COLLEGE OF PUBLIC HEALTH AND MEDICAL SCIENCES

DEPARTMENT OF ENVIRONMENTAL HEALTH SCIENCE AND

TECHNOLOGY

Simultaneous Removal of Nitrate and Phosphate Ions from Aqueous Solution Using Solid Waste from Alum and Sulphuric Acid Manufacturing Process

By

Yifru Waktole

A RESEARCH PAPER SUMMITTED TO DEPARTMENT OF ENVIRONMENTAL HEALTH SCIENCE AND TECHNOLOGY, COLLEGE OF PUBLIC HEALTH AND MEDICAL SCIENCES, JIMMA UNIVERSITY IN PARTIAL FULLFILLMENT FOR THE REQUIREMENT OF MASTERS DEGREE IN ENVIROMENTAL HEALTH SCIENCE AND TECHNOLOGY

June, 2013

Jimma, Ethiopia

i

Simultaneous Removal of Nitrate and Phosphate Ions from Aqueous Solution Using Solid Waste from Alum and Sulphuric Acid Manufacturing Process

By: Yifru Waktole

Advisors: -   Mr. Seid Tiku (PhD candidate)

                       Mr. Fekadu Fufa (PhD candidate)

June, 2013

Jimma, Ethiopia

DECLARATION

I proclaim that this piece of work is my own and all sources of materials used for this thesis work have been properly acknowledged.

Name: Yifru Waktole

Place: Jimma, Ethiopia

Signature: _____

Date of submission: _____

This thesis was submitted for examination with the approval of university advisors

Name	Signature	Date
Mr. Seid Tiku (M.Sc., PhD candidate)	_____	_____
Fekadu Fufa (M.Sc., PhD candidate)	_____	_____
Department Head	_____	_____

ABSTRACT

Nitrogen and Phosphorous are limiting nutrients for plant growth. Contrary to this, phosphorous between 20 to 100 μg/L and nitrogen between 500 to 1000 μg/L can cause eutrophication in most aquatic systems. Therefore, developing low cost and efficient method of removing these nutrients to protect the aquatic environment is mandatory. The objective of this study was to investigate simultaneous nitrate and phosphate adsorption capacity of solid waste residue collected from Awash Melkassa Aluminium Sulphate and Sulphuric Acid Factory. Batch adsorption experiments were conducted to evaluate the effect of contact time, initial solution pH, initial nitrate and phosphate ion concentration, adsorbent dose and effect of coexisting ions on simultaneous removal of nitrate and phosphate ions. Besides, adsorption isotherms and kinetics were analysed to determine the mechanism and rate determining steps during the adsorption process. After conducting batch experiment, the equilibrium time was achieved within 90 minutes while the optimum pH and adsorbent dose were found to be 7 and 20 gm/L respectively. The adsorption kinetics of nitrate and phosphate ions best fitted to the pseudo-second order equation with R^2 values 0.992 and 1 respectively. Moreover, isotherm studies showed adsorption of nitrate and phosphate fitted better to Freundlich isotherm and Langmuir isotherm with R^2 0.988 and 0.984 for phosphate and 0.991 and 0.955 for nitrate respectively. Studies on reusability of the spent adsorbent showed nearly 50% the adsorbed phosphate can be desorbed with 0.1M NaOH while that of nitrate is 99.75% showing there is a possibility of reusing. Last but not least, application on wastewater showed promising result though there is decrease in percent removal. At the optimums found during the batch experiment, AW residue collected from Awash Melkassa Aluminium sulphate and Sulphuric acid factory can potentially remove phosphate from wastewater. But, the untreated AW was not suitable to remove nitrate ion from wastewater since its percent removal was from 27-30%.

Keywords: Simultaneous removal**;** batch adsorption; chemisorption; adsorption capacity; alum waste

ACKNOWLEDGEMENT

Table of contents

LIST OF ANNEXES

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

AW – Alum waste

APHA- American Public Health Association

CDC- Centre for disease control and prevention

RFEP- relative fitting error parameter

CHAPTER ONE: INTRODUCTION

1.1 Background

Water pollution due to the excessive presence of nitrogen and phosphorus species is a serious environmental problem worldwide, as both are implicated in eutrophication of receiving surface waters (Khelifi *et al.,* 2002; Painting *et al.,* 2007; Weia *et al.,* 2008 and Tiemeyer *et al.,* 2009). Nitrogen is an important nutrient for plants and animals. According to Vitosek *et al.,* (2002) terrestrial ecosystems and headwater streams have a considerable ability to capture nitrogen or to reduce it to N_2 gas though the process of denitrification. Nitrogen cycling and retention is thus one of the most important functions of ecosystems. In contrast to the process of denitrification, when loads of nitrogen from sources such as fertilizer, septic tanks, and atmospheric deposition exceed the capacity of terrestrial systems, the excess may enter surface waters, where it may have "cascading" harmful effects as it moves downstream to coastal ecosystems (Galloway and Cowling, 2002).

Phosphorus like nitrogen is an inevitable element for the growth of animals and plants. However, several million tons of phosphorus containing wastewater is straightly discharged into the watercourses with the rapid development of industry and agriculture annually. This in turn increases phosphate concentrations and altered nutrition ratios that inevitably causes severe environmental pollution, such as the eutrophication of the waterways which frequently cause fish kills, phytoplankton blooms, and the deterioration of water quality (Song *et al.,* 2011).

1.2 Statement of the problem

Contrary to their importance, excessive presence of nutrients, i.e., nitrogen and phosphorus species is a serious environmental problem as it causes water pollution (Sibrell *et al.*, 2009). Agricultural over application of natural and synthetic fertilizers, aquaculture, and municipal wastewaters, detergent manufacturing as well as mineral processing industries are the main sources of nutrient release into the aquatic environment (Saad *et al.*, 2007; Katal *et al.*, 2012; Khelifi *et al.,* 2002 and Schick *et al.,* 2011).

These point and non-point sources of nutrients to both surface and ground water were known to cause waster quality degradation. Due to water quality degradations such as eutrophication stringent control over discharge of wastewater from municipal as well as industrial sources established. As cited by Liang (2011) eutrophication threshold for phosphorous (20 to 100 μg P/L) and for nitrogen (500 to 1000 μg N/L) in most aquatic systems. According to Zhang *et al.,* (2009), presence of trace amount of phosphorus, exceeding about 1 mg/L, in treated wastewater can stimulate algal growth (Eutrophication). Apart from water quality degradation, eutrophication can cause specific health risks appear when fresh water, extracted from eutrophic areas, is used for the production of drinking water. In such cases, the nervous, digestive, respiratory and cutaneous systems may be affected by toxins excreted by harmful algal blooms such as Cyanobacteria (CDC, 2004). Besides, presence of nitrate ions in drinking water is a potential public health hazard and can cause infant methemoglobinemia, "blue baby" syndrome (WHO, 2011).

Hence, nutrient removal from wastewater is imperative to protect eutrophication of water bodies and health of human and animal. Various techniques such as chemical precipitation, adsorption, reverse osmosis, biological removal, and constructed wetlands have been employed for removal of nutrients from wastewaters (Zeng *et al.,* 2004). According to Olgun *et al.,* (2013) and Saad *et al.,* (2007), adsorption method has become a popular method since it allows simple and economical operation resulting in less sludge production and fewer disposal problems. Other attractive feature of this method is nutrient-loaded filters can be used in agriculture as phosphate fertilizer and soil conditioner (Zeng *et al.,* 2004). In this study AW collected from manufacturing of aluminum sulphate and sulphuric acid by kaolin process was used to simultaneously remove nitrate and phosphate ions from aqueous solution.

1.3   Significance of the study

In this study, an industrial waste residue, generated during the manufacture of aluminium sulphate from kaolin by sulphuric acid process was used as an adsorbent for simultaneous removal of nitrate and phosphate from aqueous solution. A large quantity of the waste residue is generated from each batch of alum production at Awash Melkassa Aluminium Sulphate and Sulphuric Acid Factory, Ethiopia. The waste discarded is highly acidic and hence it is considered as hazardous. Presently, economically viable methods for the disposal or reuse of the solid waste are not known. The results of the present study could be used for further investigation of the adsorbent under column studies and field test of the solid waste for simultaneous removal of phosphate and nitrate ions from real wastewater. Therefore, the solid waste residue could be used for the reduction of the eutrophication of the water sources in the future after further investigations. The use of the solid waste for wastewater treatment could avoid the impact of the solid waste accumulation on the environment.

CHAPTER TWO: LITERATURE REVIEW

2.1. Forms and sources of nitrogen in the environment

Nitrogen can take different forms in the environment. Nitrogen is capable of being transformed biochemically or chemically and its transformations involve the oxidation or reduction of the nitrogen atom through both biological and chemical processes. The natural sources of nitrogen in water include biological nitrogen fixation of atmospheric nitrogen by aquatic plants, decomposition, atmospheric deposition, and weathering (Liang, 2011). Contrary to natural nitrogen cycle, anthropogenic sources have played an important role in the total amount of the nitrogen pools in aquatic environments. The sources of nitrate introduction in the surface water and ground water include agricultural fertilizers, septic tank systems, and animal waste disposal (Milmile *et al.,* 2011). Liang (2011) presented non-point sources such as fertilizer applied on agriculture land and livestock facilities, nitrogen can be transferred either by runoff directly into surface water or via leaching into groundwater, threatening the ground water quality and eventually entering surface water bodies.

2.2. Forms and sources of phosphorus in the environment

Phosphorous can exist in various phosphate species. The common forms of phosphorus in wastewater are polyphosphates (polymers of phosphoric acid), organically bound phosphates, and the most abundant orthophosphates (Kamiyango *et al.,* 2009). Similarly, (Liang, 2011) presented typical levels of phosphorous in wastewater takes different forms and were estimated by as orthophosphate 5 mg P/L (50%), tripolyphosphate 3 mg P/L (30%), pyrophosphate 1 mg P/L (10%), and organic phosphates 1 mg P/L (10%). On the one hand, orthophosphate is of significant concern because it is not only the most abundant form of P in water and wastewater, but also is the form that can be immediately utilized by organisms Agricultural over-application of fertilizers, aquaculture, agri-food industries, municipal wastewaters and detergent are the commonest sources that add phosphorous in to water bodies (Hamoudi and Belkacemi, 2012).

2.3.   Environmental impacts of nitrogen and phosphorous

Liang (2011) presented the Redfield ratio that reveals the molecular ratio of carbon, nitrogen and phosphorus in phytoplankton as C: N: P = 106:16:1. Since carbon in natural water is often considered as limitless because of the source of carbon dioxide in the atmosphere, algae growth could be limited by the deficiency of either nitrogen or phosphorus, and the limiting one is considered to be most important for eutrophication control. Generally, the limiting nutrient in most fresh waters is phosphorus, but in most sea waters is nitrogen. This is mainly because the phosphorous supply in sea waters is abundant while phosphorous levels in fresh waters are often low.

Eutrophication in its original use and etymology, 'eutrophic' meant 'good nourishment', and eutrophication meant the process by which water bodies grew more productive. It is a process driven by enrichment of water by nutrients, especially compounds of nitrogen and/or phosphorus, leading to: increased growth, primary production and biomass of algae; changes in the balance of organisms; and water quality degradation. The consequences of eutrophication are undesirable if they appreciably degrade ecosystem health and/or the sustainable provision of goods and services (Ferreira *et al.,* 2011).

(Liang, 2011) presented an estimation of the eutrophication threshold for phosphorous between (20 to 100 μg P/L) and for nitrogen to be between (500 to 1000 μg N/L) in most aquatic systems. When eutrophication takes place, the high concentrations of nutrients in water bodies promote the growth of algae and aquatic plants. The consequential bloom of algae and aquatic plants decreases the dissolved oxygen in the water body to create hypoxia (DO level < 2 mg/L). (Zhao *et al.,* 2009) also indicated a reduced oxygen level harmfully affects fish and other aquatic life, microorganism and insects' growth as well as it causes natural resorts degradation. According to (WHO, 2011) concerns for nitrogen also include health problems on humans and animals as nitrogen in ammonia form is highly toxic to fish and other aquatic life and as a result, NH_3/NH_4^+ has stringent permit limits for wastewater treatment discharge. Besides, excessive intake of nitrate by humans with drinking water or food can induce methemoglobinemia (blue baby syndrome) or carcinogenic effects in infants.

Apart from eutrophication and blue baby syndrome, nutrient enrichment can cause harmful algal bloom, which is defined as algal bloom that causes negative impacts to other organisms via production of natural toxins, mechanical damage to other organisms, or by other means (CDC, 2004). For instance, Cyanobacteria have been reported as tainting fresh water and being toxic to humans, pets and other animals. It has been reported that harmful algae blooms are global concerns and the problem is common in over 45 countries worldwide and in at least 27 U.S. States (Liang, 2011).

2.4. Nitrogen and phosphorus removal methods

2.4.1. Nitrate removal

When it is found beyond the permissible value both in the environment and drinking water, nitrate can bring in severe problems, including eutrophication and infection diseases, such as cyanosis and cancer of the alimentary canal (Wang *et al.,* 2007). Due to the above problems both in human and aquatic environment, attention has to be paid to remove nitrate from wastewater. Conventional methods used to remove nitrate include, biological de-nitrification, reverse osmosis, electro-dialysis and ion exchange. Since most of the above methods are high tech and subsequently need high cost, adsorption is the focus of this study as its potential advantages include no reagent requirements, no additional sludge generation, easy operation and low cost materials in wastewater practices.

2.4.2. Phosphate removal

Since excess phosphate and nitrate concentration in the effluent discharge can lead to eutrophication of the receiving water bodies, the amount of nutrient, i.e., nitrate and phosphate in domestic, municipal and industrial discharges must be controlled using wastewater treatment technologies. Many methods have been developed for phosphate removal and they are broadly categorized in to three as: physical, chemical and biological methods. Physical methods have proved to be either too expensive, as in the case of electrodialysis and reverse osmosis, or inefficient, removing only 10% of the total phosphorus (Zhao *et al.,* 2009). Besides, enhanced biological treatment can remove up to 97% of the total phosphorus and it is low-cost though variability in chemical composition and temperature of wastewater would make the implementation of this process not feasible for wastewater treatment (Zhao *et al.,* 2009). Last but not least, chemical removal techniques such as lime, aluminum sulfate and ferric salts are

the most effective and well-established even though cost associated with metal salts and sludge production are their inherent problems. Therefore, adsorption is the focus of this study as its potential advantages include no reagent requirements, no additional sludge generation, easy operation and low cost materials in wastewater practices.

2.5.   Aluminum sulphate and sulphuric acid factory waste

The process of manufacturing aluminium sulphate from mixture of kaolin and sulphuric acid involves digesting kaolin with sulphuric acid. After the mixture of kaolin and acid had been leached, it was cooled to room temperature and filtered to remove leach residue. The residue separated is commonly discarded within the factory's compound. The chemical composition of the alum waste (AW) collected from Awash Melkassa Aluminum sulphate and sulphuric acid factory is presented   in Table 1 as follows (Nigussie *et al.,* 2007).

