

Adsorption Kinetics, Isotherm and Equilibrium Studies of Nitrate, Nitrite, Ammonia and Phosphate from Synthetic Aqueous Solutions Using Fish Scales as Adsorbent

Veeravalli Preetham¹, G. Nani Babu²,

¹PG student, Environmental Engineering and Management, SREE, Institute of Science & Technology, JNTU Kakinada.

²Assistant Professor, School of Renewable Energy and Environmental, Institute of Science & Technology, JNTU Kakinada.

Abstract— Out of total water present on earth 97.5% is salt water and only 2.5% water is fresh water which is used for several recreational purposes which is getting polluted due the disposal of waste water directly in to the fresh water bodies. The effluents that are disposed in to the water bodies are from different sources i.e. from industries which are the major cause for the pollution of water bodies which release heavy metals and chemical wastes and the other major reasons for water pollution are effluents from the households and disposal of agricultural wastes directly in to the water bodies without treatment where major contaminants are Nitrates, Nitrites, Ammonia, Phosphates. The present study mainly focus on removal of four major pollutants from the agriculture wastes i.e. Nitrates, Nitrites, Ammonia, and Phosphates using naturally available Adsorbents with the process known as Adsorption. The adsorbents used in this study are Fish Scales and Hemi melon peels and several studies has been done to measure the efficiency of the adsorbents for the removal of contaminants such as Equilibrium studies, Kinetic studies, Isotherm studies. After complete analysis and studies the obtained results showed that 95% to 98% of the contaminants has been removed effectively with the adsorbent dosage varying from 0.2gm to 0.6gms and at the contact time varying from 0 to 110 min respectively.

Keywords— Adsorbent, Kinetic studies, Isotherm studies, Fish scales, Contaminants, Adsorption

I. INTRODUCTION

Water bodies are increasingly endangered due to water pollution climate change and rising human needs and even though stringent legislation and regulations exist in many countries to reduce pollutants bolstered by anthropogenic activities that threaten natural water bodies. Because of the limited availability of high-quality water resources, reclamation and reuse of treated wastewater have become important in the sustainable management of this natural resource. The commonly observed contaminants such as Nitrates and heavy metals etc. are added to our water resources by various human activities including domestic sewerage; agricultural practices and industrial effluents. Most of the organic and inorganic contaminants of nitrogen undergo transformation into nitrates by the nature known as nitrogen cycle. Nitrate is essential compound for normal health & hygiene. It is normally found in food stuff, leafy vegetables & proteins including purified pyrimidine & urea. It exists in different forms viz: - Nitrate (NO₃⁻), Nitrite (NO₂⁻) Ammonia (NH₄⁺). The ultimate product of biological nitrification is Nitrate. In the agricultural sector increased use of nitrogen fertilizer is the major reason for nitrate contamination. In spite of this poorly treated or untreated human and animal wastes are also responsible for contamination. Non- point sources are also responsible for nitrate contamination and which are also hard to detect. Factors such as dissolved oxygen, electron donor availability, precipitation, thickness, source availability irrigation, ground water flow etc. are also control distribution of nitrate in ground water. Blue baby syndrome (Methemoglobinemia) especially occur in infants is due to increase in the concentration of nitrate in water & it is due to high solubility of nitrate in water. High concentration also causes gastric & intestinal cancer. According To WHO 45 ppm is the permissible limit of Nitrate for human consumption. According to W.H.O. the guideline value for nitrate nitrogen is 10 ppm (mg/L of nitrate –nitrogen). The Indian council of medical research has recommended a highest desirable level of 20ppm of nitrate-nitrogen in the drinking water while maximum permissible level recommended for drinking water is 50 ppm.

Phosphorus (P) is another major nutrient contaminant in water. It also enters water bodies through mining, industrial and agricultural activities, and sewage discharges. Excessive concentrations of which is defined as the enrichment of water bodies by nutrients and the consequent deterioration of quality due to the luxuriant growth of plants such as algae and its repercussions on the ecological balance of the waters affected. Although both nitrogen (N) and P are considered to be the limiting nutrients for eutrophication, some algae are efficient in the fixation of atmospheric N and hence P often becomes the potentially limiting nutrient in freshwaters. In advanced stages of eutrophication, dissolved oxygen can become depleted to dangerously low levels causing fish death when algae decay. The large algae biomass produced by eutrophication can also affect water treatment by blocking filters or passing through them causing bad odour and taste in treated water. Blue-green algae can produce compounds that are toxic to fish and other aquatic life. These conditions are also potentially risky to human health, resulting from consumption of shellfish contaminated with algal toxins or direct exposure to waterborne toxins. To control eutrophication the U.S. Environmental Protection Agency has recommended

that total P should not exceed 0.05 mg P/L in a stream at a point where it enters a lake or reservoir and should not exceed 0.1 mg/L in streams that do not discharge directly into lakes or reservoirs.

