for elimination of eutrophication. Phosphorous removal from municipal and industrial wastewater has received more attentions since 1960. Various processes such as Physical, biological and chemical have been practiced for this purpose while every method has its advantages and disadvantages. Physical methods consist of filtration, ultra filtration, reverse osmoses, ion-exchange and electro dialysis. Some of these methods are expensive and in-efficient. The maximum phosphorous removal in biological wastewater treatment processes is about 30 % (Davarkhah et al*.,* 2012). Thus, additional treatment may be required. Chemical processes have some disadvantages for example too much usage of chemicals, more complex feeding equipment, and more operation and maintenance difficulties and costs. Figure 1 presents efficacies of the treatment techniques in removing phosphate from various categories of textile wastewaters (typical and synthetic). From figure 1, efficacies of the treatment techniques range from 0.92 to 1.00 for

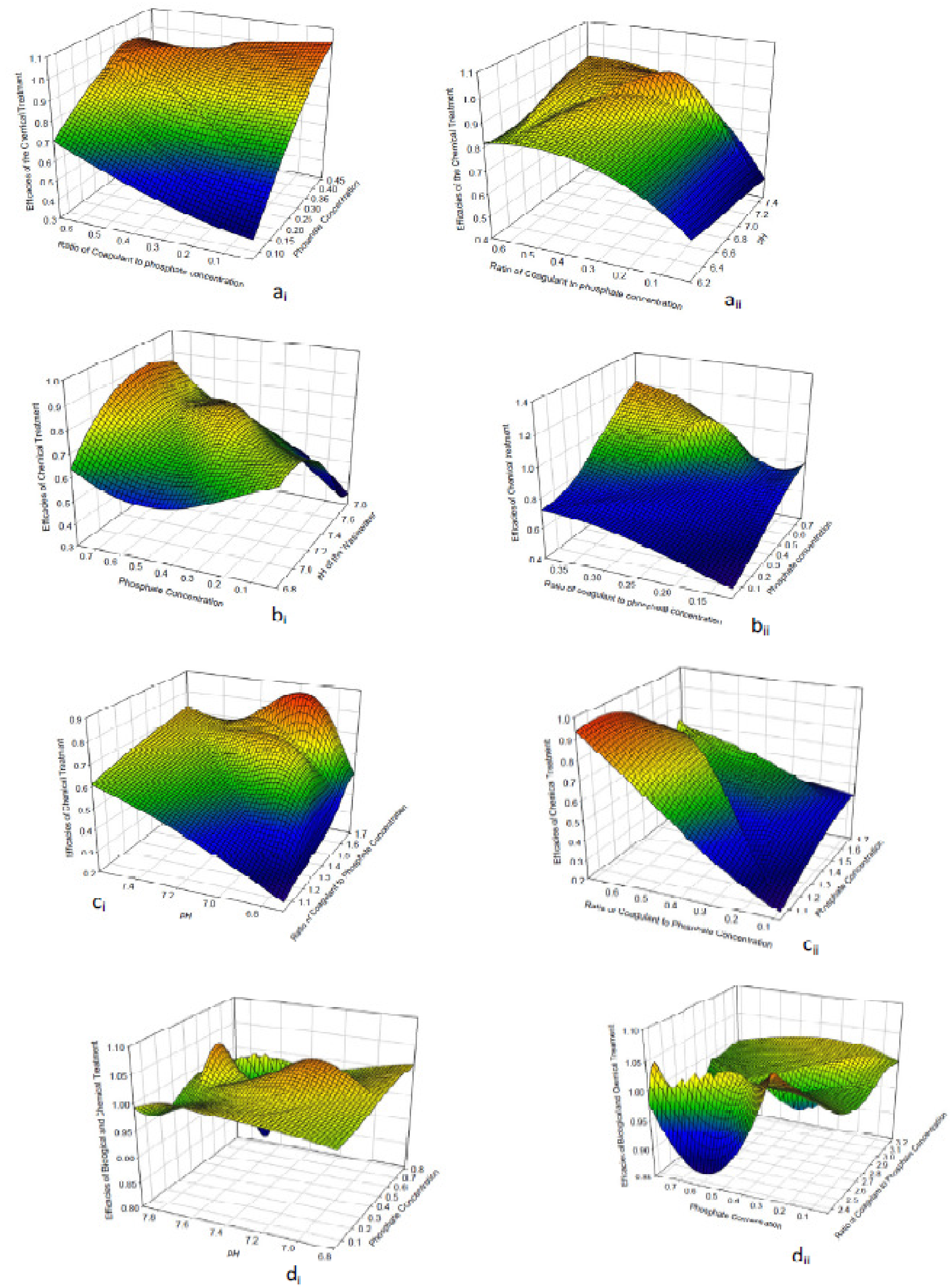

Figure 1. Efficacies of the treatment techniques and processes in removing phosphate from textile wastewaters.
(a) Synthetic textile wastewater (orthophosphate, 100 %).
(b) Synthetic textile wastewater (orthophosphate and poly phosphate).
(c) Typical raw textile wastewater treated with chemical only.
(d) Typical raw textile wastewater treated with chemical only and biological.

Table 1. Analysis of Variance of the Efficacies.

Source of Variation	Sum of Squared	Degree of Freedom	Mean Squared	F- Value	p-value
Processes	0.329	11	0.0299	3.626	0.002
Efficacies	0.922	3	0.3075	37.339	0.000
Error	0.272	33	0.0082		
Total	1.523	47			

treatment combination of biological and chemical treatment (using alum) of typical textile wastewater, 0.24 to 0.70 for chemical treatment (using alum) only for typical textile wastewater, 0.59 to 0.88 and 0.40 to 0.93 for chemical treatment of synthetic textile wastewaters with poly phosphate and orthophosphate. These results show that combination of biological and chemical treatments are effective in removing phosphate from textile wastewaters. These results revealed that efficacies of the treatment techniques is a function of many factors such as alum dose, composition of the wastewater, treatment technique, phosphate concentration, pH and other factors. Mechanism of alum hydrolysis and polymerization in water, which support phosphate removal can be expressed as follows (Sawsan et al., 2009):