Table 1 Percentage composition of the chemical constituents in AW.

Chemical composition	Percent (wt. %)
Kaolin	8.883
$Al_2(SO_4)_3$	1.778
$Al(OH)_3$	0.878
$CaSO_4$	0.194
$Fe_2(SO_4)_3$	0.023
Fe_2O_3	0.001
$MgSO_4$	0.008
Na_2SO_4	0.007
K_2SO_4	0.005

A physical property of AW as presented by Negassa (2012) shows the adsorbent is acidic and it has high percent porosity. The data on physical properties of the adsorbent are given on Table 2.

Table 2 Physical properties of alum waste

Properties	Value
pH $_{in\ water}$	3.57
pH $_{in\ KCl}$	3.37
Conductivity (μS/cm)	4.04
Bulk density (g/cm^3)	0.26
Particle density(g/cm^3)	2.10
Porosity (%)	87.7

CHAPTER THREE: OBJECTIVES OF THE STUDY

3.1. **General objective**

- to assess common health and health related problems in Jiren Kebele, Jimma town Ethiopia.

3.2. Specific objectives

- to assess iec and bcc activities in jiren kebele by 2012

- to assess sanitation and hygienic practice in jirenkebele by 2012.

- to assess health service utilization among the community at jiren kebele by 2012

- to assess safe water supplying the jirenkebele by 2012

- to design possible interventions on those identified problems in jiren kebele by 2012

CHAPTER FOUR: MATERIALS AND METHOD

4.1. Study area and period

This study was conducted in Jimma town, Oromia Regional State at Jimma University in graduate and staff research laboratory. The town has latitude and longitude of 7°40′N 36°50′E. It has heavy rainfall and warm climate with a mean annual temperature of 24.9^0C. The study was conducted from January to May, 2013.

4.2. Study design

The study design was batch adsorption experiment.

4.3. Study variables

Dependent variables	Independent variables
Amount of nitrate or phosphate removed (mg/g)	Contact time
	Initial solution pH
	Initial concentration
Percent removal (%)	AW dose
	Coexisting ions

4.4. Conceptual framework
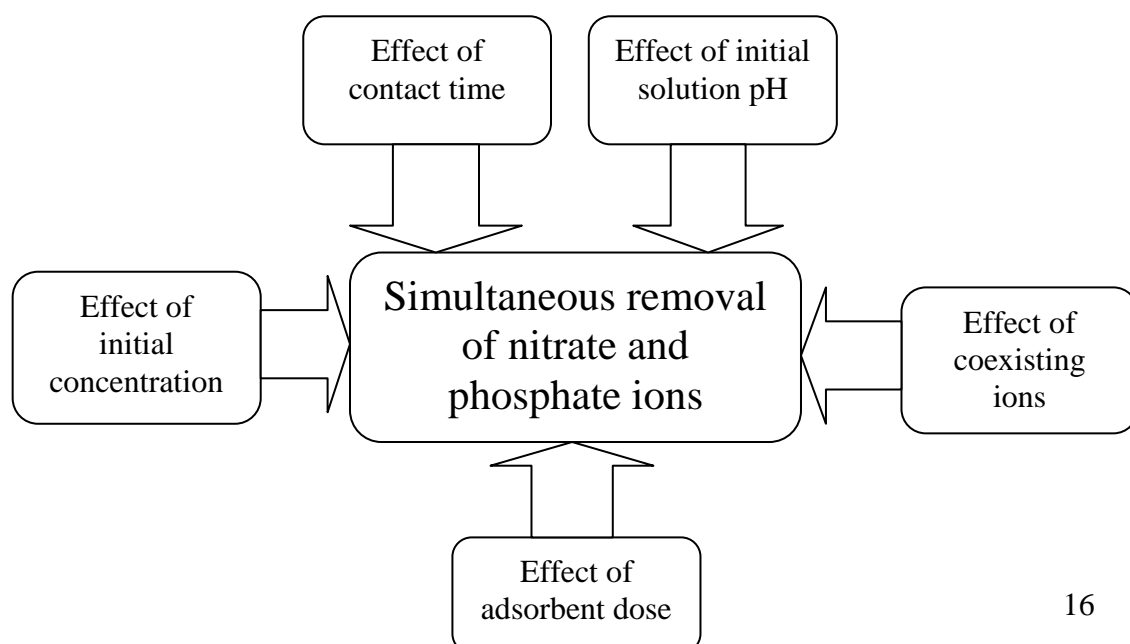
Fig. 1 Conceptual framework

4.5. Adsorbent preparation

A composite sample from different batches of alum solid waste residue was collected from Awash Melkassa Alum Factory, East Shewa Zone, and Oromia Regional State, Ethiopia. The collected samples were mixed and dried at laboratory room temperature. The dried residue was ground using mortar and sieved using sieves of mesh sizes (212 µm). Then, particle size of less than 212 µm was stored in an air tight plastic bottle for further experimental uses.

4.6. Effect of contact time

Determination of equilibrium time was conducted using 100 ml test solution containing 19.3 mg/L orthophosphate and 5.14 mg /L NO_3-N with 20g/L adsorbent dose in 250 ml Erlenmeyer flask. The pH of the solution was adjusted using pH meter (HQ40D Hatch multi parameter PHC101 probe) and shaked at 150 rpm for 5, 10, 20, 30, 40, 50, 60, 90 and 120 minutes; the supernatant liquid was collected using Whatman filter paper of pore size 0.45µm. Finally, the nitrate-nitrogen and orthophosphate ion concentrations were determined by using UV screening method and stannous chloride method respectively.

4.7. Effect of initial pH

Optimum pH for simultaneous removal of nitrate and phosphate ions was conducted using 100ml test solution containing 11.83 mg/L orthophosphate and 3.36 mgNO_3-N/L with 20 g/L adsorbent dose in Erlenmeyer flask of volume 250ml. The pH considered to see effect of initial solution pH were 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12; after shaking speed (150 rpm) for equilibrium time the supernatant liquid was collected using Whatman filter paper of pore size 0.45 µm.

4.8. Effect of adsorbent dose

The effect of adsorbent dose was investigated by varying the dose of AW from 4 g/L to 32 g/L. Measured weights of the AW using analytical balance were added to 100ml test solution containing 3.33 mgNO_3-N/L and 10.38 mg/L orthophosphate in 250 ml Erlenmeyer flask and shaked (150 rpm) for equilibrium time at optimum pH 7 for

simultaneous removal of nitrate and phosphate ions. After shaking was complete, the supernatant liquid was collected using Whatman filter paper of pore size 0.45µm.

4.9.   Effect of initial concentration

Effect of initial nitrate and phosphate ion concentration on simultaneous removal of nitrate and phosphate ions was investigated by varying concentration of nitrate (3, 5, 9, 11, 12, 13, 14, 15, 17 and 19 $mgNO_3$-N/L) and (0.2, 50, 80, 110, 140, 170, 200, 230and 260mg/L orthophosphate) in 250 ml Erlenmeyer flask and shaked (150 rpm) for equilibrium time at optimum pH and optimum AW dose. After shaking was complete, the supernatant liquid was collected using Whatman filter paper of pore size 0.45 µm.

4.10.   Effect of coexisting ions

Effect of three coexisting ions commonly found in domestic and municipal waste water; chloride, bicarbonate and sulphate on simultaneous nitrate and phosphate adsorption was examined by adding (5, 50 and 100 mg/L) of the respective anions prepared from sodium chloride, potassium sulphate and sodium bicarbonate respectively. Initial concentrations of phosphate and nitrate used were $[PO_4^{3-}]_0$: 19.3 mg/L and $[NO_3$-$N]_0$: 5.14 mg/L.

4.11.   Desorption experiment

First, a known concentration of adsorbate (19.3 mg/L orthophosphate and 5.14 mg NO_3-N/L with 20 g/L AW dose in Erlenmeyer flask of volume 250ml) was allowed to adsorb at equilibrium time. Then, the supernatant was analyzed for residual adsorbate after separating the adsorbent by filtration preceded by centrifugation. After separating the adsorbate loaded adsorbent, it was dried for 24 h at 105^0C and shaked to contact time with varying concentration of NaOH (0.1, 0.5 and 1.0 M) separately.

4.12. Adsorption experiment on wastewater

Adsorption experiment using AW for real wastewater was conducted after collecting wastewater from wastewater discharge point near Jimma University. The adsorption experiment on wastewater was carried out with 7.17 mg/L orthophosphate, 1.3 mg /L NO_3-N, pH ~ 7.24, 90 min contact time and 20 g/L AW dose in 250 ml Erlenmeyer flask.

4.13. Chemical analysis

Concentration of the adsorbates (nitrate and phosphate ions) in the stock, standard and supernatant solutions were analyzed by Ultra violet screening method for nitrate ions and stannous chloride method for phosphate ions by UV-Vis spectrophotometer (DR 500) at 220nm and 690 nm respectively according to standard method for examination of water and wastewater, American public health association (APHA, 1995). The calibration curves used during reading of phosphate (stannous chloride method) and nitrate (UV-screening method) are shown in Fig. 2a and Fig. 2b respectively.

$$y = 0.330x - 7.143E-5$$
$$R^2 = 0.999$$

(b)

y = 0.22738x - 0.0038
$R^2 = 0.999$
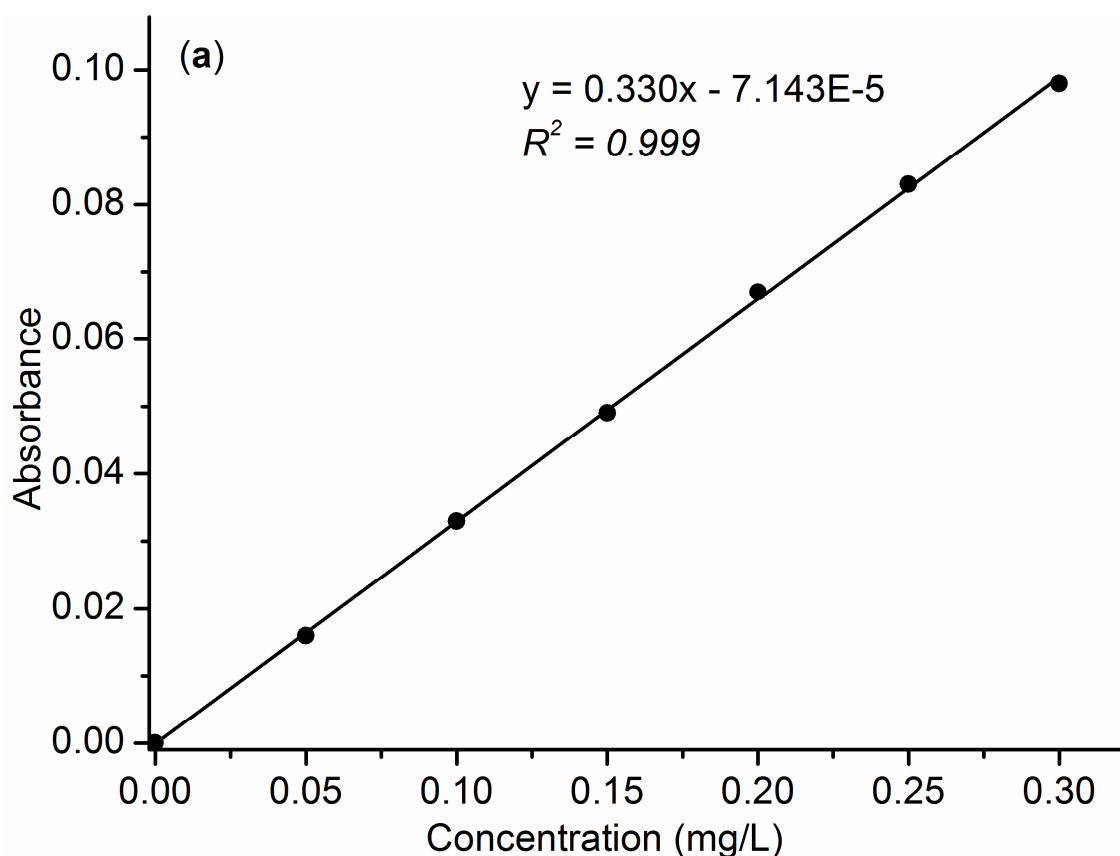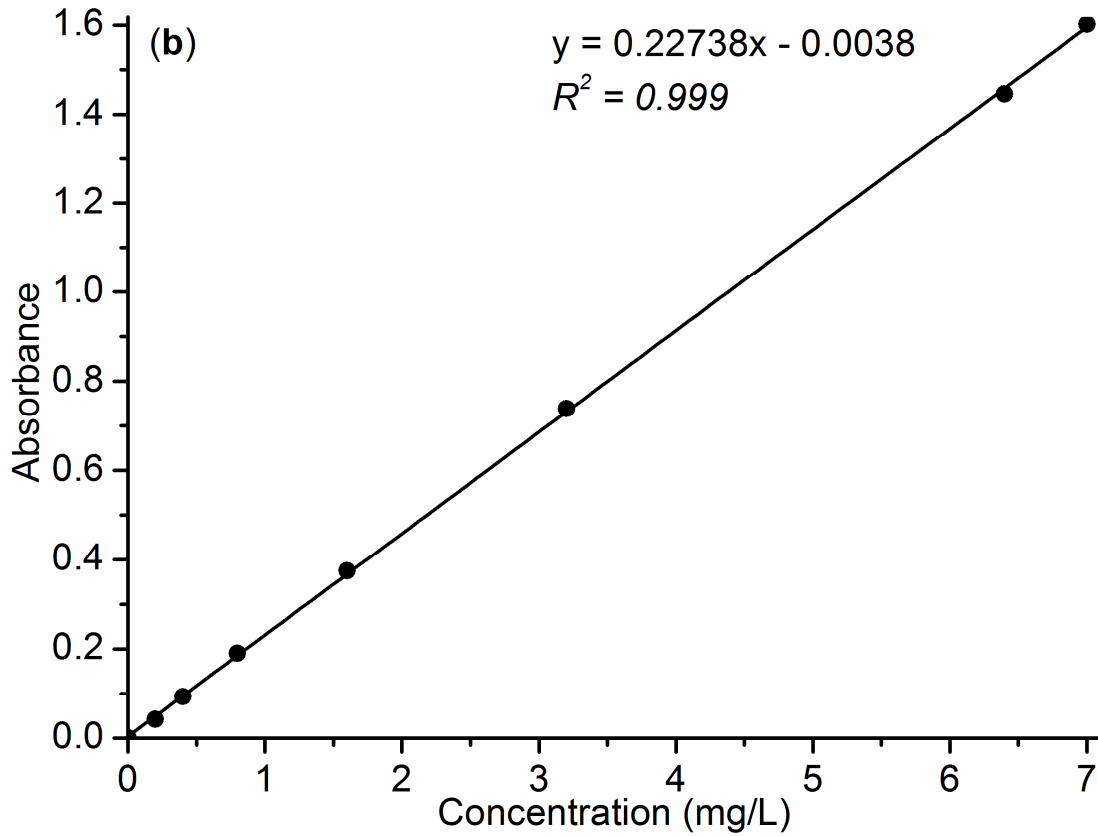
Fig. 2 Calibration curves for (a) orthophosphate and (b) nitrate-nitrogen used in stannous chloride method and UV-screening methods respectively.