II. OBJECTIVES

1. To check the Fish Scales powder suitability as an adsorbent to remove phosphates, Nitrates, Nitrites and Ammonia.
2. The following parameters were taken to study the various parameters effects for the removal of Phosphates, Nitrates, Nitrites and Ammonia using Fish scales
 - Contact time (min)
 - Adsorbent dosage (gm)
 - Initial concentration of different compounds (mg/L)
3. To study the available biosorption kinetic suitability models for the removal of phosphates, Nitrates, Nitrites and Ammonia using Fish scales
 - Lagergren pseudo first-order
 - Pseudo second-order
4. To study the adsorption capacity and intensity using isotherms for the removal of phosphates, Nitrates, Nitrites and Ammonia using Fish scales.
 - Langmuir isotherm
 - Freundlich isotherm
 - Temkin isotherm

III. MATERIALS AND METHODOLOGY

A. Preparation of Adsorbent:

1. Fish Scales: Waste fish scales were obtained from the fish market near bus stand Kakinada. The fish scales are first washed with either tap water to remove dusts, dirt and other unwanted particles. The scales were further washed with distilled water then dried in an oven at 100°C until they became constant weight. The dried scales were ground with a mortar grinder, and the pulverized scales were sieved through mesh to retain on 850 μm particle size.



Fig. 1 Fish scales



Fig. 2 Fish scales powder

B. Preparation of Adsorbate:

1. Phosphate stock solution:

Phosphate stock solution were prepared by dissolving a known amount of 1.0g potassium dihydrogen orthophosphate (KH_2PO_4 , purity > 99 %) in 1000ml of distilled water. The aqueous solution was diluted with distilled water to obtain the PO_4^{3-} synthetic solution of desired concentration. The KH_2PO_4 agent used was of analytical grade and without further purification. All experiments employed distilled water.

2. Nitrate stock solution:

Nitrate stock solution was prepared by dissolving a known amount of 1.62g of potassium nitrate salt (KNO_3 , Fluka, purity > 99 %) in 1000ml of distilled water. The aqueous solution was diluted with distilled water to obtain the NO_3^- synthetic solution of desired concentration. The KNO_3 agent used was of analytical grade and without further purification. All experiments employed distilled water.

3. Nitrite stock solution:

Nitrite stock solution was prepared by dissolving a known amount of 1.62g of Sodium nitrite salt (NaNO_2 , purity > 99 %) in 1000ml of distilled water. The aqueous solution was diluted with distilled water to obtain the NO_2^- synthetic solution of desired concentration. The NaNO_2 agent used was of analytical grade and without further purification. All experiments employed distilled water.

4. Ammonia stock solution :

Ammonia stock solution was prepared by dissolving a known amount of 1g of Ammonium chloride salt (NH_4Cl , purity > 99 %) in 1000ml of distilled water. The aqueous solution was diluted with distilled water to obtain the NH_4^+ synthetic solution of desired concentration. The NH_4Cl agent used was of analytical grade and without further purification. All experiments employed distilled water.

C. Adsorption:

Adsorption of molecules often proceeds in two stages. The first state has all the characteristics of physisorption, but the state is unstable. In this state the molecule may re evaporate or it may stay on the surface long enough to transfer irreversibly into a chemisorbed state. The transition is rather dramatic, usually resulting in splitting of the molecule and adsorbing the individual atoms called dissociative chemisorption. The adsorption energies for the first phase are similar to physisorption of rear gases, but may contain additional contributions from the dipole and quadruple movements of the molecules. The dissociation stage can be explosive- literally. The heat of adsorption is given up suddenly, and can be imparted resulting atoms.

1. *Types of Adsorption:* At a molecular level, adsorption is due to attractive interactions between a surface and the species being adsorbed. Two types of adsorption are
 - 1.1 *Physisorption:* The dissolved molecules are small particles of adsorbate are attracted and attached to the surface of the adsorbent. In this type of adsorption binding is only by weak Vander Wall's force. It is also called Vander Wall's adsorption.
 - 1.2 *Chemisorption:* Adsorption in which the dissolved molecules are small particles are attracted and penetrated into the surface of the adsorbent is called chemisorption.

2. *Factors Affecting Adsorption*

- 2.1 *Contact time:* The removal efficiency of the pollutants get increased with an increase in contact time before the final equilibrium is reached. The total amount that got adsorbed when the equilibrium time reached reflects the maximum adsorption capacity of the adsorbent under the operating conditions.
- 2.2 *pH:* The pH of the solution was one of the important parameter that can control the adsorption process. The effect of pH also depends on the charge on the adsorbent surface.
- 2.3 *Concentration:* Different initial pollutant concentrations and a fixed concentration of biomass were used to calculate adsorption capacity. The initial and final concentrations of the solutions were measured by HACH apparatus or by the spectrophotometer. These data were used in the calculation of the adsorption capacity of the adsorbent.
- 2.4 *Adsorbent dose:* The adsorbent dosage is another important parameter because this determines the capacity of an adsorbent. The removal of pollutants gets increased with an increase in the adsorbent dosage. The effect of adsorbent dosage on adsorption can be studied by varying the amount of adsorbents and by keeping the other parameters as constant.
- 2.5 *Temperature and Pressure:* Increase of temperature and decrease of pressure will increase the extent of adsorption. This fact that heat gets absorbed in the process of adsorption can be implied by the Le Chatliers principles. As in the case of the heat of the solution the different heats of adsorption, viz, the differential and integral heat must be distinguished. If accurate values were to be obtained the results would probably throw much light on the adsorption phenomena.
- 2.6 *Surface area (particle size):* The adsorbents with smaller particle size have a higher ability in the adsorption process with large external surface. Therefore more metal ions could be removed than the large particles. The adsorption increases as the particle size decreases, because the surface area increases when the particle size decreases. Such an effect is probably due to the inability of the large ions to penetrate all the initial pore structure of the adsorbent.