$$Al(OH_2)_6^{3+} \rightleftharpoons Al(OH)(OH_2)_5^{2+} + H^+ \quad (9)$$

$$2Al(OH)(OH_2)_5^{2+} \rightleftharpoons Al_2(OH)_2(OH_2)_8^{+} + 2H_2O \quad (10)$$

$$Al_2(OH)_2(OH_2)_8^{+} + 2H_2O \longrightarrow Al_6(OH)_{12}^{6+} + 12H_2O \quad (11)$$

$$Al_6(OH)_{12}^{6+} + 12H_2O \longrightarrow Al_{10}(OH)_{22}^{8+} + 16H_2O \quad (12)$$

$$Al_{10}(OH)_{22}^{8+} + 16H_2O \longrightarrow Al_{24}(OH)_{60}^{12+} + 24H_2O \quad (13)$$

$$Al_{32}(OH)_{82}^{14+} + 28H_2O \longrightarrow Al_{54}(OH)_{144}^{18+} + 36H_2O \quad (14)$$

Mechanism of phosphate removal from textile wastewater can be summaries as follows:

$$Al^{3+} + (PO_4)^{3-} \xrightarrow{H_2O} Al_3(OH)_3(PO_4)_3Al(OH)_3 \quad (15)$$

Amount alum required for phosphate removal can be expressed as follows:

$$Y = \frac{a}{1 + b\exp^{cX_c}} \quad (16)$$

Where

Y is the mole of aluminium required per mole of soluble phosphate removal; a = 0.80; b = -0.95; c = 1.9; exp is exponential and X_c is the initial concentration of phosphate in the aqueous solution.

These equations revealed that removal of phosphate can be influence by hydrolysis and polymerization processes of alum. Table 1 shows analysis of variance of the efficacies and the treatment techniques. The table revealed that there is a significant difference between the efficacies of the treatment techniques at 95 % confidence level (F = 37.339; p = 0.000). Also, from the Table it can be seen that there is a significant difference between the treatment processes at 95 % confidence level (F = 3.626; p = 0.002). These show that in selection of technique for phosphate removal from textile wastewater, process and factors selections are important ingredients that must be considered.

Model equations and statistical evaluation of the models

Table 2 presents coefficients of the selected factors in the model equations for the various treatment techniques. Table 2 revealed that the coefficients can be grouped into two (positive and negative coefficients), which indicates that a factor is negative factors (k_4) while others are positive factors (k_2 and k_3). Negative factors are the factors that reduce efficacies with increasing value of the factors. Positive are factors that increase efficacies with increasing value of the factors. The value of k_1 (mean) as positive indicates that alum can be used to remove phosphate from textile wastewaters.