4.14. Data analysis

4.14.1. Adsorption Kinetics

The uptake of anions (nitrate and phosphate ions) by the alum residue was determined by mass balance, as follows:

$$q_t = \frac{(C_0 - C_t) * V}{M}$$ (1)

Where C_0 (mg/L) and C_t (mg/L) are nitrate and phosphate concentrations at time 0 and t, respectively, V is the volume of the solution (L), and M is the mass of alum waste (g) (Boparai *et al.*, 2010). The removed anions in percent were calculated by the following formula:

$$A(\%) = \frac{(C_0 - C_t)}{C_0} * 100$$ (2)

where C_0 (mg/L) and C_t (mg/L) are initial and concentration at time, t, of nitrate and phosphate, respectively.

Kinetics of adsorption, in terms of solute uptake rate, which governs the residence time, is one of the important characteristics defining the efficiency of adsorption (Krishnan and Haridas, 2008). Several kinetic models have been developed to predict the adsorption kinetics and rate controlling step. In order to evaluate the kinetics of simultaneous nitrate and phosphate adsorption, pseudo-first-order and pseudo-second-order models were computed.

4.14.1.1. *Pseudo-First order kinetics*

Lagergren presented a first-order rate equation to describe the kinetic process of liquid-solid phase adsorption pseudo-first-order model is expressed as:

$$\frac{d_{qt}}{d_t} = k_1(q_e - q_t) \tag{3}$$

Where qe (mg/g) and qt (mg/g) are the amounts of the nitrate and phosphate adsorbed on the adsorbent at equilibrium and at any time t, respectively; and k_1 (min^{-1}) is the rate constant of the first order adsorption. After integration and applying boundary conditions $q_t = 0$ at t = 0 and $q_t = q_t$ at time = t, the integrated form of Eq. (3) becomes;

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

The value of k_1 and q_e can be obtained from the slope and intercept of the linear plot of ln (q$_e$– q$_t$) versus t, respectively.

4.14.1.2. *Pseudo-second order kinetics*

The Pseudo-second order kinetic model presented by Ho and McKay is expressed as:

$$\frac{d_{qt}}{d_t} = k_2(q_e - q_t)^2 \tag{5}$$

Where K_2 (g.mg^{-1}.min^{-1}) is the rate constant of the second-order equation; q$_e$ (mg.g^{-1}) is the maximum adsorption capacity; q$_t$ (mg/g) is the amount of adsorption at time t (min). After definite integration by applying the conditions qt =0 at t=0 and qt =qt at t = t it becomes the following;

$$\frac{t}{q_t} = \frac{1}{k_2}\frac{1}{q_{e^2}} + \frac{t}{q_e} \tag{6}$$

The value of q$_e$ and K_2 can be obtained from the slope and intercept of the linear plot of t/q$_t$ versus t, respectively.

4.14.2. Adsorption Isotherm

As Foo and Hameed (2010) described, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous media or aquatic environments to a solid-phase at a constant temperature and pH. In addition, adsorption isotherm describes the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium (Boparai *et al.,* 2010). In order to evaluate the relationship between the amount of anion adsorbed and the anion concentration remaining in solution three isotherm models; Langmuir, Freundlich isotherms and Dubinin and Radushkevich were considered.

4.14.2.1. Langmuir isotherm

In 1916 Langmuir developed a theoretical equilibrium isotherm relating the amount of gas sorbed on a surface to the pressure of the gas (Langmuir, 1916). Langmuir isotherm is based on the assumption that the point of valance exists on the surface of the adsorbent and that each of these site is capable of adsorbing one molecule. It is assumed that the adsorption sites have equal affinities for molecules of adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir equation is commonly written as:

$$q_e = \frac{q_{max} b C_e}{1 + b C_e}$$ (6)

Where, q_e is the amount adsorbed (mg/g) and c_e is equilibrium concentration of adsorbate (mg/L) while q_{max} and b are constants related to adsorption capacity and energy of adsorption, respectively (Zeng *et al.,* 2004).

Moreover, a dimensionless constant, commonly known as separation factor (R_L) defined by Webber and Chakkravorti can be represented as:

$$R_L = \frac{1}{1 + K_L C_0}$$ (7)

where K_L (L/mg) refers to the Langmuir constant and Co is denotes to the adsorbate initial concentration (mg/L). R_L value indicates the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < RL < 1$) or irreversible ($R_L = 0$) (Foo and Hameed, 2010).

4.14.2.2. *Freundlich isotherm*

In 1906, Freundlich presented the earliest known sorption isotherm equation. This empirical model can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption (Freundlich, 1906). This model is based on the assumption that the number of active sites available for adsorption is dependent upon the concentration of sorbate particles. That is, as the concentration of target species increases, then the number of active sites increases until the point of saturation is reached. The Freundlich equation is basically empirical but it is often useful as a means for data description. The general form of Freundlich isotherm is given in the following equation (Zeng *et al.,* 2004).

$$q_e = k_f C_e^{1/n} \tag{8}$$

Where k_f and n are Freundlich isotherm constants related to adsorption capacity and adsorption intensity, respectively and C_e is the equilibrium concentration (mg/L).

4.11.3. Dubnin and Radushkehvich *isotherm*

Another equation used during analysis was the Dubinin-Radushkevich (D-R) model which is written as (Nigussie *et al.,* 2007):

$$q_e = q_m \exp\left(- \beta \varepsilon^2\right) \tag{9}$$

Where q_m is D-R constant.

The sorption data was modeled by D-R isotherm to determine the adsorption type as physical or chemical. The linear form of D-R model is expressed by the following equation.

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{10}$$

Where q_e is the amount of nitrate or phosphate adsorbed per unit dosage of the adsorbent (mol/g), q_m the monolayer capacity (mol/g), C_e the equilibrium concentration of nitrate or phosphate (mol/L), β is the activity coefficient related to mean sorption energy (mol²/kJ²), and ε is the Polanyi potential described as:

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \tag{11}$$

The mean sorption energy, E (KJ/mol), can be calculated as:

$$E = \frac{1}{\sqrt{- 2\beta}} \tag{12}$$

4.11.4. Intraparticle diffusion equation

Intraparticle diffusion model based on the theory proposed by Weber and Morris was tested to determine if the particles diffusion is the rate-limiting step for the nitrate and phosphate adsorption onto AW (Benghalem *et al*., 2010). According to this theory (Anand *et al*., 2009):

$$q_t = k_p t^{0.5} \tag{13}$$

Where q_t is the amount of nitrate or phosphate adsorbed (mg/g) at a given time t (min); k_p (mg g^{-1} min$^{-1/2}$) is the intraparticle diffusion rate constant. The K_P value was obtained from plotting of q_t versus $t^{0.5}$.

4.11.5. Relative fitting error parameter

The best fit model was determined by evaluating the relative fitting error parameter (*RFEP*) value which was computed using the equation:

$$RFEP = \left(\frac{SSR/n-2}{q_{ave}} \right)^{0.5} \tag{14}$$

where, q_{ave} is average q_e, n is number of data point and SSR is squared sum of residuals (Han, 2012).

4.15. Data quality management

Data quality was maintained by conducting triplicate experiments and mean values were reported. Calibration of the analytical equipment was conducted at each set of analysis using freshly prepared standard solution. Blank and Control experiments were conducted; blank and control corrected values were reported.

4.16. Ethical consideration

Formal letter was written from Jimma University to Awash Melkassa aluminium sulphate and sulphuric acid factory and all concerned bodies and institutions.

4.17. Dissemination plan

The final result of the study will be presented to Jimma university scientific community and Department of Environmental Health Science and Technology. The

manuscript will be sent for consideration of publication on an international peer reviewed journal.

CHAPTER FIVE: RESULT

5.1. Effect of contact time

The experimental result showed that the removal of phosphate ion increased from 0 mg/g to 0.0962 mg/g within the first 60 min and almost remained constant afterwards until equilibrium time while the amount adsorbed for nitrate ion increased from 0 to 0.07 mg/g in the first 60 min and showed the same pattern as phosphate (Fig. 3). The equilibrium time was achieved at 90 min for both adsorbates. Therefore, 90 min was taken as equilibrium time for the rest of the experiments.
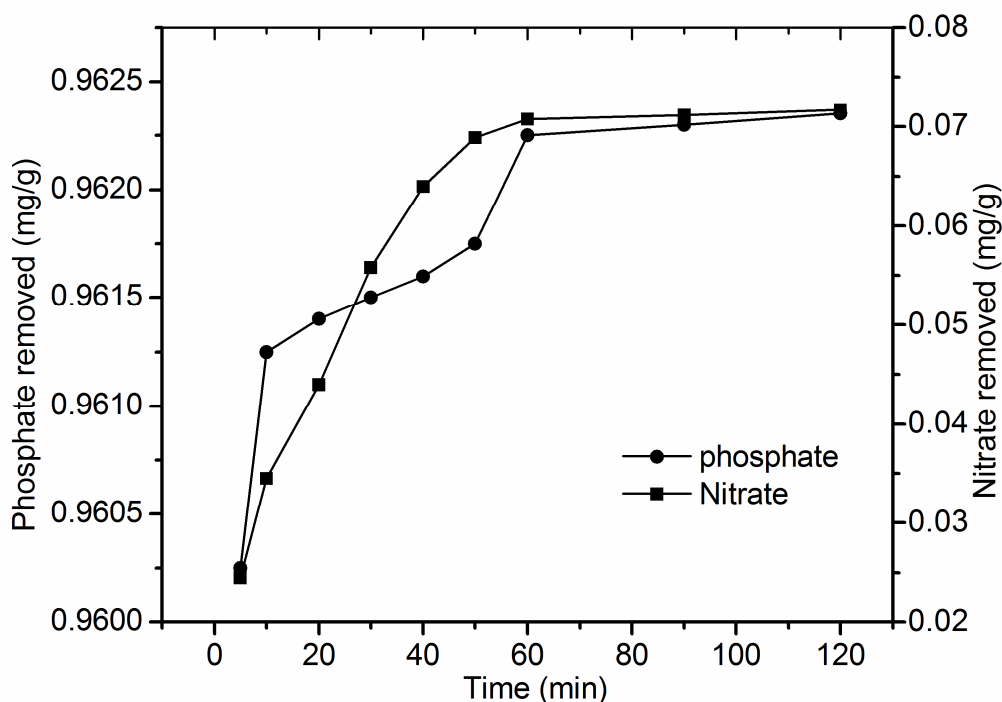
Fig. 3 Effect of contact time on simultaneous removal of nitrate and phosphate ions ($[PO_4^{3-}]_0$: 11.83 mg/L, $[NO_3\text{-}N]_0$: 3.36 mg/L, dose: 20 g/L, pH~7 and agitation rate: 150 rpm)

5.2. Adsorption kinetics

Adsorption kinetics for simultaneous nitrate and phosphate removal was examined by applying the pseudo-first and pseudo-second order kinetics. From Tables 3 and 4, the kinetic data well fitted to pseudo-second order kinetics with R^2 1 and 0.992 for phosphate and nitrate respectively (Figs. 5a and 5b). Similarly, R^2 value for the

pseudo-first order kinetics of phosphate was 0.698 while that of nitrate was 0.915 (Figs. 4a and 4b). This indicates the kinetics data better fitted to pseudo-second order kinetics than pseudo-first order kinetics for both adsorbates. The plots of pseudo-first and pseudo-second order kinetics for phosphate and nitrate ions are given in Figs. 4 and 5, respectively. The parameters of the pseudo-first and pseudo-second order equations for phosphate and nitrate adsorption on AW are given in Tables 3 and 4, respectively.
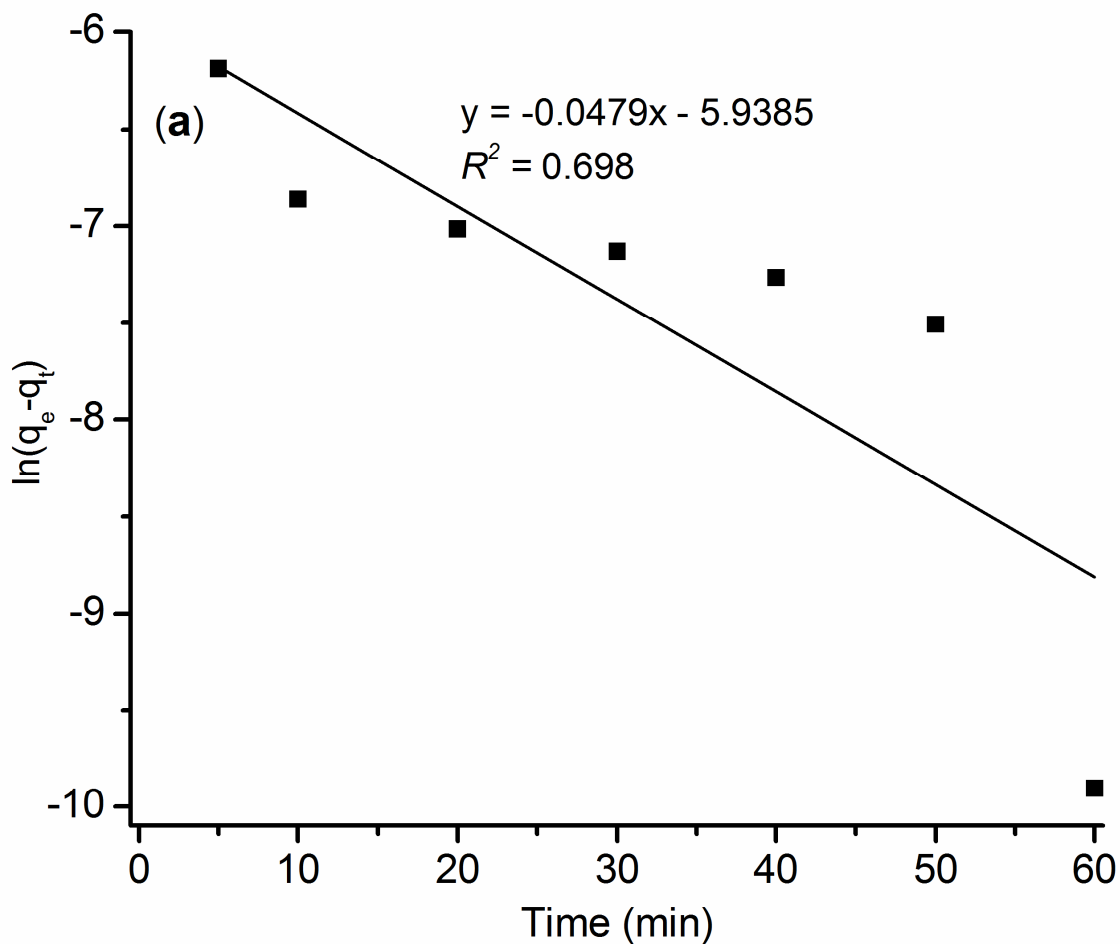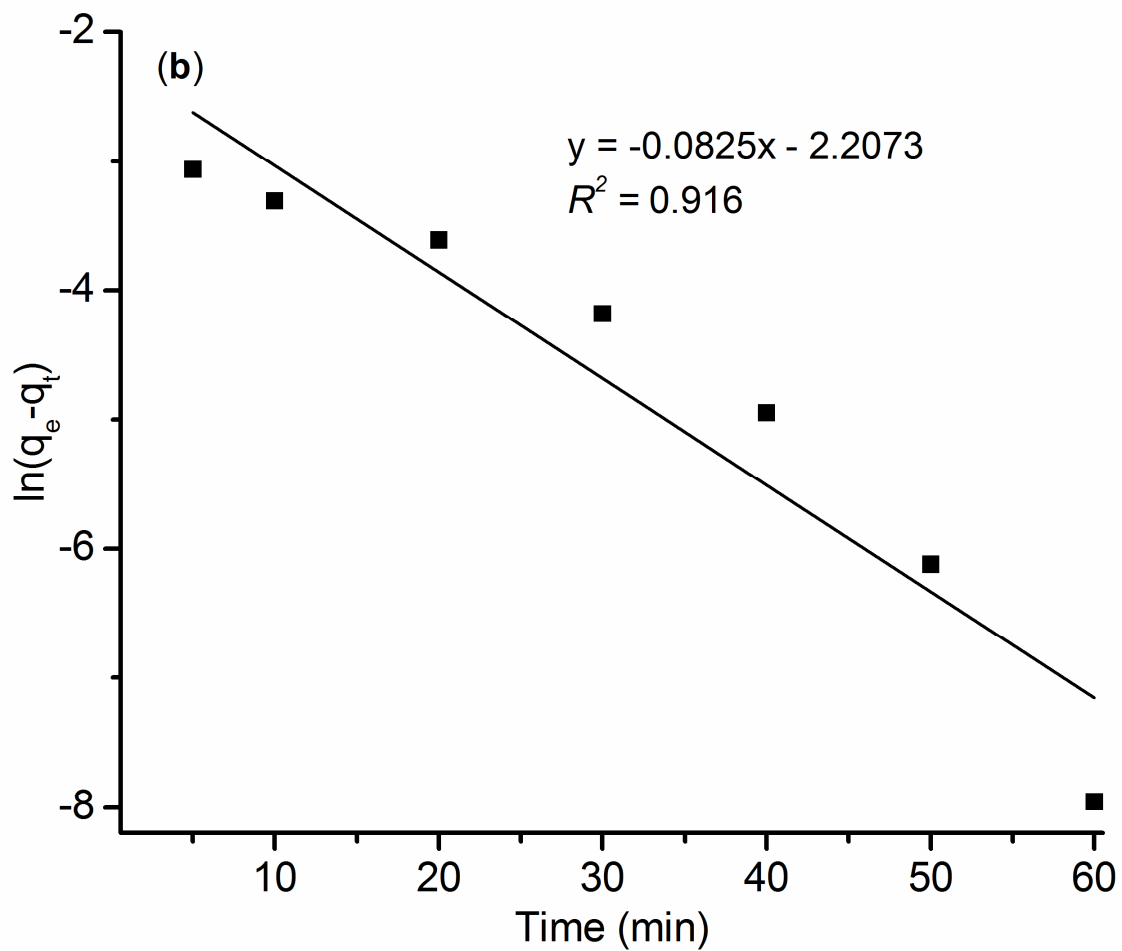
(a)