D. Equilibrium Models

1. *Langmuir Isotherm:* The most widely used isotherm equation for modeling the equilibrium is the Langmuir equation which is valid for monolayer sorption on to a surface with a finite number of identical sites and is given by equation

$$q_e/q_m = bC_e / (1+bC_e)$$

This equation can be re arranged as

$$C_e/q_e = 1/(bq_m) + C_e/q_m$$

The plot is drawn between C_e/q_e and C_e , the slope ($1/q_m$) and intercept ($1/(bq_m)$) are calculated. Further analysis of Langmuir equation is made on the basis of separation factor, (R_L), which is defined as $R_L = 1/(1+bC_e)$.

2. *Freundlich Isotherm:* The empirical Freundlich model also considers mono molecular layer coverage of solute by the adsorbent. However, it assumes the adsorbent has a heterogeneous surface so that binding sites are not identical. This model takes the following form for a single component adsorption. Freundlich presented an empirical biosorption isotherm equation that can be applied in case of low and intermediate calculation ranges.

The Freundlich isotherm is given by

$$Q_e = K_f C_e^n$$

Where K_f represents the biosorption capacity when metal equilibrium concentration and n presents the degree of dependence of biosorption with equilibrium concentration taking logarithms on both sides, we get

$$\ln q_e = \ln K_f + n \ln C_e$$

3. *Temkin isotherm:* Temkin and Pyzhev isotherm describes the behavior of many biosorption systems on the heterogeneous surface and it is based on the following equation

$$q_e = RT \ln (A_T C_e) / b_T$$

The linear form of temkin isotherm can be re arranged as

$$q_e = (RT/b_T) \ln(A_T) + (RT/b_T) \ln(C_e)$$

$$Y = m X + c$$

E. Kinetic studies: For the kinetic theory, the experiment was conducted in batch studies under optimum conditions. These flasks were put in a orbital shaker at a constant rotational speed of 165 rpm at a different temperature and different time intervals. These conical flasks after shaking were filtered in centrifuge and analysed for metal concentration. Wide no. of models has been developed with their varying degrees of complexities to achieve the metal adsorption kinetics. In the present work, Pseudo first order and Pseudo second order kinetics were studied to analyse the adsorption kinetics for the given Nitrate Nitrite Ammonia and Phosphate using Hemi melon, Fish scales and combination of Fish scales and Neem powders as adsorbents.

1. *Pseudo-first order kinetic model:* The pseudo-first order kinetic model was presented by Lagergren, which is suited mostly for the solutes of lower concentrations. The pseudo-first order kinetic model can be expressed as

$$dq_t/dt = k_f (q_e - q_t)$$

Where q_t (mg/g) is the bio sorption intensity at time t;
 q_e (mg/g) is the bio sorption intensity at equilibrium time;
 k_f (min⁻¹) is the rate constant of the first-order bio sorption.

Integrating the equation and applying boundary conditions

$$q_t = 0 \text{ at } t = 0 \text{ \& } q = q_t \text{ at } t = t,$$

The resultant equation becomes,

$$\text{Log} (q_e - q_t) = - k_f t + \text{log} q_e$$

A plot of log (q_e - q_t) vs t will be a straight line with k_f as slope and log q_e as an intercept.

2. *Pseudo second order kinetics:* The pseudo-second order kinetic model was proposed by Ho and McKay can be used to explain the biosorption kinetics, if the rate of bio sorption is found to be a second order mechanism. The pseudo-second order model can be written as:

$$dq_t/dt = k_s (q_e - q_t)^2$$

where k_s is the rate constant for the pseudo second order system

For the boundary conditions $q_t = 0$ at $t = 0$ and $q = q_t$ at $t = t$;

The equation can be derived as

$$t/q_t = 1/q_e (t) + 1/(k_s q_e^2)$$

IV. ANALYSIS AND RESULTS

A. *Effect of contact time:* The effect of contact time was analysed by shaking 0.4g of given adsorbents in 200ml of Nitrate Nitrite Ammonia and Phosphate solution concentration 50 mg/L. This operation was carried out for different time intervals like 10, 20, 30, 40, up to 140 min. at constant agitation speed of 165 rpm. After each interval of time the sample is centrifuged, separated and the supernatant (clear liquid) is analysed for calculating the amount of Nitrate Nitrite Ammonia and Phosphate present in the solution. Analysis is stopped when the final concentration values obtained are same, which means there is no further adsorption indicating equilibrium time has reached.