K_2 is the ratio of alum dose to phosphate concentration, which indicates that high value of the ratio (alum dose to phosphate concentration) with increase H^+ (forward reaction in equation (9); more $Al(OH)(OH_2)_5^{2+} + H^+$) and more phosphate concentration will be precipitated. Low ratio of alum dose to phosphate concentration will support backward reaction (equation (9), more of $Al(OH_2)_6^{3+}$) and concentration of phosphate removed will be small. Sawsan et al. (2009) reported that a rise in alum dosage to optimum dose increases the phosphate removal. Further addition of alum beyond optimum dose leads to a decrease in the phosphate removal efficiency. The decrease in phosphate removal efficiency after the optimum dosage was due to the restablization of colloidal suspension (Ahmed et al., 2006). This is due to the fact that an increase in the dosage shifts the optimum pH to

Table 2. Coefficients of the factors in the model equation.

Model Coefficient	Industrial Wastewater Treated using Biological and Chemical Treatment			Industrial Wastewater Treated using Chemical treatment only			Synthetic Wastewater (50 % ortho-phosphate and 50% poly phosphate) Treated using Chemical treatment only			Synthetic Wastewater (100 % ortho-phosphate) Treated using Chemical treatment only		
	Microsoft Excel Solver	Elimination	Least Squared	Microsoft Excel Solver	Elimination	Least Squared	Microsoft Excel Solver	Elimination	Least Squared	Microsoft Excel Solver	Elimination	Least Squared
K_1	0.952	0.622	1.134	0.035	-0.077	0.227	-0.161	0.769	0.547	0.344	0.782	0.319
K_2	0.074	0.074	0.023	0.399	0.399	0.389	0.701	0.827	0.863	1.034	1.034	1.123
K_3	0.046	0.046	0.016	0.344	0.344	0.370	0.256	0.384	0.417	0.439	0.439	0.492
K_4	0.025	0.025	0.027	0.033	0.033	0.060	-0.087	0.000	0.024	-0.003	-0.003	-0.001

Table 3. Statistical Evaluation of the Coefficients (F- values) in the model equations.

Model Coefficient	Industrial Wastewater Treated using Biological and Chemical Treatment			Industrial Wastewater Treated using Chemical treatment only			Synthetic Wastewater (50 % ortho-phosphate and 50% poly phosphate) Treated using Chemical treatment only			Synthetic Wastewater (100 % ortho-phosphate) Treated using Chemical treatment only		
	Microsoft Excel Solver	Elimination	Least Squared	Microsoft Excel Solver	Elimination	Least Squared	Microsoft Excel Solver	Elimination	Least Squared	Microsoft Excel Solver	Elimination	Least Squared
K_2	142.563	142.563	13.929	142.784	142.784	135.580	1620.262	2251.957	2452.756	640.4	640.4	755.8
K_3	56.689	56.689	6.741	105.988	105.988	122.659	216.036	485.664	572.670	115.2	115.2	145.1
K_4	16.071	16.071	19.196	0.972	0.972	3.226	24.857	0.000	1.897	0.007	0.007	0.000

Table 4. Effects of the selected factors in the model equations.

Model Coefficient	Industrial Wastewater Treated using Biological and Chemical Treatment			Industrial Wastewater Treated using Chemical treatment only			Synthetic Wastewater (50 % ortho-phosphate and 50% poly phosphate) Treated using Chemical treatment only			Synthetic Wastewater (100 % ortho-phosphate) Treated using Chemical treatment only		
	Microsoft Excel Solver	Elimination	Least Squared	Microsoft Excel Solver	Elimination	Least Squared	Microsoft Excel Solver	Elimination	Least Squared	Microsoft Excel Solver	Elimination	Least Squared
K_1	0.952	0.622	1.134	0.035	-0.077	0.227	-0.161	0.769	0.547	0.344	0.782	0.319
K_2	0.147	0.147	0.046	0.798	0.798	0.778	1.403	1.654	1.726	2.067	2.067	2.246
K_3	0.093	0.093	0.032	0.688	0.688	0.740	0.512	0.768	0.834	0.877	0.877	0.984
K_4	0.049	0.049	0.054	0.066	0.066	0.120	-0.174	0.000	0.048	-0.007	-0.007	-0.002