$y = -0.0479x - 5.9385$
$R^2 = 0.698$

Fig. 4 Pseudo-first order kinetics of (a) phosphate and (b) nitrate adsorption ($[PO_4^{3-}]_0$: 19.3 mg/L, $[NO_3\text{-}N]_0$: 5.14 mg/L, dose: 20 g/L, pH ~ 7 and agitation rate: 150 rpm)

(a)

$y = 1.0390x + 0.0262$
$R^2 = 1$

(b)

$y = 11.8791x + 165.9443$
$R^2 = 0.992$
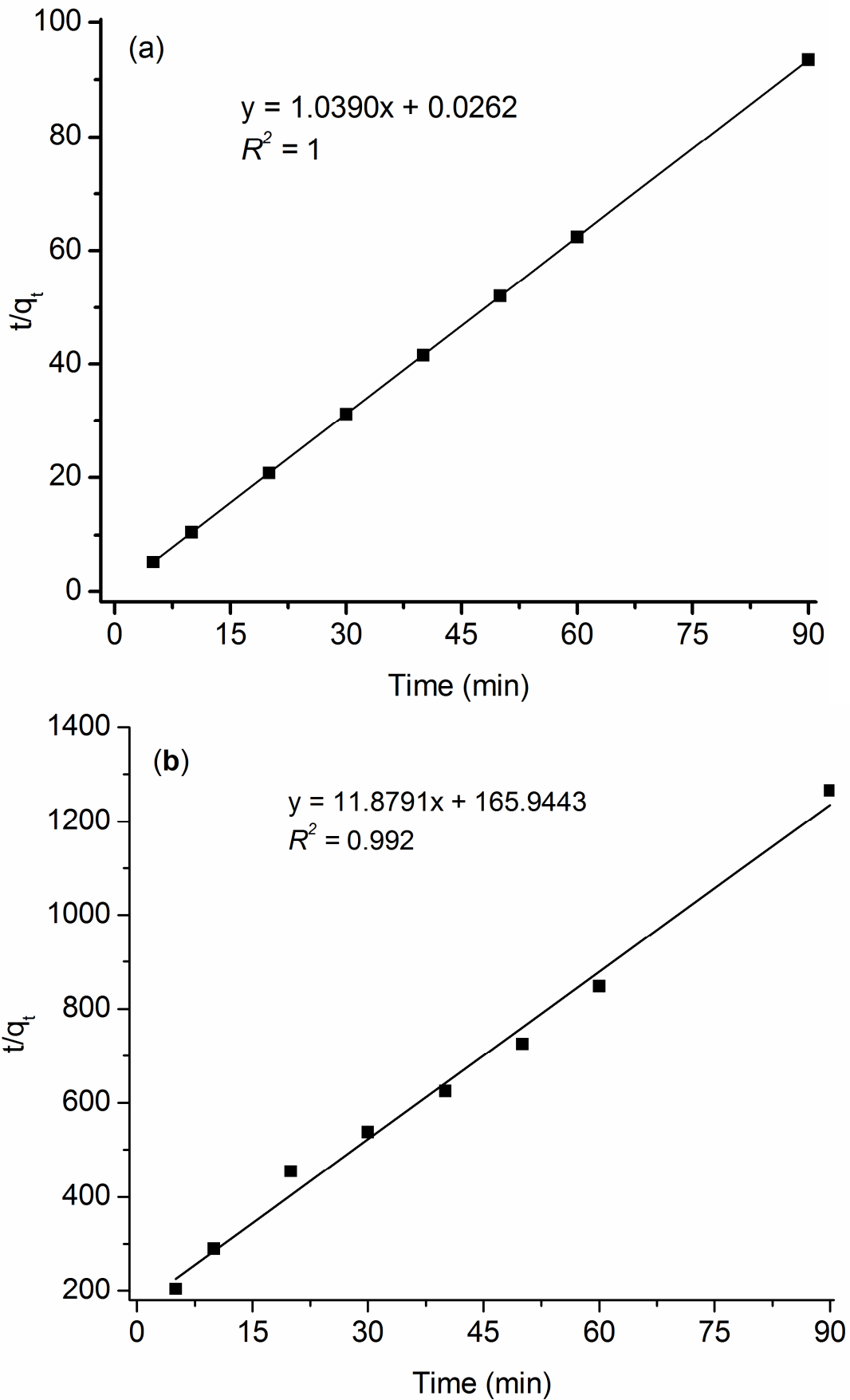
Fig. 5 Pseudo-second order kinetics of (a) phosphate and (b) nitrate adsorption ($[PO_4^{3-}]_0$: 19.3 mg/L, $[NO_3\text{-}N]_0$: 5.14 mg/L, dose: 20 g/L, pH ~ 7 and agitation rate: 150 rpm)

Table 3 Parameters of pseudo-first and pseudo-second order of phosphate adsorption kinetics

Pseudo-first order		Pseudo-second order	
Parameters	Value	Parameters	Value
q_e (mg/g)	0.962	q_e (mg/g)	0.962
$q_{e, cal}$ (mg/g)	0.003	$q_{e, cal}$ (mg/g)	0.962
K_1 (min^{-1})	0.048	K_2 (g/(mg.min)	41.206
R^2	0.698	R^2	1

Table 4 Parameters of pseudo-first and pseudo-second order of nitrate adsorption kinetics

Pseudo-first order		Pseudo-second order	
Parameters	Value	Parameters	Value
q_e (mg/g)	0.071	q_e (mg/g)	0.071
$q_{e, cal}$ (mg/g)	0.110	$q_{e, cal}$ (mg/g)	0.006
K_1 (min^{-1})	0.082	K_2 (g/(mg.min))	2318.144
R^2	0.915	R^2	0.992

5.3. Effect of initial pH

Fig. 6 reveals that high phosphate removal efficiency (0.5887 – 0.5885 mg/g) between pH 5-9 where as high nitrate removal was achieved at pH 7 (0.046 mg/g NO_3-N). The removal of phosphate in the pH range mentioned was found to be to be 0.589 mg/g. These shows simultaneous removals of both adsorbates were found to be higher at pH 7. Hence, pH 7 was selected as optimum pH to conduct the rest adsorption experiments so as to simultaneously remove nitrate and phosphate ions.
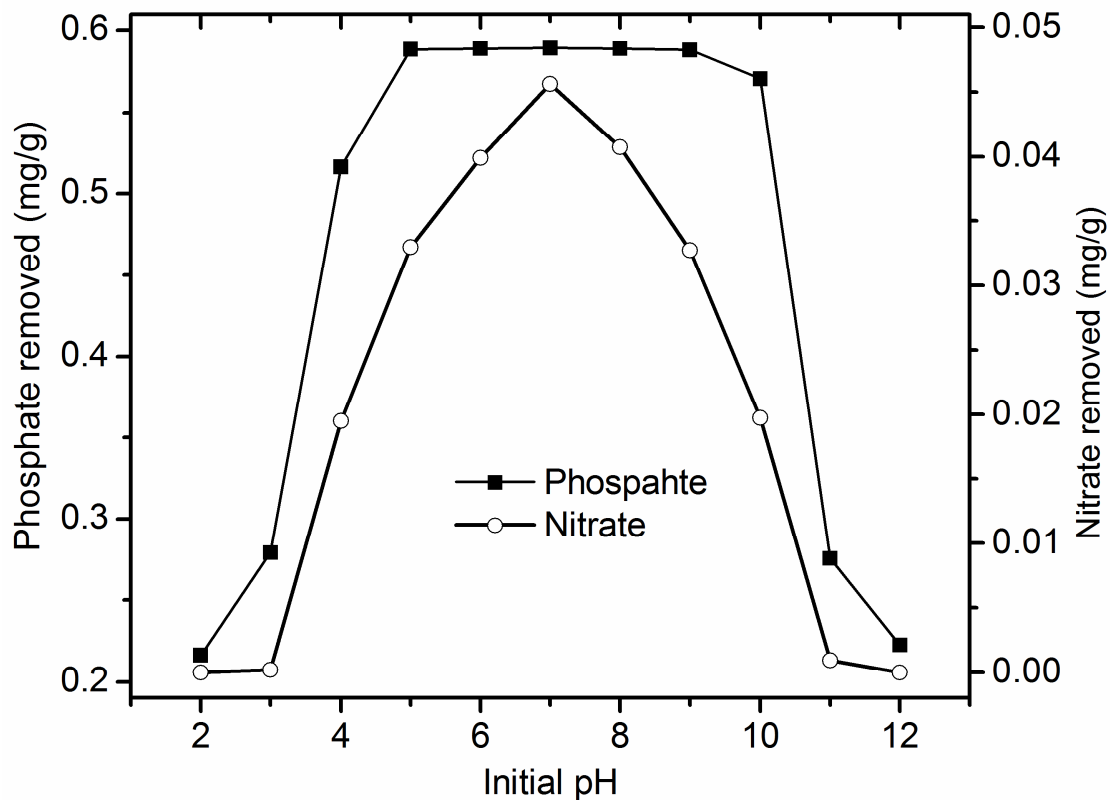
Fig. 6 Effect of pH on simultaneous removal of nitrate and phosphate ions ($[PO_4^{3-}]_0$: 11.83 mg/L, $[NO_3\text{-}N]_0$: 3.36 mg/L, adsorbent dose: 20g/L, pH~7 and agitation rate: 150 rpm)