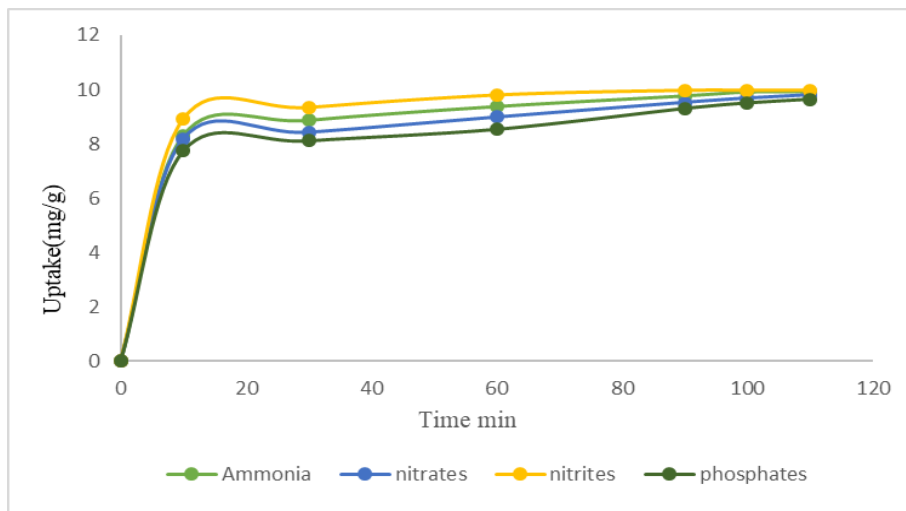


Fig. 3 Pollutants uptake capacities at varying time intervals

B. *Effect of Adsorbent dose:* 50 mg/L Nitrate Nitrite Ammonia and Phosphate solutions each of 200mg/L with a known amount of different adsorbent dosages ranging from 0.2 g to 0.6 g, is agitated with constant agitation speed 165

rpm for equilibrium time at constant temperature. The concentration of Nitrate Nitrite Ammonia and Phosphate for each individual samples are determined by HACH analyser and Spectrophotometer

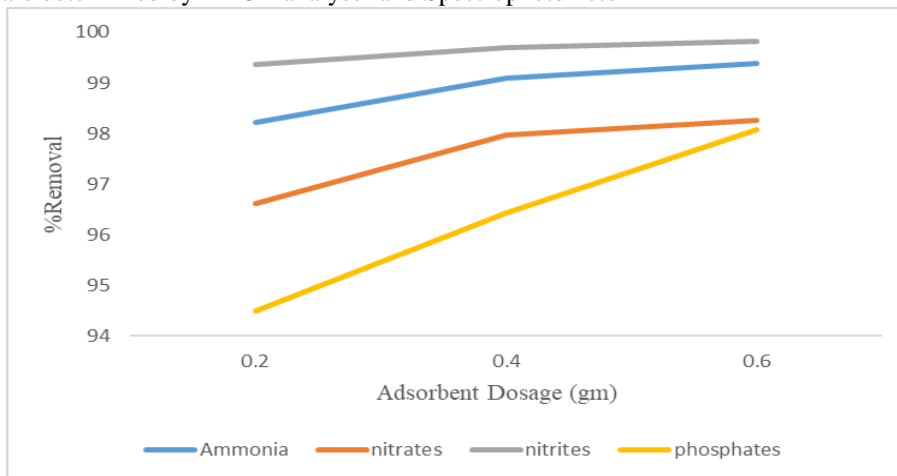


Fig. 4 Effect of adsorbent dose on Different contaminants adsorption

C. *Effect of Initial pollutants concentration (C_o):* Different pollutant concentrations of 30 mg/L, 40 mg/L, 50 mg/L, 60 mg/L and 70 mg/L were taken in 250 ml conical flasks each of 100ml. 0.4g of Fish scales powder is added to each of those beakers. The beakers were then rotated in a jar apparatus at 165 rpm for optimum contact time at room temperature. The samples further collected are centrifuged, separated and supernatant was analysed for the remaining amount of Nitrate Nitrite Ammonia and Phosphate present in the aqueous solution.

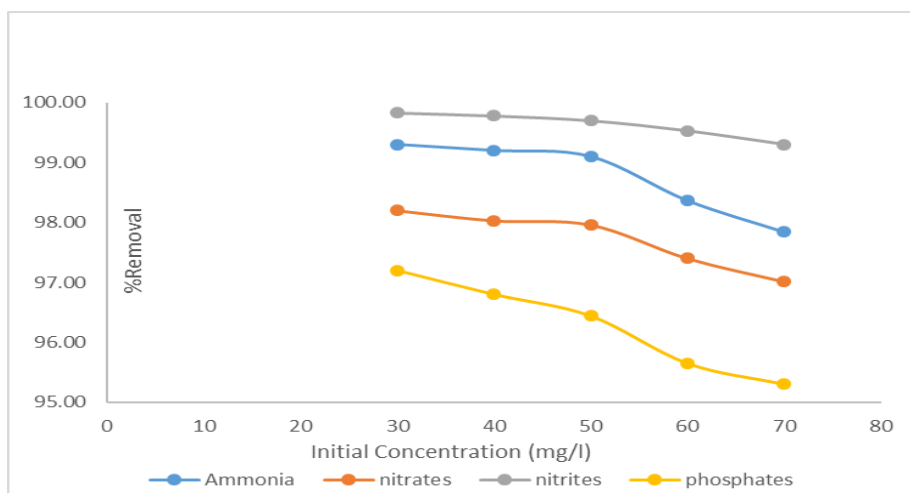


Fig. 5 Effect of varying concentration of Different pollutants

D. *Adsorption isotherms:*

1. *Langmuir Isotherm:*

TABLE 1
LANGMUIR ISOTHERM PARAMETERS

Pollutant	Equation	Q_{max} (mg/g)	b, L/mg	R^2
Nitrate	$(C_{eq}/Q_{eq}) = 0.0399 C_{eq} + 0.0689$	25.062	0.579	0.9870
Nitrite	$(C_{eq}/Q_{eq}) = 0.0645 C_{eq} + 0.0029$	15.503	22.241	0.9878
Phosphate	$(C_{eq}/Q_{eq}) = 0.0428 C_{eq} + 0.1096$	23.364	0.391	0.9923
Ammonia	$(C_{eq}/Q_{eq}) = 0.0597 C_{eq} + 0.0214$	16.750	2.790	0.9950