an unfavorable range for phosphate removal, so the increase in the dosage is meaningless and it actually decreases the performance of the coagulant. K_3 is the coefficient for the phosphate's concentration in aqueous solution. It can be explained that increase in the phosphate's concentration indicates an increase in the charges in aqueous solution, which will increase attraction force between alum and the phosphate concentration (equation 15). The value of k_4 as negative value can be explained through equation (9), as the value of H^+ increase the reaction shift backward for more $Al(OH_2)_6^{3+}$ which will not support the phosphate concentration removal. Sawsan et al. (2009) stated that after alum was added into water, the pH of solution decreased. This is due to the fact that a part of alum was precipitated as the hydroxide forms and H^+ was formed (equation 9). Below a pH range of 5.5 the aluminium ions are soluble and do not participate in the hydration, coagulation, precipitation and oxidation reactions necessary to make alum effective as a coagulant. Sawsan et al. (2009) studied effects of selected factors on removal of phosphate from textile and it was reported that that phosphorus removal was not affected by slow mixing time. The reason may be due to the fact that the phosphorus removal is relatively fast and equilibrium had been reached in less than 5 minutes. Sawsan et al. (2009) reported that a similar behaviour was observed by Szabo et al., (2008) and Georgantas and Grigoropoulou, (2003). Tables 3 and 4 present statistical evaluation of these selected factors. From (Table 3) for industrial wastewater treatment using

Table 5. Statistical Evaluation of the methods for solving the models.

Model Coefficient	Industrial Wastewater Treated using Biological and Chemical Treatment			Industrial Wastewater Treated using Chemical treatment only			Synthetic Wastewater (50 % ortho-phosphate and 50% poly phosphate) Treated using Chemical treatment only			Synthetic Wastewater (100 % ortho-phosphate) Treated using Chemical treatment only		
	Microsoft Excel Solver	Elimination	Least Squared	Microsoft Excel Solver	Elimination	Least Squared	Microsoft Excel Solver	Elimination	Least Squared	Microsoft Excel Solver	Elimination	Least Squared
Total error	0.00579	0.03101	0.00844	0.00575	1.47052	0.00620	0.0038	1.6816	0.0020	0.00614	1.83246	0.00989
MSC	-0.26923	-1.94744	-0.6464	3.11837	-2.42603	3.04302	2.23454	-3.86187	2.87702	3.45509	-2.24395	2.97838
Mean Error	0.01578	0.04335	0.01722	0.0181	0.3488	0.0195	0.0145	0.3741	0.0112	0.01601	0.39011	0.01903
Absolute error	0.18936	0.52026	0.20667	0.2175	4.1851	0.2338	0.1740	4.4898	0.1338	0.19214	4.68134	0.22835
Root Mean Squared error	0.07609	0.17608	0.09188	0.07582	1.21265	0.07873	0.0615	1.2967	0.0446	0.07834	1.35368	0.09943

Table 6. Parameters for the model.

Treatment Process	Constant 'a'	Constant 'b'	correlation coefficients	coefficient of determination	F-Value	p- value
Chemical Treatment of typical textile wastewater	6.95	8.77	0.932	0.868	65.66	<0.0001
Chemical Treatment of synthetic textile wastewater (Orthophosphate)	120.38	130.82	0.936	0.876	70.73	<0.0001
Chemical Treatment of synthetic textile wastewater (Poly and Orthophosphate)	979.54	1270.61	0.216	0.047	0.49	0.500
Combination of Biological and Chemical Treatment of typical textile wastewater	-1481.64	-1508.60	0.214	0.058	0.62	0.451

combination of biological and chemical treatment processes all the factors are significant at 95 % confidence level. The can be attributed to the fact that in biological treatment of wastewaters pH and phosphorus are needed for the growth of the microorganisms. For other typical and synthetic wastewaters, pH is not a significant factor. This can be attributed to effectiveness of alum in a wide range of pH value. Detail of these computations are as presented at the appendices.