5.4. Effect of adsorbent dose

The effect of adsorbent dose was studied by varying the dose between 4 and 32 g/L. It was observed that the percent removal of phosphate ions onto AW increased from 99.364% to 99.932% with increasing AW dose from 4 to 32 g/L. Similarly, percent removal of nitrate increased from 22.34% to 32.20% with the increased dose of AW (Figs. 7a and 7b). Based on this result 20 g/L was selected as optimum dose to conduct the rest adsorption experiment during simultaneous removal of nitrate and phosphate.
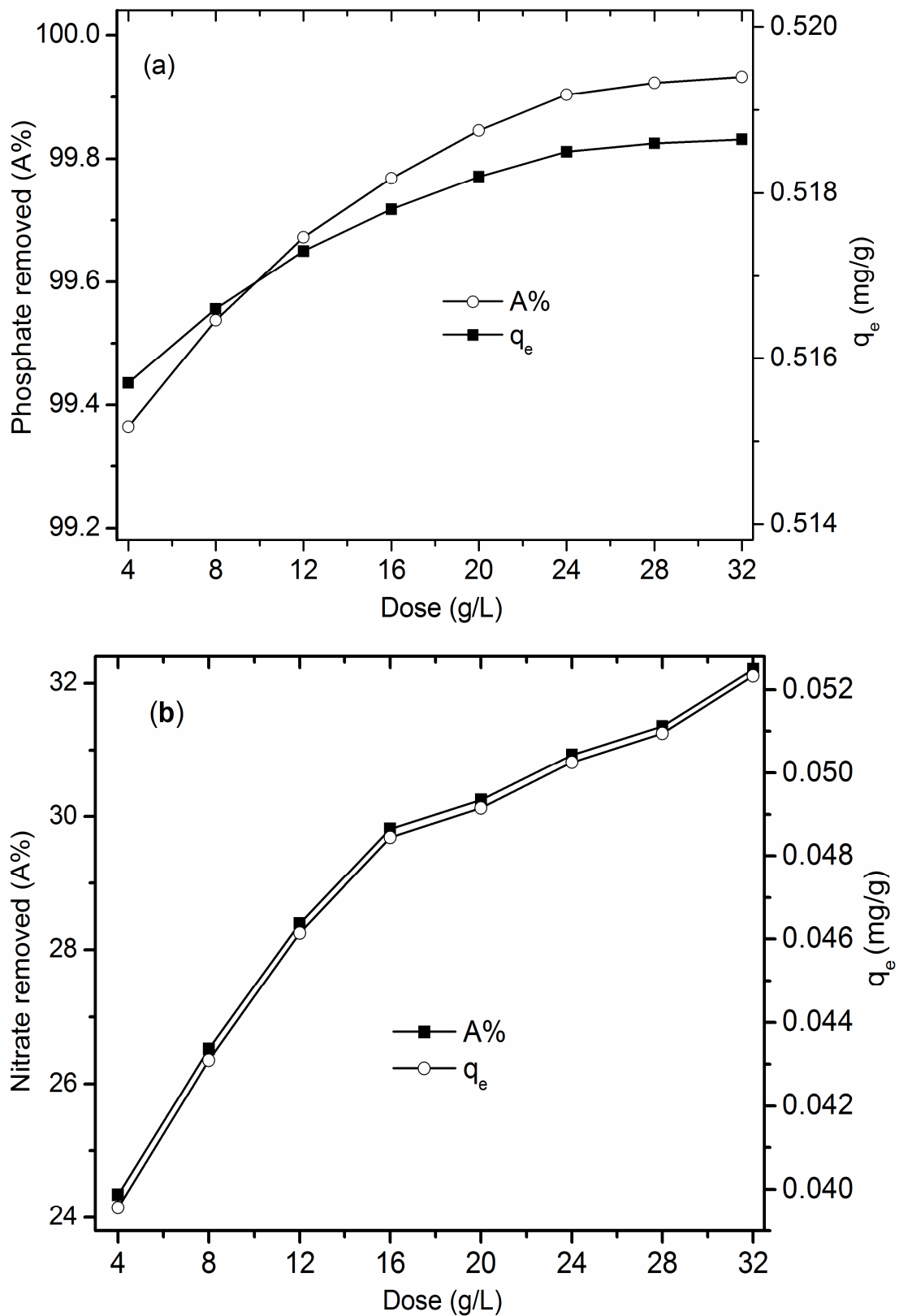
Fig. 7 Effect of adsorbent dose on the simultaneous remvoal of (a) phosphate and (b) nitrate ($[PO_4^{3-}]_0$: 10.38 mg/L, $[NO_3\text{-}N]_0$: 3.33 mg/L, dose: 4-2 g/L, pH~7 and agitation rate: 150 rpm)

5.5. Effect of initial concentration

The effect of initial adsorbate concentration on the adsorption was investigated by varying the initial concentration of phosphate between 0.2 mg/L and 260 mg/L and that of nitrate-nitrogen between 3 and 19 mg/L. The results showed that the percentage removal increased from 70 to 99.97% with an increase in the phosphate concentration from 0.2 to 260 mg/L (Fig. 8a) while that of nitrate decreased from 26.33 to 6.53% with the increase in the concentration of nitrate-nitrogen (Fig. 8b).
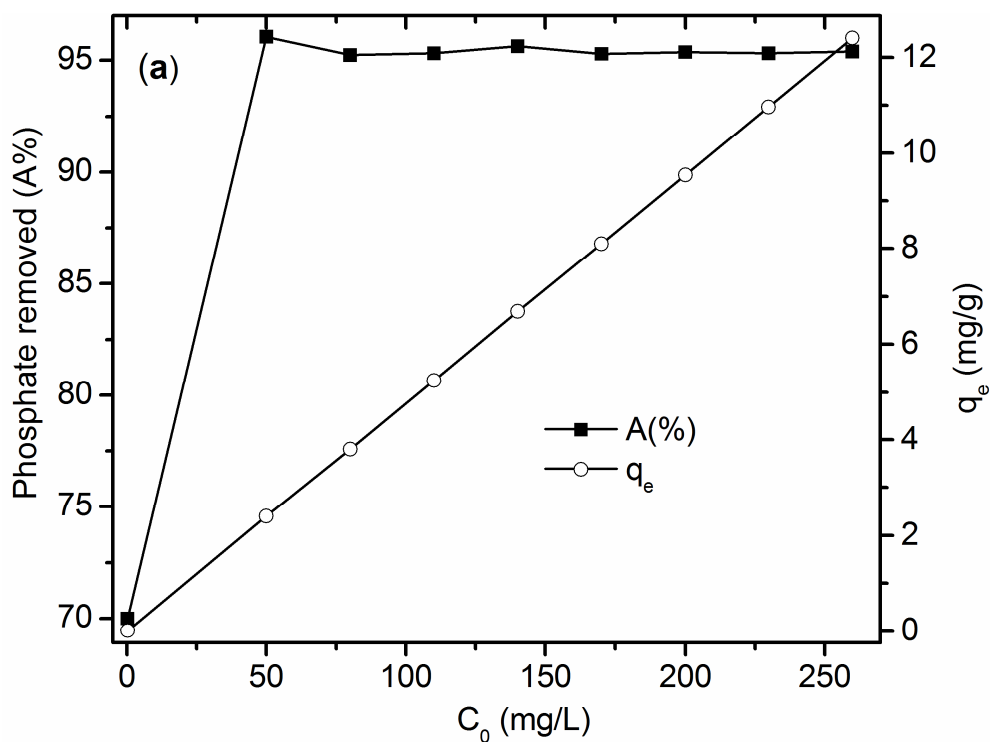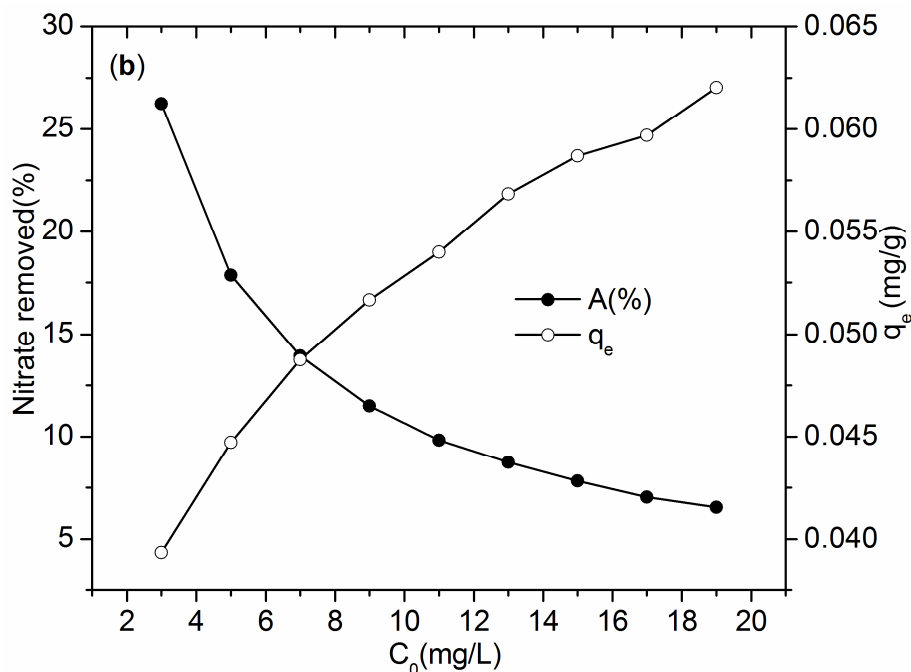
Fig. 8 Effect of initial concentration on the simultaneous removal of (a) phosphate and (b) nitrate ($[PO_4^{3-}]_0$: 0.2 to 260 mg/L, $[NO_3\text{-}N]_0$: 3 to 19 mg/L, dose: 20 g/L, pH~ 7 and agitation rate: 150 rpm)

5.6. Adsorption isotherm

The adsorption data obtained from simultaneous removal of nitrate using AW were analysed according to the two commonly used non-linear isotherms, Langmuir isotherm and Freundlich isotherm. The result showed adsorption of phosphate and nitrate well fitted to Freundlich isotherm with R^2 values 0.988 and 0.991 respectively. Likewise, experimental data of both adsorbates well fitted to Langmuir isotherm with R^2 equals 0.984 for phosphate and 0.955 for nitrate. Moreover, Freundlich and Langmuir isotherm constants determined by non-linear regression are given in Tables 5 and 6. The isotherm plots of the equilibrium adsorption of phosphate and nitrate are respectively given in Fig. 9a and Fig. 9b.
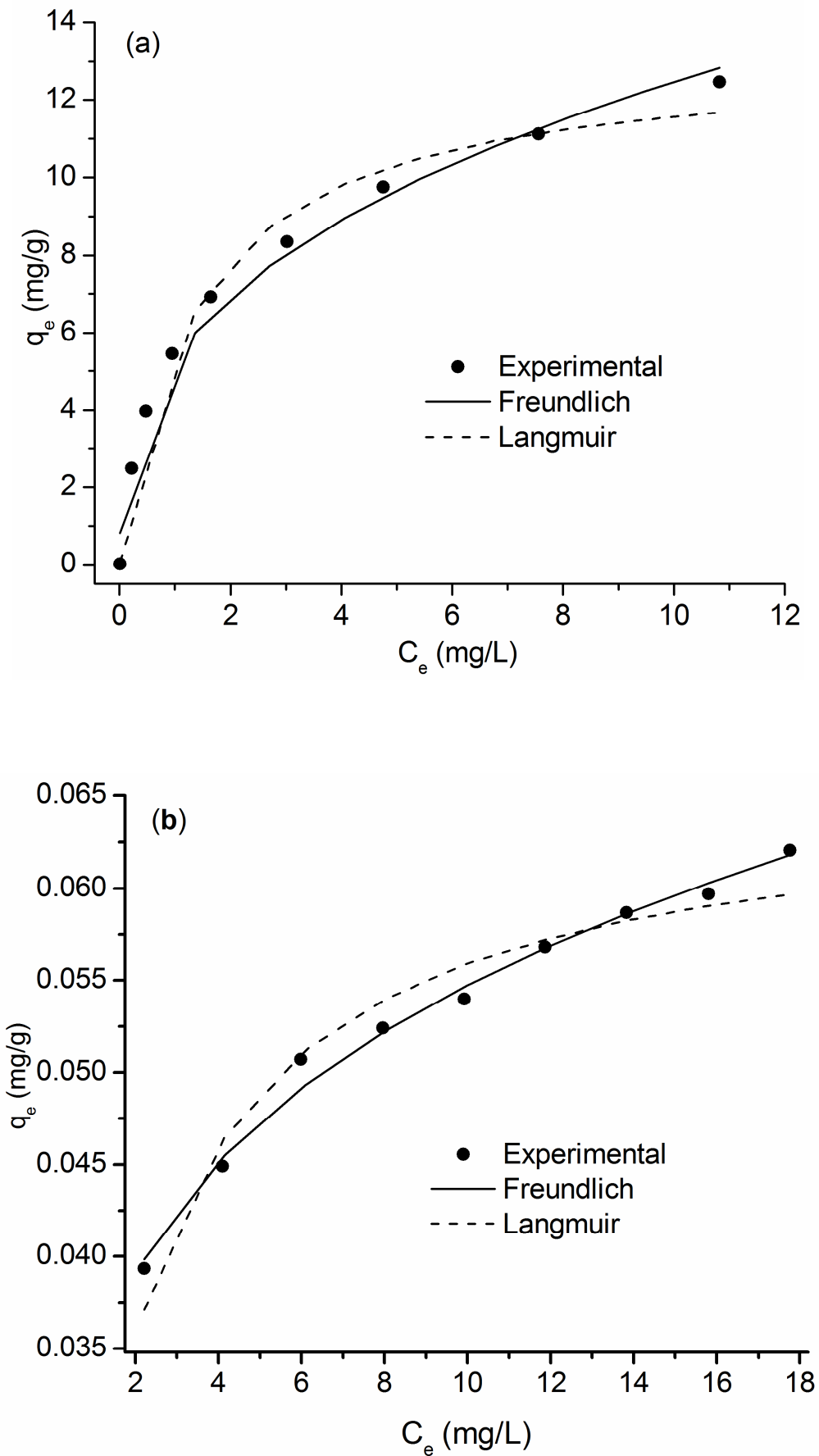
Fig. 9 Isotherm plots for (a) phosphate and (b) nitrate equilibrium adsorption ($[PO_4^{3-}]_0$: 0.2 to 260 mg/L, $[NO_3\text{-}N]_0$: 3 to 19 mg/L, dose: 20 g/L, pH~7, agitation rate: 150 rpm and temperature: 299K)

Table 5 Isotherm parameters for the removal of phosphate by untreated AW

Freundlich isotherm		Langmuir isotherm	
Parameters	Value	Parameters	Value
k_f (mg/g)	5.361	$q_{max\ (mg/g)}$	13.150
n	2.727	b (L/mg)	0.367
R^2	0.988	R^2	0.984
RFEP	1.619	R_L	0.010-0.932
		RFEP	2.199

Table 6 Isotherm parameters for the removal of nitrate ions by untreated AW

Freundlich isotherm		Langmuir isotherm	
Parameters	Value	Parameters	Value
k_f (mg/g)	0.034	$q_{max\ (mg/g)}$	0.065
n	4.740	b (L/mg)	0.594
R^2	0.991	R^2	0.955
RFEP	3.825E-6	R_L	0.081-0.359
		RFEP	1.931E-5