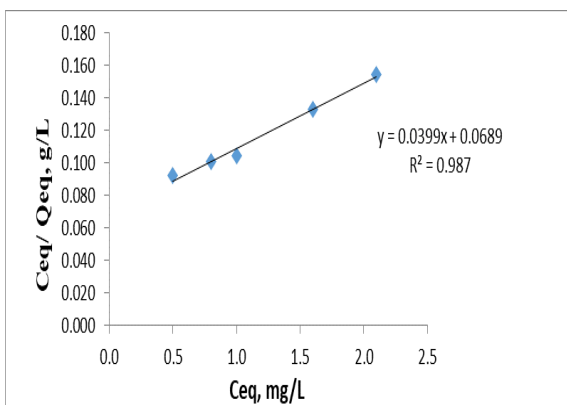


Fig.6. Langmuir Isotherm for %absorption of Nitrate

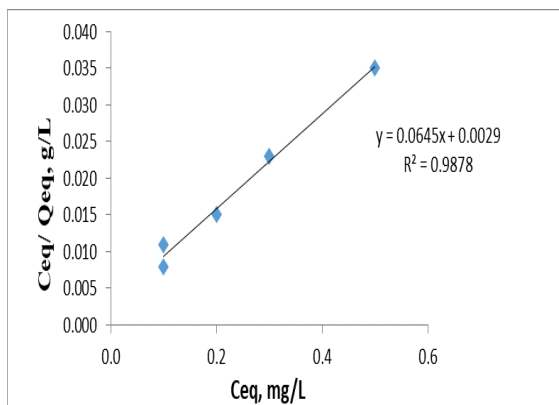


Fig.7. Langmuir Isotherm for %absorption of Nitrite

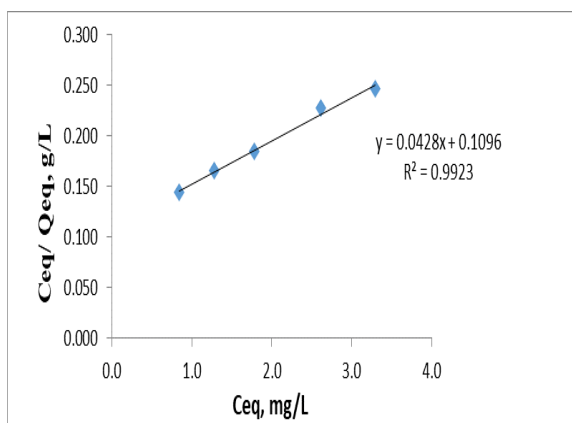


Fig.8. Langmuir Isotherm for %absorption of Phosphate

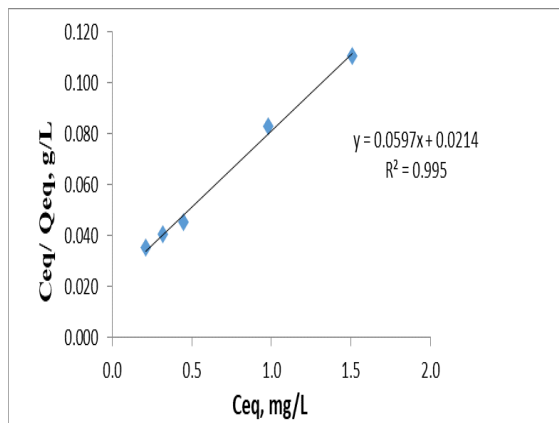


Fig.9. Langmuir Isotherm for %absorption of Ammonia

2. Freundlich Isotherm:

TABLE 2
 FREUNDLICH ISOTHERM PARAMETERS

Pollutant	Equation	K_f	M	R^2
Nitrate	$\log Q_{eq} = 0.5965 \log C_{eq} + 0.9581$	9.8090	1.676	0.9845
Nitrite	$\log Q_{eq} = 0.3724 \log C_{eq} + 1.2799$	18.819	2.735	0.9762
Phosphate	$\log Q_{eq} = 0.596 \log C_{eq} + 0.8199$	3.302	1.677	0.9949
Ammonia	$\log Q_{eq} = 0.3954 \log C_{eq} + 1.0826$	12.094	2.529	0.9435