Effects and Statistical Evaluation of the models

Table 4 shows effect of these selected factors in removing phosphate concentration from aqueous textile wastewaters. The detailed computations are as presented at the appendices (Appendices A, B, C and D). From the table effects of these factors varied with the wastewaters, method of solving the model and with the treatment techniques. The table revealed that effect of these factors are in order of k_1 greater than (>) k_2 ; $k_2 > k_3$ and $k_3 > k_4$. Table 5 shows statistical evaluation of the methods for solving the models. The table revealed that accuracy of the methods are in order of Microsoft Excel Solver > Least Squared > Elimination based on the lower values of errors and values of model of selection criterion. This indicates that in solving model equation for phosphate removal from textile wastewater for applications in environmental pollution control, Microsoft excel solver method is the best based on highest value of model of selection criterion and lowest value of errors.

Relationship between alum concentration and phosphate removed

A model that relates concentration of phosphate removed (Y) to alum dose (C) was obtained from literature as follows (Oke and Okuofu, 2000):

$$Y = \frac{aC}{1 + bC} \quad (17)$$

Where;
a and b are model constants.
The values of the model constants are as presented

in Table 6. Table 6 shows correlation coefficients, coefficient of determination (CD), F-values and probability can be obtained. From these values it is clear that the model is significant for removal of phosphate from typical textile wastewater ($F = 65.66$; $p < 0.0001$; $a = 6.95$ and $b = 8.77$) and from synthetic orthophosphate wastewater ($F = 70.73$; $p < 0.0001$; $a = 120.38$ and $b = 130.82$). The correlation coefficients, coefficient of determination (CD) are 0.932 and 0.868; 0.936 and 0.878 respectively. This shows that phosphate removal from these wastewaters followed Langmuir isotherm equilibrium model, which the other two did not followed the model.

Conclusion

In this study, removal of phosphate from typical and synthetic textile wastewaters was studied based on chemical treatment (using alum and combination of biological and chemical treatment).The coefficients of selected factors in the models, methods of determining the coefficients in the models and effects of the selected factors were evaluated statistically.

It was concluded that:

(a) Initial concentration of the pollutant and pH have effects on effluent quality. Pre-treatment and coagulant dose were significant factors in the treatment of textile wastewaters.

(b) In solving model equation for phosphate removal from textile wastewater for applications in environmental pollution control, Microsoft excel solver method is the best based on highest value of model of selection criterion and lowest value of errors.

REFERENCES

Ahmet B, Ayfer Y, Doris L, Nese N, Antonius K (2003). Ozonation of high strength segregated effluents from a woollen textile dyeing and finishing plant, Dyes and Pigments, 58:93-98.

APHA (1998). Standard Methods for the Examination of Water and Wastewater (20th ed.). American Public Health Association, Washington, DC.

Arash D, Mitra G, Ahmad J, Niyaz MM (2011). Dye Removal, Energy Consumption and Operating Cost of Electrocoagulation of Textile Wastewater as a Clean Process. *Clean* – Soil, Air, Water, 39(7):665–672.

Arslan IA, Isil AB (2002). The effect of preozonation on the H_2O_2 / UV – C treatment of raw and biologically pre-treated textile industry wastewater, Water Science and Technology, 45: 297- 304.

Arslan IA, Isil AB, Detlef WB(2002). Advanced oxidation of a reactive dyebath effluent: comparison of O3, H_2O_2/UV-C and TiO_2/UV-A processes, Water Research, 36: 1143-1154.

Autret E, Berthier F, Luszezanec A, Nicolas F (2007). Incineration of municipal and assimilated wastes in France: Assessment of latest energy and material recovery performances. Journal of Hazardous Materials, 139(3): 569–574.

Azbar N, Yonar T, Kestioglu K (2004). Comparison of various advanced oxidation processes and chemical treatment methods for COD and colour removal from a polyester and acetate fiber dying effluent, Chemosphere, 55:35-43 .

Balasubramanian J, Sabumon PC, Lazar JU, Ilangovan R (2006). Reuse of textile effluent treatment plant sludge in building materials. Waste Management, 26(1): 22–28.

Balogh SJ, Nollet YH (2008). Mercury mass balance at a wastewater treatment plant employing sludge incineration with off gas mercury control. Science of the Total Environment, 389(1):125–131.

Behbahani M, Moghaddam AMR, Arami M (2011). A Comparison Between Aluminum and Iron Electrodes on Removal of Phosphate from Aqueous Solutions by Electrocoagulation Process. *Int. J. Environ. Res.*, 5(2):403-412,

Corella J, Toledo JM (2000). Incineration of doped sludges in fluidized bed. Fate and partitioning of six targeted heavy metals. I. Pilot plant used and results. Journal of Hazardous Materials, 80(1-3): 81–105.