5.7. Mean sorption energy

The D-R isotherm can be used to model the adsorption process. This can be achieved by computing the mean sorption energy according to Eq. (11), where sorption energy less than 8 KJ/mol shows physiosorption, while value of mean sorption energy greater than 8 KJ/mol shows chemisorption. The D-R isotherm plots for phosphate and nitrate are given in Fig. 10a and 10b. The mean sorption energy computed from the D-R

equation for phosphate was found to be 8.506 KJ/mol while that of nitrate was 3.272 KJ/mol (Table 7).
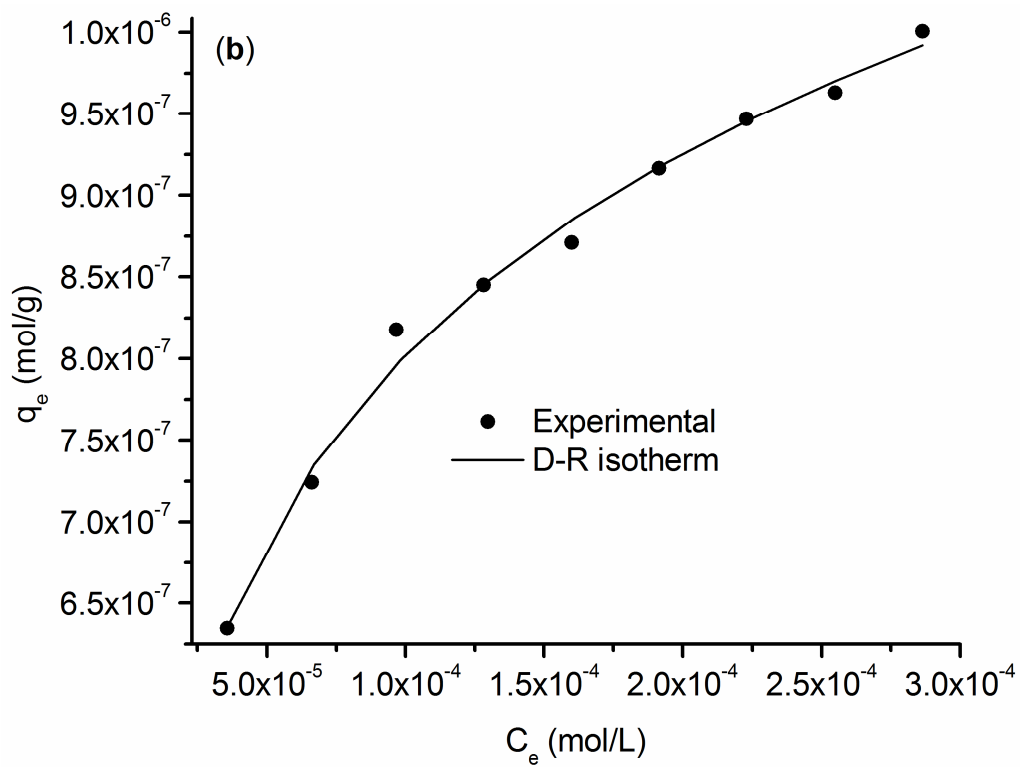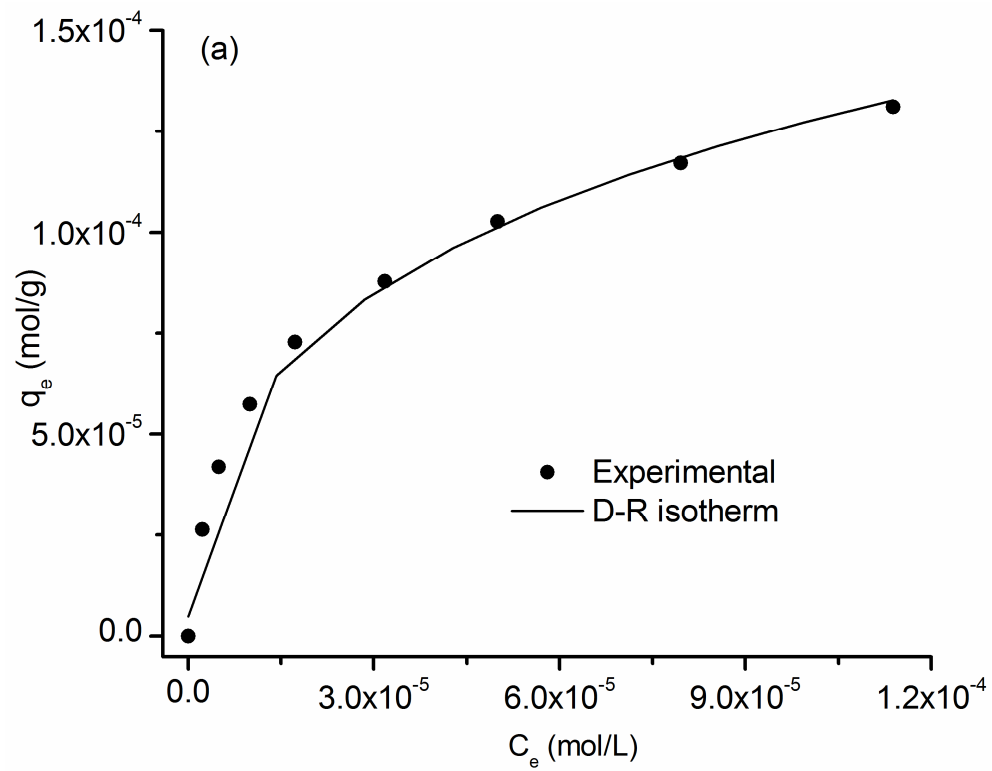
Fig. 10 D-R plot for (a) phosphate and (b) nitrate ($[PO_4^{3-}]_0$: 0.2 to 260 mg/L, $[NO_3\text{-}N]_0$: 3 to 19 mg/L, dose: 20 g/L, pH ~ 7, agitation rate: 150 rpm and temperature: 299K)

Table 7 Isotherm parameters for the removal of nitrate ions by untreated AW

D-R phosphate		D-R nitrate	
Parameter	Value	Parameter	Value
q_m	5.474E-4	q_m	2.150E-6
β (mol^2/KJ^2)	0.00691	β (mol^2/KJ^2)	0.0467
R^2	0.996	R^2	0.992
E_{D-R} (KJ/mol)	8.506	E_{D-R} (KJ/mol)	3.272
RFEP	6.128E-11	*RFEP*	8.659E-16

5.8. Intraparticle diffusion equation

Analysis of equilibrium data using intraparticle diffusion model depicted, intraparticle diffusion is not the rate determining step as the graph of q_t versus $t^{0.5}$ did not pass through the origin as shown in Figs. 11a and b.
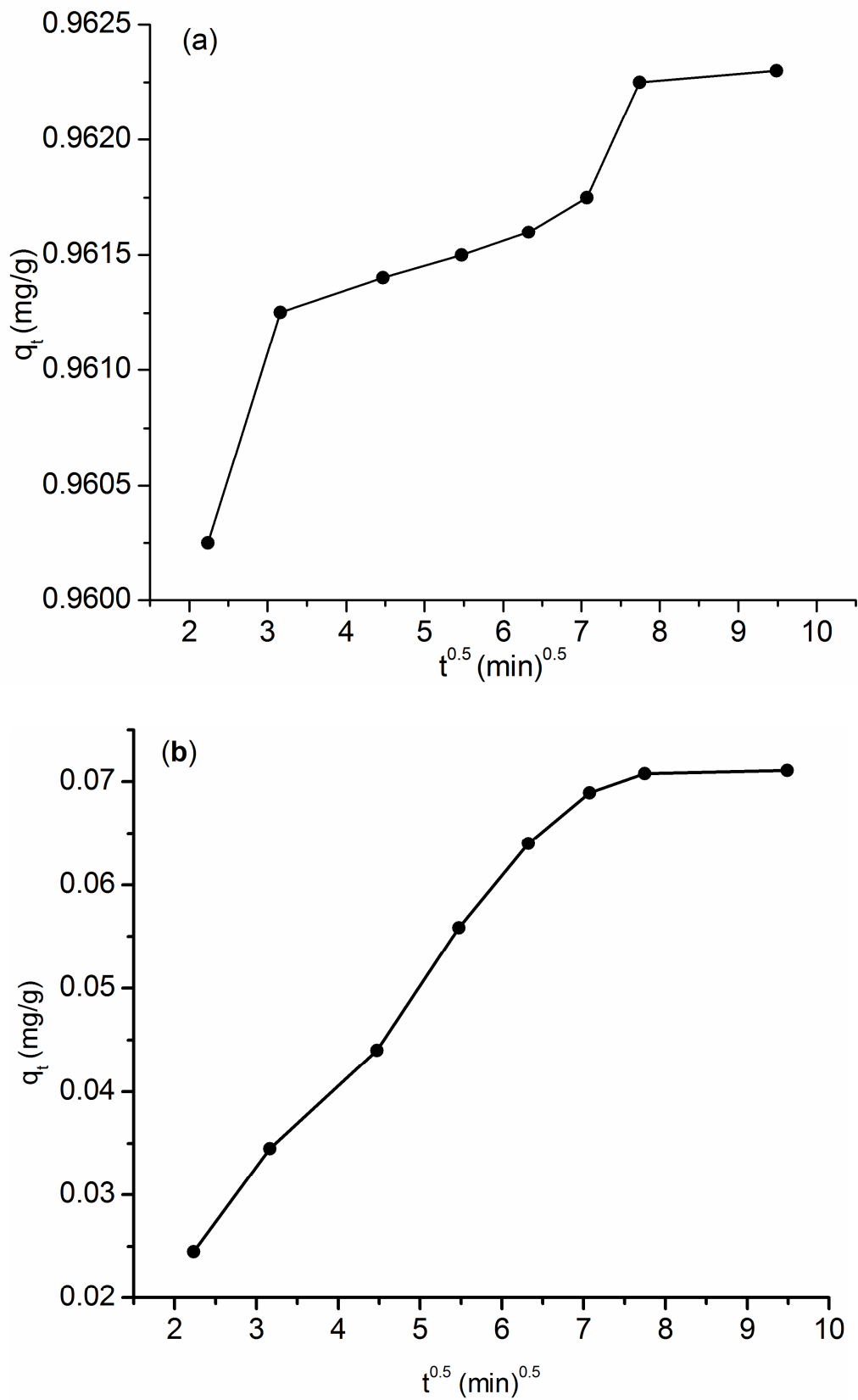
Fig. 11 Effect of contact time on simultaneous removal of nitrate and phosphate ions ([PO_4^{3-}]$_0$: 11.83 mg/L, [NO_3-N]$_0$: 3.36 mg/L, dose: 20 g/L, pH ~ 7 and agitation rate: 150 rpm)

5.9.   Effect of co-existing ions

The effect of common coexisting ions such as chloride, sulfate, and bicarbonate in wastewater on the simultaneous adsorption of phosphate and nitrate was investigated by varying the concentration of the anions from 5 to 100 mg/L in the solution. The result showed that the presence of individual or the mixture of the three ions in the solution did not significantly affect the removal efficiency of phosphate when compared with the removal efficiency of phosphate without the presence of the ions in the solution (Fig. 12a). The removal efficiency of phosphate without the presence of the ions was represented by 'control' in Fig. 12a. On the contrary, increase in concentration of all the coexisting ions had significantly affected the removal efficiency though the effect of chlorides are not as prominent as bicarbonate and sulfate indicated in Fig. 12b.
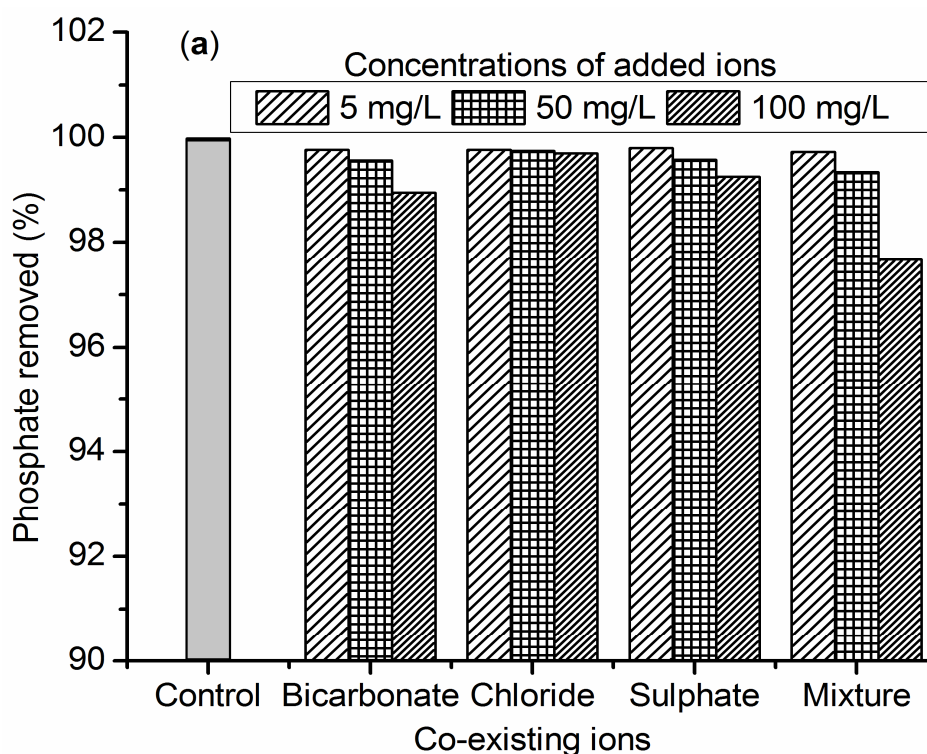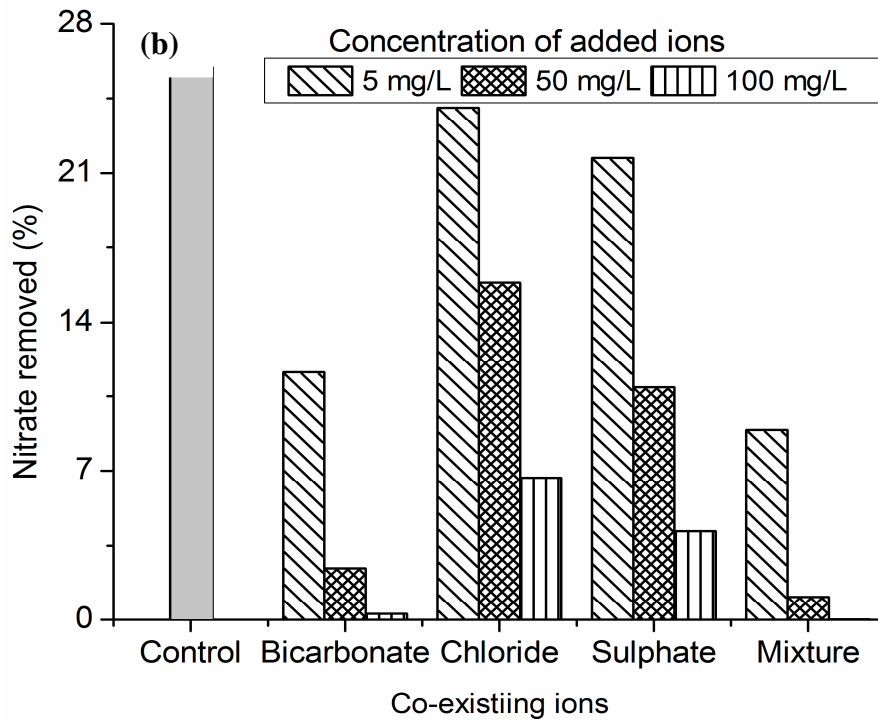
Fig. 12 Effect of co-existing ions on the simultneous removal of (a) phosphate and (b) nitrate ($[PO_4^{3-}]_0$: 19.3 mg/L, $[NO_3\text{-}N]_0$: 5.14 mg/L, dose: 20g/L, pH ~ 7 agitation rate: 150 rpm)