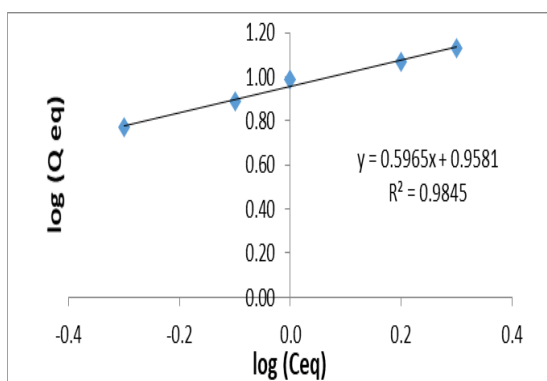


Fig.10. Freundlich Isotherm for %absorption of Nitrate

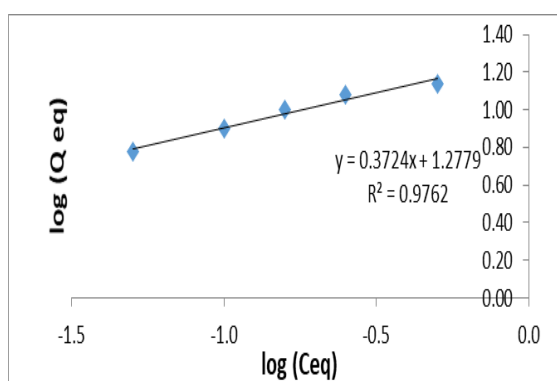


Fig.11. Freundlich Isotherm for %absorption of Nitrite

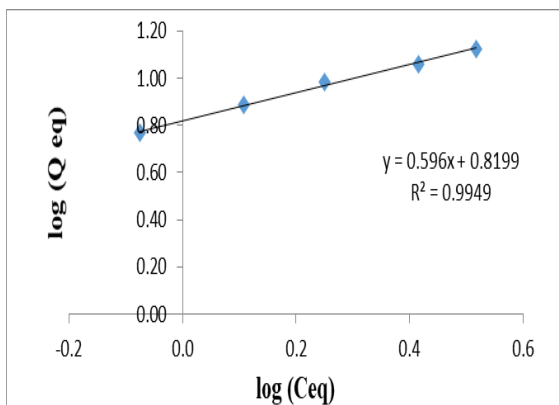


Fig.12. Freundlich Isotherm for %absorption of Phospates

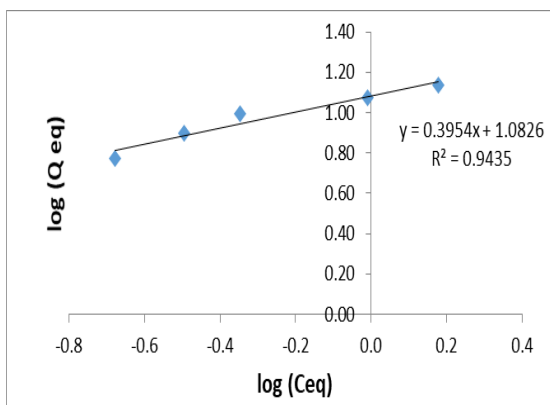


Fig.13. Freundlich Isotherm for %absorption of Ammonia

3. Temkin Isotherm:

TABLE 3
 TEMKIN ISOTHERM PARAMETERS

Pollutant	Equation	A_T , L/mg	b_T	R^2
Nitrate	$Q_{eq} = 0.3296 \ln C_{eq} - 1.5418$	0.807	7150.55	$R^2 = 0.9907$
Nitrite	$Q_{eq} = 0.570 \ln C_{eq} - 4.71$	0.885	4372.55	$R^2 = 0.9991$
Phosphate	$Q_{eq} = 0.3673 \ln C_{eq} - 1.2047$	0.737	6858.54	$R^2 = 0.9927$
Ammonia	$Q_{eq} = 0.5229 \ln C_{eq} - 3.1995$	0.849	4817.63	$R^2 = 0.9799$