Davarkhah R, Mohammad BM, Samaneh D, Fatemeh M (2012). Polyphosphate Removal from Synthetic Wastewater by Electrochemical Process. 2012 2nd International Conference on Biotechnology and Environment Management IPCBEE vol. 42 IACSIT Press, Singapore.

Dhaouadi H, M'Henni F (2008). Textile mill effluent decolorization using crude dehydrated sewage sludge. Chemical Engineering Journal, 138(1-3): 111–119.

Fatoki OS, Ogunfowokan AO (2002). "Effect of Coagulant Treatment on the Metal Composition", Water SA, 28(3): 293-297.

FEPA (1991)."Guidelines to Standards for Environmental Pollution Control in Nigeria", Federal Environmental Protection Agency (FEPA), Lagos.

Georgantas DA, Grigoropoulou HP (2003)."Phosphorus Removal from Synthetic Wastewater Using Spent Alum Sludge",8th International Conference on Environmental Science an Technology, Lemnos island, Greece, 8 – 10 September.

George ZK, Jie F, Kostas AM (2013). The Change from Past to Future for Adsorbent Materials in Treatment of Dyeing Wastewaters. Materials 6:5131-5158.

Georgiou D, Melidis P, Aivasidis A, Gimouhopoulos K (2002). Degradation of azo-reactive dyesby ultraviolet radiation in the presence of hydrogen peroxide, Dyes and Pigments, 52: 69-78.

Greben HA, Maree JP, Eloff E, Murray K(2005). Improve of Sulphate Removal rates at increased Sulphide Concentration in the Sulphidogenic bioreactor. Water SA, 31(3): 351- 358.

Hala YE, Laila AM (2014). Bioremediation of the textile waste effluent by Chlorella vulgaris. Egyptian Journal of Aquatic Research, 40:301–308.

Hala Y, Kassas L, Abdelfattah M (2014). Bioremediation of the textile waste effluent by Chlorella vulgaris. Egyptian Journal of Aquatic Research 40:301–308.

Horan NJ(1993). Biological Wastewater Treatment System, Theory and Operation, 1st edn, John Wiley and Sons, New York.

Karamalidis A K, Voudrias EA (2007). Release of Zn, Ni, Cu, $SO_4^{2+}$and CrO_4^{2+} as a function of pH from cement-based stabilized/solidified refinery oily sludge and ash from incineration of oily sludge. Journal of Hazardous Materials, 141(3): 591–606.

Kikuchi R, 2001. Recycling of municipal solid waste for cement production: pilot-scale test for transforming incineration ash of solid waste into cement clinker. Resources, Conservation and Recycling, 31(2): 137–147.

Klimiuk E, Filipkowska U, Libecki B (1999). Coagulation of Wastewater Containing Reactive Dyes with the Use of Polyaluminium Chloride (PAC). Polish Journal of Environmental Studies. 8(2):81-88.

Kyzas GZ, Jie F, Kostas AM (2013). The Change from Past to Future for Adsorbent Materials in Treatment of Dyeing Wastewaters. Materials 6:5131-5158.

Leader JW, Reddy KR, Wilkie AC (2005). Optimization of low-cost phosphorus removal from wastewater using co-treatments with constructed wetlands. Water Science and Technology, 51(9):283–290.

Li CW, Lin JL, Kang SF, Liang CL (2005). Acidification and alkalization of textile chemical sludge: volume/solid reduction, dewater ability, and Al(III) recovery. Separation and Purification Technology, 42(1): 31–37.

Lin SH, Peng CF, (1996). Continuous treatment of textile wastewater by combined coagulation, electrochemical oxidation and activated sludge. Water Research, 30(3): 587–592.