5.10. Desorption experiment

From the experimental results of the effect of pH given in *subsection 5.4*, the adsorption of phosphate and nitrate significantly decreased in the extreme pHs. This could suggest that desorption of the adsorbates can be effective using either extreme acidic or basic pH. The data found from the desorption experiment showed nearly 50% of the adsorbed phosphate was desorbed by 1.0 M NaOH. Unlike phosphate 100% desorption of nitrate was observed using 1 M NaOH. The results of desorption experiments are given in Fig. 13.
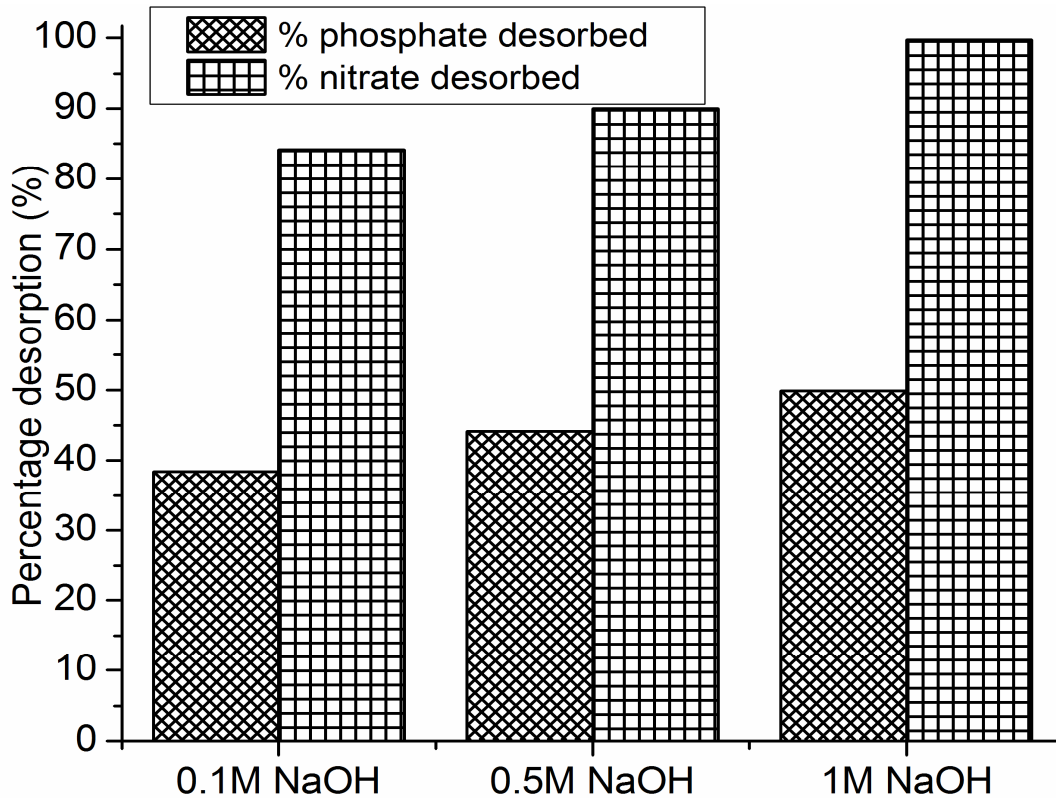
Fig. 13 Effect of increasing NaOH concentration on simultaneous desorption of phosphate and nitrate ($[PO_4^{3-}]_0$: 19.3 mg/L, $[NO_3-N]_0$: 5.14 mg/L, agitation rate: 150 rpm)

5.11. Removal of phosphate and nitrate from wastewater

Applicability of the adsorbent for simultaneous removal of phosphate and nitrate collected from wastewater discharge point near Jimma University was investigated. The physicochemical characterization and adsorption experiments of the wastewater were conducted at Jimma University, department of environmental health science and technology graduate and staff research laboratory. Adsorption experiment on the wastewater revealed 77.5% and 4.6% phosphate and nitrate removal from the sample, respectively. The analysed physico-chemical characteristics of the wastewater are shown in Table 8.

Table 8 Physico-chemical characteristics of the wastewater

Physicochemical characteristics	Value
DO (mg/L)	1.46
BOD (mg/L)	1530
pH	7.24
DO in percent saturation (%)	24.00
Conductivity (µs/cm)	958
Temperature (^{0}C)	22.9
Turbidity (NTU)	46.8
Total dissolved solid (mg/L)	479
Total suspended solid (mg/L)	114
Chloride (mg/L)	8.9
Orthophosphate (mg/L)	7.17
Nitrate-nitrogen (mg/L)	1.3

CHAPTER SIX: DISCUSSION

This survey also found that 16(11.85%, N=135) of them were pregnant and among these, 13(81.2%) were attended ANC at least once and the rest (18.8%) of them did not attend ANC. This finding is not similar with the finding in Yem special Woreda(14) in which about28.5% women have received antenatal care at least once during their last pregnancy with the majority 71.5% reported that they did not attend ANC for their last pregnancy. This difference could be due to the presence of additional NGOs that work on maternal health in addition to governmental health institute. Despite of this fact still some (18.8%) did not attend antenatal care which is in contrary to WHO recommendation for all pregnant women to attend ANC at least four times. And the finding in Awetu Mendera is still not similar with the 2010 DTTP report conducted in Ginjo gudru kebele, Jimma town, on which among all of the total pregnant women attended ANC at least once. This could be due to absence of urban health extension worker in Awetu Mendera.

Concerning to delivery service utilization, on the other hand, among the total deliveries 18(5.6%) in the last 12 months, 16(88.9%) of them gave birth at health institution and 2(11.1%) of them were at home and of these all of them were conducted by TBA by using gloves. This finding is incomparable with the findings in North Gondar Zone (15), in which the magnitude of home delivery in this finding was less relative to the previous finding indicating some improvement and this could be due to government effort to achieve the MDG but still there are some women (11.1%) who did not use safe delivery service.

Among the total surveyed households, 88.9% of them had ITN during survey with the mean number of ITN 1.96. Among these, 189(65.6%) of them used ITN always, 90(31.2%) of them used it sometimes and 9(3.1%) of them did not use ITN due to different reasons like the problem of allergy responded by majority of them. This finding is inconsistent with the study conducted in Arbaminch Town (19) in which ITN coverage rate was 58.8% and utilization rate was 73%. The difference could be due to an improved emphasis on malaria prevention by distributing ITNs for the community even though the problem of utilization is there.

The finding on waste disposal system in this survey revealed that majority (35.5%) of households dispose in open field, in garbage or waste container (31.5%), by burning (22.8%) with the least (10.2%) using pit and this finding is comparable with the previous findings conducted in Ethiopia which indicated lack of adequate access to public solid waste management services, and in Addis Ababa about 37% use open dumping, 22% burning, 33% burying and 11% composting for waste disposal but not consistent with findings of Kersa Demographic Surveillance and Health Research Centre (KDS-HRC) in which only 6.9% used garbage or temporary storage site (7,8).

Concerning to the HIV test, only 118(36.4%) of the respondents were tested for HIV/AIDS and 206(63.6%) of them did not tested for HIV/AIDS which is almost consistent with the previous study conducted in Addis Ababa(20)and the common reasons forwarded for not being tested were feeling of not being exposed for the risks of acquiring HIV/AIDS 85(41.26%), afraid to had HIV/AIDS test 79(38.35%) and being married and feeling of none concern for married 42(20.39%) which indicates community awareness on HIV/AIDS was less which is also similar with the previous study. From the totally surveyed HHs, about 8(2.5%) mentally ill client was found. Out of this, 3(37.5%) had medical follow up but the rest did not.

CHAPTER SEVEN: CONCLUSION AND RECOMMENDATION

7.1.   Conclusions

Simultaneous phosphate and nitrate removal from aqueous solutions was studied using AW. Based on the results of this study, the following conclusions were drawn.

Static test were conducted with macro invertebrate larvae in 150 ml glass beaker with in different dilutions. The de-chlorinated tap water was used as the diluent medium (prepared by passing tap water through a distiller). Experimental vessels were filled with de-chlorinated tap water and allowed to cool to laboratory temperature to ensure constant temperature of diluent medium. The sewage concentration series used in the dilution in this study was 0 (control), 10, 30, 50, 70 and 90 % (reference) for a time period of 1, 3, and 7 hour. Each test solution had three replicates. Each replicates has ten (10) organisms. The mortality of the organisms was recorded at the end of the specified exposure times. Dead organisms were collected at each interval, labeled and preserved in 70% ethanol. Surviving organisms at the end of the 7 hour period were collected, labeled and preserved in 70% ethanol. At the end of each interval the identification of the macro invertebrate was undertaken to the family level using different identification key ( ). Laboratory temperatures were controlled with the use of air-conditioners to around room temperature.

7.2.   Recommendations

Various studies have shown that macroinvertebrates are often sensitive to toxicants, and represent a large proportion of the biomass in aquatic systems (Buikema et al., 1982). Macro invertebrate larvae were collected by rinsing rocks into a jug of river water and with kick net mesh size 250µm by wading at the middle of the stream of Ofale in Dedo District, Jimma Zone, Ethiopia. The stream passes through agricultural area and is not prone to industrial and domestic waste pollution since there is no indication of such pollution. The stream bed was mainly silt, pebble and cobble stones. It has on average a riparian vegetation of about 1 m on both sides of the stream.

Macro invertebrates were gently rinsed off the net with river water into a 10 L bucket filled with aerated stream water. The transit time to the laboratory was approximately one hour. Collected organisms were placed in the buckets containing stream water from the sample site and transferred to the laboratory around the icepack to prevent

overheating. The majority of the test organisms were mainly (there were also other families) from the families of the mayflies (Ephemeroptera); Hepetageniidae, Canidae and Baetidae and from Odonata family; Coenagriidae. Macroinvertebrate, are sensitive to handling, and were gently transferred to the laboratory streams. The macro invertebrates were not identified until the end of the experiment.

REFERENCES

Anand, S., Soma, G., Sujana, M. and Vasumathi, N., (2009). Studies on fluoride adsorption capacities of amorphous Fe/Al mixed hydroxides from aqueous solutions, *Journal of Fluorine Chemistry* **130**(8): 749-754.

APHA (1995). Standard Methods for Examination of Water and Wastewater. 4500-P and 4500-NO$_3$.   USA.

Baraka, M. A., El-Tayieb, M. M., El Shafai, M. and Mohamed, Y. N., (2012). Sorptive Removal of Phosphate from Wastewater Using Activated Red Mud. *Australian Journal of Basic and Applied Sciences* **6**(10): 500-510.

Benghalem, A., Ghaffour, N., Ramdani, A. and Taleb, S. (2010). Removal of excess fluoride ions from Saharan brackish water by adsorption on natural materials. *Desalination* **250**(1): 408-413

Boparai, K. H., Joseph, M. and O'carroll, D., (2010). Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. *Journal of Hazardous Materials* **xxx:** xxx-xxx.

CDC (2004). About Harmful Algal Blooms. http://www.cdc.gov/nceh/ciguatera/

Cengeloglu, Y., Tor, A., Ersoz, M. and Arslan, G., (2006). Removal of nitrate from aqueous solution by using red mud. *Separation and Purification Technology* **51**(2): 374-378.

Dai, J., Yang, H., Yan, H., Shangguan, Y., Zheng, Q. and Cheng, R., (2011). Phosphate adsorption from aqueous solutions by disused adsorbents: Chitosan hydrogel beads after the removal of copper (III). *Chemical Engineering Journal* **166**: 970-977.

Ferreira, G. A., Andersen, H.J., Borja, A., Bricker, B. S., Campa, J., Da Silva, C.M., Garces, E., Heiskanen A., Humborg, C., Ignatiades, L., Lancelot, C., Menesguen, A., Tett, P., Hoepffner, N. and Claussen, U., (2011). "Overview of eutrophication indicators to assess environmental status within the European Marine Strategy Framework Directive." *Estuarine, Coastal and Shelf Science* **93**(2): 117-131.

Foo, Y. K and Hameed, H. B., (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal* **156**: 2–10.

Freundlich, H. M. F., (1906). Over the adsorption in solution. *Journal of physical chemistry* **57**:385–470.

Galloway, J. and Cowling, E., (2002). Reactive nitrogen and the world: 200 years of change. *Ambio* **31**: 64-71.

Hamoudi, H. and Belkacemi, K., (2012). Adsorption of nitrate and phosphate ions from aqueous solutions using organically-functionalized silica materials: Kinetic modeling. *Fuel* **xxx**: xxx-xxx.

Han, S, D., Batchelor, B., Park, H, S. and Abdel-Wahab., (2012). As(V) adsorption onto nanoporous titania adsorbents (NTAs): Effects of solution composition. *Journal of Hazardous Materials* **229– 230**: 273-281.

Kamiyango, W. M., Masanba, L.R.W., Sajidu, I.M.S. and Fabiano, E., (2009). Phosphate removal from aqueous solutions using kaolinite obtained from Linthipe, Malawi. *Physics and Chemistry of the Earth* **34**: 850–856.

Katal, R., Baei, S. M., Rahmati, T.H. and Esfandian, H., (2012). Kinetic, isotherm and thermodynamic study of nitrate adsorption from aqueous solution using modified rice husk. *Journal of Industrial and Engineering Chemistry* **18:**295–302.

Khelifi, O., Kozuki, Y., Murakami, H., Kurata, K., Nishioka, M., (2002). Nutrients adsorption from seawater by new porous carrier made from zeolitized fly ash and slag. *Marine Pollution Bulletin* **45**: 311–315

Kose, E. T. and Kivanc, B., (2011). Adsorption of phosphate from aqueous solutions using calcined waste eggshell. *Chemical Engineering Journal* **178:**34– 39

Krishnan, A. K., and Haridas, A., (2008). Removal of phosphate from aqueous solutions and sewage using natural and surface modified coir pith. *Journal of Hazardous Materials* **152**: 527-535.

Langmuir, I., (1916). The adsorption of gases on plane surface of glass, mica and platinum. *Journal of American chemical society* **40**:1361–1368.

Liang, Q., (2011). Simultaneous phosphorus and nitrogen removal using aluminum based water treatment residual. Fort Collins Colorado State University 1-100. *Unpublished research.*

Milmile, N.S., Pande, V.J., Karmakar, S., Bansiwal, A., Chakrabarti, T. and Biniwale, B.R., (2011). Equilibrium isotherm and kinetic modeling of the adsorption of nitrates by anion exchange Indion NSSR resin. *Desalination* **276**: 38-44.

Negassa, S., (2012). Phosphate sorption capacity of solid residue of Awash Melkassa Aluminum Sulphate and Sulphuric Acid Factory. *Unpublished research.*

Nigussie, W., Zewge, F. and Chandravanshi, S.B., (2007). Removal of excess fluoride from water using waste residue from alum manufacturing process. *Journal of Hazardous Materials* **147**: 954-963.

Olgun, A., Atar, N. and Wang, S., 9 (2013). Batch and column studies of phosphate and nitrate adsorption on waste solids containing boron impurity. *Chemical engineering journal* **222**:108–119

Özacar, M., (2003). Adsorption of phosphate from aqueous solution onto alunite. *Chemosphere* **5**: 321-327.

Painting, J.S., Devlin, J.M., Malcolm, J. S., Parker, R. A., Mills, K.D., Mills, C., Tett, P., Wither, A., Burt, J., Jones, R. and Winpenny, K., (2007) Assessing the impact of nutrient enrichment in estuaries: Susceptibility to eutrophication. *Marine Pollution Bulletin* **55**:74–90

Saad, R., Belkacemi, K. and Hamoudi, S., (2007). Adsorption of phosphate and nitrate anions on ammonium-functionalized MCM-48: Effects of experimental conditions. *Journal of Colloid and Interface Science* **311**(2): 375-381.

Schick, J., Caullet, P., Paillaud, J., Patarin, J., and Mangold-Callarec, C., (2011). Nitrate sorption from water on a Surfactant-Modified Zeolite. Fixed-bed column experiments. *Microporous and Mesoporous Materials* **142**: 549-556.