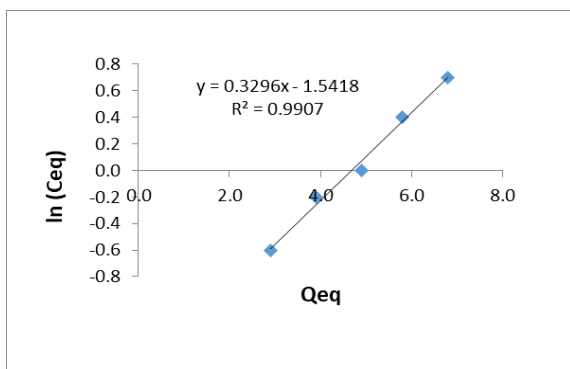


Fig.14. Temkin Isotherm for %absorption of Nitrate

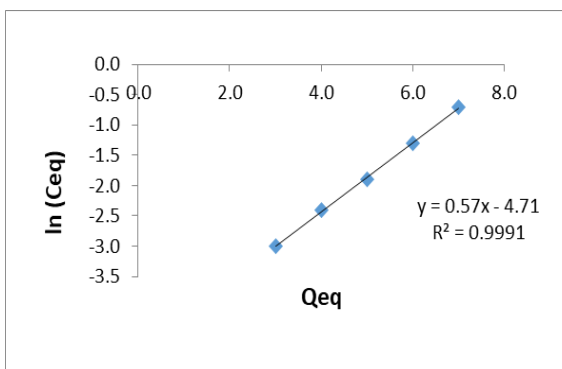


Fig.15. Temkin Isotherm for %absorption of Nitrite

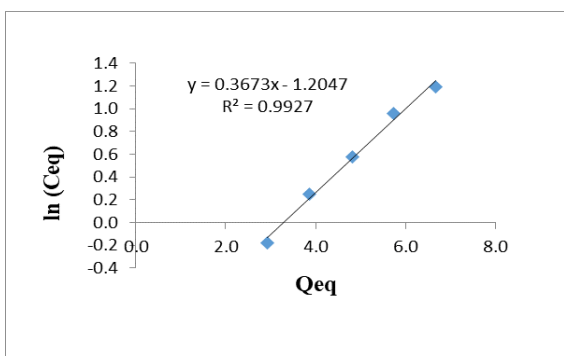


Fig.16. Temkin Isotherm for %absorption of Phosphate

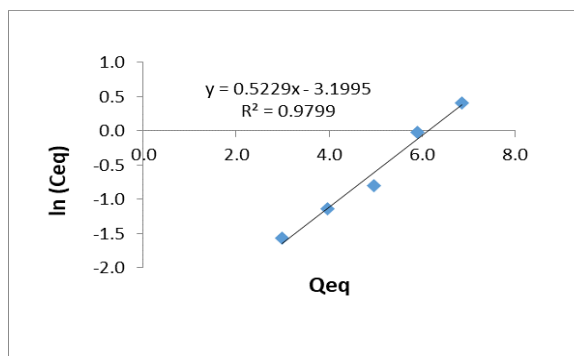


Fig.17. Temkin Isotherm for %absorption of Ammonia

- E. Adsorption kinetics
 1. Pseudo-first order kinetic model:

TABLE 4
FIRST ORDER EQUATION AND COEFFICIENTS

Kinetics	Pollutant	Model equation	R ²	Rate constant, K ₁
First order	Nitrate	$\log(Q_{eq}-Q_t) = -0.027 t - 1.0125$	0.7284	0.0621 min ⁻¹
First order	Nitrite	$\log(Q_{eq}-Q_t) = -0.033 t - 0.7652$	0.8473	0.0759 min ⁻¹
First order	Phosphate	$\log(Q_{eq}-Q_t) = -0.0275 t - 1.1091$	0.7043	0.0633 min ⁻¹
First order	Ammonia	$\log(Q_{eq}-Q_t) = -0.0308 t - 0.9549$	0.776	0.0709 min ⁻¹