Lubello C, Caffaz S, Gori R, Munz G (2009). A modified activated sludge model to estimate solids production at low and high solids

retention time. Water Research, 43(18): 4539–4548.
Mahdi A, Azni I, Aofah A (2007). Combined anaerobic-aerobic system for treatment of textile wastewater. Journal of Engineering Science and Technology, 2(1):55-69.
Manhong H, Liang C, Donghui C, Saijie Z (2011). Characteristics and aluminum reuse of textileafter acidification Journal of Environmental Sciences, 23(12):1999- 2004.
Mehmet F.S. and Z.S. Hasan, 2002. Ozone treatment of textile effluents and dyes: effect of applied ozone dose, pH and dye concentration, Journal of Chemical Technology and Biotechnology, 77: 842-850.
Murakami T, Suzuki Y, Nagasawa H, Yamamoto T, Koseki T, and Hirose H., 2009. Combustion characteristics of sewage sludge in an incineration plant for energy recovery. Fuel Process Technology, 90(6): 778–783.
Oke IA, Okuofu CA (2000). Mathematical modeling of Phosphorous Removal from Textile Wastewater With Aluminum Sulphate (Alum; $Al_2(So_4)_3$–YH_2O).Nigerian Journal of Engineering, 8 (2), 59- 67
Oke IA, Okuofu CA, Otun JA (2006). A Statistical Classification of Textile Wastewaters in Northern Nigeria. Journal of Applied Sciences Research 2(4): 209-216.
Olcay, T., K. Isik, E. Gülen and O. Derin, 1996. Color removal from textile wastewaters, Water Science and Technology, 34: 9-11.
Ozmihci S, Kargi F (2006). Utilization of powdered waste sludge (PWS) for removal of textile dyestuffs from wastewater by adsorption. Journal of Environment Management, 81(3): 307–314.
Pala A, Tokat E (2002). Color removal from cotton textile industry wastewater in an activated sludge system with various additives. Water Research, 36(11): 2920–2925.
Rosa EVC, Mater L, Souza-Sierra MM, R¨orig LR, Vieira LM, Radetski CM (2007a) Textile sludge application to non-productive soil: Physico-chemical and phytotoxicity aspects. Ecotoxicology and Environmental Safety, 68(1):91–97.
Rosa EVC, Giuradelli TM, Corrˆea AXR, R¨orig LR, Schwingel PR, Resgalla CJr, (2007b). Ecotoxicological evaluation of the short term effects of fresh and stabilized textile sludges before application in forest soil restoration. Environment Pollution, 146(2): 463–469.
Rossle, W.H and W.A. Pretorius, 2001. A Review of characterization requirements for on line prefermenters, Paper1: Wastewater Characterization. Water SA, 27: (3), 405-412.
Sawsan AM, Mohammed HA, Haider AS (2009). Phosphorus Removal from Water and Waste Water by Chemical Precipitation Using Alum and Calcium Chloride. Iraqi Journal of Chemical and Petroleum Engineering.10 (2):35-42.
Sheng, H.L. and M.L. Chi, 1993. Treatment of textile waste effluents by ozonation and chemical coagulation, Water Research, 27: 1743-1748.
Stanistaw L, Monika G (1999). Optimization of oxidants dose for combined chemical and biological treatment of textile wastewater, Water Research, 33: 2511-2516.
Szabo A, Taka´cs, I.,Murthy, S., Daigger, G. T.,Licsko, I., Smith, S., 2008, “Significance of Design and Operational Variables in Chemical Phosphorus Removal”, Water Environ. Res., 80(5).407- 416
Taib MR, Swithenbank J, Nasserzadeh V, Ward M, Cottam D (1999). Investigation of sludge waste incineration in a novel rotating fluidized bed incinerator. Process Safety and Environmental Protection, 77(5): 298–304.
Tang P, Zhao YC, Xia FY(2008). Thermal behaviors and heavy metal vaporization of phosphatized tannery sludge in incineration process. Journal of Environmental Sciences, 20(9): 1146–1152.
Toledo J, Corella M, Corella LM (2005). The partitioning of heavy metals in incineration of sludges and waste in a bubbling fluidized bed: 2. Interpretation of results with a conceptual model. Journal of Hazardous Materials, 12613): 158–168.
Wong W Y, Lu Y, Nasserzadeh V S, Swithenbank J, Shaw T, Madden M (2000). Experimental investigation into the incineration of wool scouring sludges in a novel rotating fluidised bed. Journal of Hazardous Materials, 73(2): 143– 160.
Zhang FS, Yamasaki S, Nanzyo M (2001). Application of waste ashes to agricultural land – effect of incineration temperature on chemical characteristics. Science of the Total Environment, 264(3): 205–214.
Zodi S, Potier O, Lapicque F, Jean PL (2009). Treatment of the textile wastewaters by electrocoagulation: Effect of operating parameters on the sludge settling characteristics.Separation and Purification Technology, 69(1): 29–36.