Sibrell, L. P., Montgomery, A.G., Ritenour, L. K. and Tucker, W. T., (2009) Removal of phosphorus from agricultural wastewaters using adsorption media prepared from acid mine drainage sludge. *Water research* **43:** 2240-2250.

Song, X., Pan, Y., Wu, Q., Cheng, Z. and Ma, W., (2011). Phosphate removal from aqueous solutions by adsorption using ferric sludge removal from aqueous solutions by adsorption using ferric sludge. *Journal of desalination* **280**: 384-390.

Tiemeyer, B., Kahle, P. and Lennartz, B., (2009). Phosphorus losses from an artificially drained rural lowland catchment in North-Eastern Germany. *Agricultural water management* **96**:677 - 690.

Vitousek, P., Mooney, H., Olander, L. and Allison. S., (2002). Nitrogen and nature. *Ambio* 31:97-101.

Wang, Y., Gao, B., Wen-Wen Yue, W. W. and Yue, Q., (2007). Adsorption kinetics of nitrate from aqueous solutions onto modified wheat residue. *Colloids and Surfaces A: Physicochemical Engineering. Aspects* **308**: 1-5.

Weia, X., Viadero, C. R., and Bhojapp, S., (2008). Phosphorus removal by acid mine drainage sludge from secondary effluents of municipal wastewater treatment plants. *Water research* **42**:3275 – 3284.

WHO (2011). Nitrate and nitrite in drinking-water.

www.who.int/**water_**sanitation_health/dwq

Zeng, L., Lia, X. and Liu, J., (2004). Adsorptive removal of phosphate from aqueous solutions usingiron oxide tailings. *Water Research* **38**: 1318-1326.

Zhang, G., Liu. H., Liu, R. and Jiuhui, Q., (2009). Removal of phosphate from water by a Fe-Mn binary oxide adsorbent. *Journal of Colloid and Interface Science* **335**(2): 168-174.

Zhang, J., Shen, Z., Shan, W., Chen, Z., Mei1, Z., Yangming Lei1,Y. and Wang, W., (2010). Adsorption behavior of phosphate on Lanthanum(III) doped mesoporous silicates material. *Journal of Environmental* **22**(4) :507–511

Zhao, Y., JunWang, Luan, Z., Peng, X., Liang, Z. and Shi, L., (2009). Removal of phosphate from aqueous solution by red mud using a factorial design. *Journal of Hazardous Materials* **165**: 1193–1199.

ANNEXES

Annex 1 Laboratory wares were cleaned following the steps mentioned below

1. Rinse material with tap water

2. Soak in detergent overnight

3. Rinse with tap water

4. Soak in 2% HNO_3 over night

5. Rinse with distilled water

6. Dry plastic wares at $55\pm5°C$ and glass wares at $105\pm5°C$ in oven for 12 hrs

Annex 2 Determination of orthophosphate

I. Apparatus

A). Glassware: 1000mL volumetric flask, 250 ml Erlenmeyer flasks, 10 ml Mohr pipette, clean quartz spectrophotometric cuvettes, 100mL graduated cylinder and 250mL were used.

B). Spectrophotometer: DR 500 UV-Vis spectrophotometer

II. Reagent

A) Phenolphthalein Indicator: 0.2g phenolphthalein was dissolved into 200mL deionized water and 200mL ethanol.

B) Ammonium Molybdate Reagent: 25g $(NH_4)_6 MO_7O_{24} .4H_2O$ was dissolved in 175 ml distilled water. Cautiously add 280 ml con. H_2SO_4 was cautiously added to 400 ml distilled water. Then cooled to add molybdate solution, and afterwards diluted to 1litter.

C) Stannous Chloride Reagent: 2.5 g fresh stannous chloride dissolved in 100mL glycerol (also known as glycerine) and heated on water bath for 2 h; stirred with rod to enhance dissolution. This reagent is stable and requires neither preservatives nor special storage.

D) Stock phosphate solution: Dissolve in distilled water 0.7165 anhydrous KH_2PO_4 and dilute to 1000 ml; 1.00ml = 500 μg PO_4^{3-}- P

E) Standard Phosphate Solution: 219.5mg of KH_2PO_4 dissolved and dilute to 1000ml; 1 ml=50.0 $\mu g PO_4^{3-}$ - P).

F) Strong-acid solution: 300 ml concentrated H_2SO_4 was slowly added to about 600 ml distilled water. After cooling, 4.0 ml concentrated HNO_3 added and diluted to 1L.

Procedure for stannous chloride method

A) Determination of Orthophosphate:

1. The following series of phosphate standards were prepared by measuring the indicated volume of standard phosphate solution in to separate 100 ml volumetric flasks (graduated cylinders).

Standard phosphate solution (ml)	Phosphate (PO_4^3) μg/100 ml
0	0
1	5
2	10
3	15
4	20
5	25
6	30

1. To the sample, 0.05 ml (1 drop) of phenolphthalein indicator solution was added. When the sample turned pink, strong acid solution was added drop wise until the colour disappeared.
2. With a measuring pipette, 4 ml acid-molybdate solution was added to each of the standards and sample.
3. Thoroughly mixing was carried out by inverting each flask four to six times
4. With medicine dropper, 0.5 ml (10 drops) of stannous chloride solution was added to each of the standards and sample
5. The flasks were stoppered and mixed by inverting each flask four to six times.
6. After 10 minutes, but before 12 minutes, the colour was photometrically measured at 690 nm using distilled water as a blank.
7. A calibration curve was constructed using the standards and the amount of phosphate in μg in the sample was determined from the curve.

8. Calculation: $mg\ PO_4^{3-}/L = \mu g\ PO_4^{3-}/ml$ of sample

Annex 3 UV- Screening method

Apparatus

- DR 500 UV-Vis spectrophotometer with curette that transmits UV light.

Reagents

- ❖ **Nitrate-free water**: Deionized water was used to prepare all solutions and dilutions.

- ❖ **Stock nitrate solution**: KNO_3 was dried in an oven at 105°C for 24 h and 0.7218 g was dissolved in water and dilutee to 1000 ml; 1.00 ml = 100 $\mu g\ NO_3^-$-N.

- ❖ **Intermediate nitrate solution**: 100 ml stock nitrate solution was diluted to 1000 ml with water, 1.00 ml = 10.0 $\mu g\ NO_3^-$-N.

- ❖ **Hydrochloric acid solution**: HCl = 1 N.

Procedure

- ❖ **Treatment of sample**

  1 ml 1 N HCl was added to 50 ml clear sample solution and mixed thoroughly.

- ❖ **Preparation of standard curve**

  Calibration standard was prepared in the range of 0 to 7 mg NO_3^--N/L by diluting to 50 ml the following volumes of intermediate nitrate solution: 0, 1.00, 2.00, 4.00, 7.00… 35.0 ml. NO_3^- standards were treated in same manner as samples.

- ❖ **Spectrophotometric measurement**

  Absorbance was read using distilled/deionized water as the reference at a wavelength of 220 nm to obtain NO_3^- reading and a wavelength of 275 nm to determine interference due to dissolved organic matter.

- ❖ **Calculation**
  - Two times the absorbance reading at 275 nm was subtracted from the reading at 220 nm to obtain absorbance due to NO_3^-.

- A standard curve was constructed by plotting absorbance due to NO_3^- against NO_3^--N concentration of standard.

- Using corrected sample absorbance, obtain sample concentrations was obtained directly from standard curve. Note: If correction value is more than 10% of the reading at 220 nm, do not use this method.

Annex 4 Argentometric method

Reagent

A) Potassium chromate indicator solution:

- ❖ 50 g K_2CrO_4 was dissolved in a litre of distilled water.
- ❖ $AgNO_3$ was added to the solution until a definite red precipitate was formed.
- ❖ The solution was allowed to stand for 12 h.
- ❖ The solution was filtered and dilute to 1 L with distilled water.

B) Standard silver nitrate titrant, 0.0141 N:

- ❖ 2.395g $AgNO_3$ was dissolved in distilled water and dilute to 1000 ml.
- ❖ Standardized against 0.0141 N NaCl solution. 1.00 ml = 500 µg Cl⁻ and stored in a brown bottle.

C) Standard sodium chloride, 0.0141 N:

- ❖ 824g NaCl (dried at 140^Oc) was dissolved in distilled water and dilute to 1000 ml, 1.00 ml = 600 µg Cl⁻

D) Special reagents for removal of interference:

i. Aluminum hydroxide suspension: dissolve 125 g Aluminum potassium sulphate or aluminium ammonium sulphate, in 1L distilled water. Warm to 60^0c and add 55 ml conc. NH_4OH slowly with stirring. Let stand about 1 hr transfer to a large bottle, and wash precipitate by successive additions, with thorough mixing and decanting with distilled water, until free from chloride.

ii. Phenolphthalein in indicator solution .

iii. Sodium hydroxide 1 N.

iv. Sulphuric acid, 1 N.

v. Hydrogen peroxide, 30%

Procedure argentometric method

1. The appropriate sample volume was measured for the indicated chloride range using the following table and transfer to a 250 ml Erlenmeyer flask.

Sample Volume ml	Alkalinity Range mg/L as $CaCO_3$
100	1-50
50	51-100
25	101-200
10	201-500

2. The total volume was brought to 100 ml with distilled water if the sample size was less than 100 ml.
3. A colour comparison blank was prepared by placing distilled water in a similar flask and the volume must be equal to that of the sample.
4. One ml potassium dichromate indicator solution was added to the blank and the sample and afterwards mixed.
5. Silver nitrate tartant was carefully added drop by drop to the colour comparison blank until the yellow colour changes to a brownish tine.
6. The ml silver nitrate titrant consumed was recorded
7. If the sample was turned yellow, gradually add silver nitrate titrate was gradually added from a burette. Shaken the flask continuously and continue adding the titrant until the sample turns the same.
8. The ml silver nitrate titrant consumed was recorded
9. Calculation

$$mg\ Cl/L = (A-B)\ \frac{X\ N\ X\ 35,450}{ml\ of\ sample}$$

Where

A= ml nitration for sample

B= ml titration for blank and

N= normality of silver nitrate

mg NaCl/L = (mg Cl/L) x 1.65

Note:

1. Titrate directly sample in the PH range 7 to 10. Adjust sample PH to 7 to 10 with H_2SO_4 or NaOH if not in this range

2. For highly collared samples clarification with aluminium hydroxide suspension is necessary

3. If sulphide, sulphite thiosulphate is present, add 1 ml hydrogen peroxide and stir for 1 minute.

Annex 5 Determination of BOD_5

Reagent and Apparatus

- BOD bottles; 300 ml capacity
- Incubator ($20^O C \pm 1^O C$)
- Stir plate, stir bar, ring stand, burette, 200 ml beaker, and burette holder
- 250 ml Graduated Cylinder
- Containment vessel, baking soda, wash beaker, solution beaker, and pipette for handling concentrated sulphuric acid.

a). Phosphate buffer solution: Dissolve 8.5g KH_2PO_4, 21.75 g K_2HPO_4 33.4g Na_2HPO_4 $7H_2O$, and 1.7g NH4Cl in about 500 ml distilled water and dilute to 1L. The PH should be 7.2 without further adjustment. Discard reagent (or any of the following reagent) if there is any sign of biological growth in the stock bottle.

b). Magnesium sulphate solution: Dissolve 22.5g MgS_4. $7H_2O$ in distilled water and dilute to1L.

c). Calcium chloride solution: dissolve 27.5g $CaCl_2$ in distilled water and dilute to 1L.

d). Ferric Chloride solution: dissolve 0.25g $FeCl_3$. $6H_2O$ in distilled water and dilute to 1L

e). Acid and alkali solutions, IN: for neutralization of caustic or acidic waste sample.

f). Sodium sulphite solution 0.025N: Dissolve 1.575g Na_2SO_3 in 1000 ml distilled water. This solution is not stable; prepare on the day of use.

g). Nitrification inhibitor: 2-chloro-6- (trichloro methyl) pyridine.

h).Glucose-glutamic acid solution: Dry reagent-grade glucose and reagent-grade glutamic acid at 103^OC for 1h. Add 0.150 g glucose and 0.150g glutamic acid to distilled water, dissolve and dilute to 1 1iter. Prepare fresh immediately before use.

Procedure

1. a) Using your best engineering judgment, determine the dilution for the glucose-glutamic acid control (BOD5= 198 mg/L) and for the raw and treated wastewater samples.

b) Check proposed dilutions with instructor before proceeding.

2. a) Prepare four dilution water blanks by filling each bottle with the dilution water/seed mixture.

b) Prepare four raw wastewater samples. Add the appropriate volumes of raw effluent, X1 ml, as determined in step 1. Add (300-X1) ml of dilution water. Make sure you shake the sample bottle thoroughly prior to pipetting sample. Samples for this lab can be pipetted directly from the sample bottle to assure that uniform samples are pipetted. Shake bottle between additions of raw wastewater to different BOD bottles.

c) Prepare four treated wastewater samples as in part b with appropriate volumes of treated wastewater, X2, and dilution water (300-X2) as determined in step 1. Make sure you shake the sample bottle thoroughly prior to pipetting sample as in part b above.

d) Prepare eight glucose-glutamic acid samples as in part b, with appropriate volumes of glucose-glutamic acid, X3, and dilution water (300-X3) as determined in step 1.

3. Add water to the reservoir at top of BOD bottle. Refill during incubation period to avoid total evaporation of water.

4. Determine the DO (day = 0) on one bottle of raw wastewater, treated wastewater, and dilution water blank, and two bottles of the glucose-glutamic acid control. (See DO determination below).

5. Put remaining samples in incubator (20^OC).

6. Repeat step three for days 3, 4, and 5.

Annex 6 Gravimetric method: Total suspended solids

Preparation of glass-fibber disk

1) Insert disk with wrinkled side up in filtration apparatus

2) Apply vacuum and wash disk with three successive 20-mL portions of distilled water continue suction to remove all traces of water.

3) Remove filter from filtration apparatus along with the Gooch crucible, and dry in an oven at 103 to 105^0C for 1 hour. If volatile solids are to be measured, ignite at 550 ± 50^0C for 15 minutes in a muffle furnace.

4) Cool in desiccators to balance temperature and weighing until a constant weight is obtained or until weight loss is less than 0.5 mg between successive weightings.

SAMPLE ANALYSES

I) Assemble filtering apparatus and filter by suction. The filter paper was wetted with small volume of distilled water to moisten it.

2). Filter a measured volume of well mixed sample through the glass fibre filter.

3). Wash with three successive 10-mL volumes of distilled water, allowing complete drainage between washings and continue suction for about 3 minutes after filtration is complete.

4) Remove the crucible and filter combination from the crucible adapter if a Gooch crucible is used.

5) Dry for at least I hour at 103 to 105^0C in an oven, cool in desiccators to balance temperature, and weigh.

6) Calculation

mg suspended solids/L = $\dfrac{(A-B)\times1000}{\text{ml sample}}$

   Where:

   A= Weight of filter + dried residue, mg

   B= Weight of filter, mg