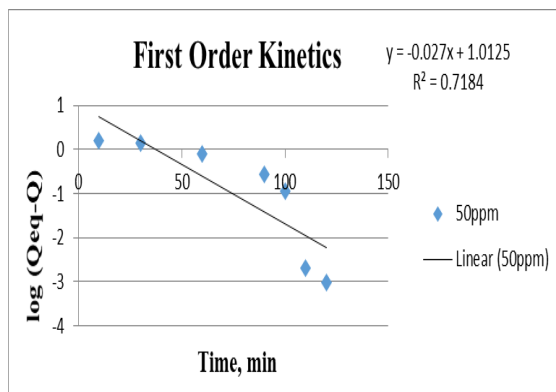


Fig.18. First order kinetics of Nitrate on %absorption

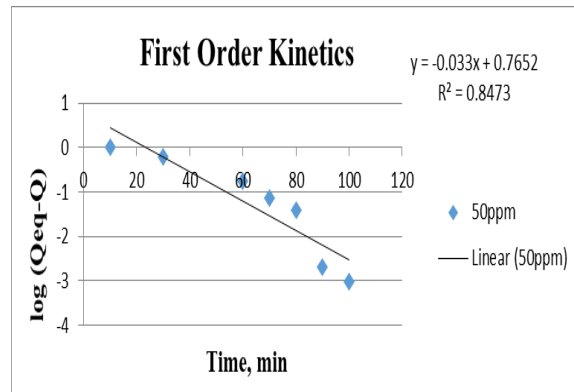


Fig.19. First order kinetics of Nitrite on %absorption

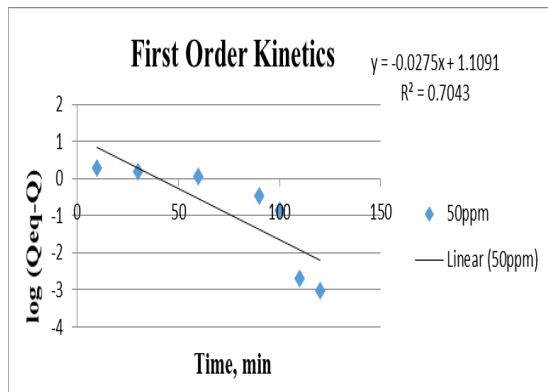


Fig.20. First order kinetics of Phosphates on %absorption

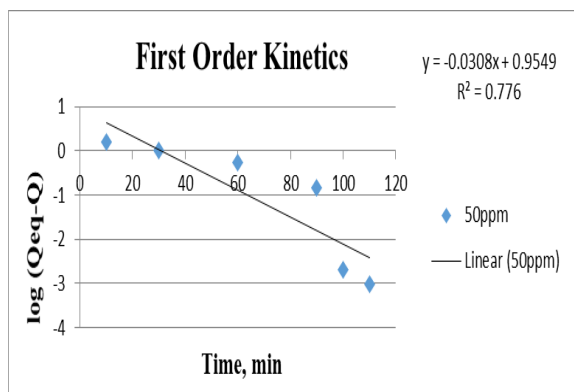


Fig.21. First order kinetics of Ammonia on %absorption

2. Pseudo-first order kinetic model:

TABLE 5
SECOND ORDER EQUATION AND COEFFICIENTS

Kinetics	Pollutant	Model equation	R ²	Rate constant, K ₂
Pseudo Second order	Nitrate	$t/Q_t = 0.0987 t + 0.4869$	0.9983	0.0200 gm.(mg.min) ⁻¹
Pseudo Second order	Nitrite	$t/Q_t = 0.0984 t + 0.1947$	0.9999	0.0497 gm.(mg.min) ⁻¹
Pseudo Second order	Phosphate	$t/Q_t = 0.0994 t + 0.6247$	0.9966	0.0159 gm.(mg.min) ⁻¹
Pseudo Second order	Ammonia	$t/Q_t = 0.098 t + 0.3635$	0.9992	0.0264 gm.(mg.min) ⁻¹

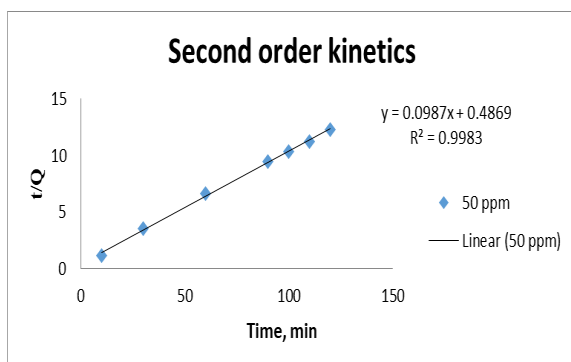


Fig.22. Second order kinetics of Nitrate on %absorption

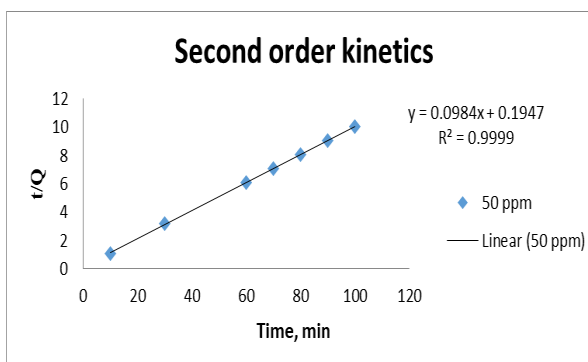


Fig.23. Second order kinetics of Nitrite on %absorption

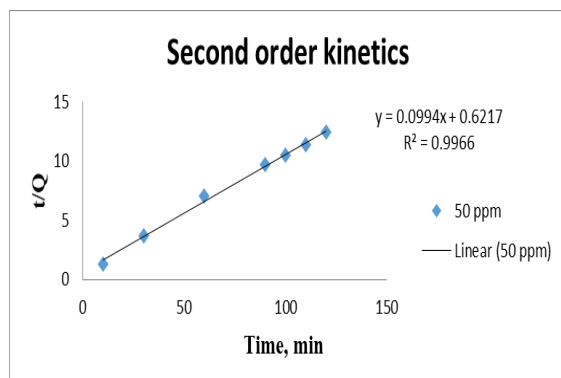


Fig.24. Second order kinetics of Phosphates on %absorption

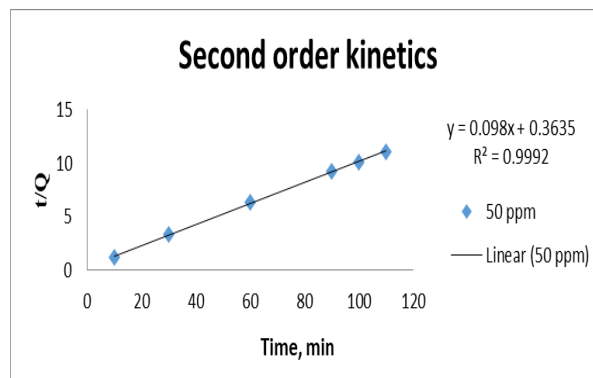


Fig.25. Second order kinetics of Ammonia on %absorption

V. CONCLUSIONS

After completion of different studies and final assessment of this study resulted in to the final conclusions which are as follows:

- The percentage removal efficiency of Nitrates with Fish Scales as adsorbent resulted as 97.76%.
- The percentage removal efficiency of Nitrites with Fish Scales as adsorbent resulted as 99.70%.
- The percentage removal efficiency of Phosphates with Fish Scales as adsorbent resulted as 99.10%.
- The percentage removal efficiency of Ammonia with Fish Scales as adsorbent resulted as 96.44%.
- The results Obtained by Fish Scales as Adsorbent are phenomenal because the uptake abilities of scales from different fish species should be similar and most fish scales contain significant portions of organic protein (collagen), and the structure of collagen shows that it contains the possible functional groups, such as phosphate, carboxyl, amine and amide, that are involved in the adsorption of different pollutants
- Langmuir, Freundlich and Temkin isotherms were observed to fit the equilibrium data and the model parameters were calculated at room temperature using linearized equations which showed that Langmuir isotherm model ($R^2 \approx 1$) is in good agreement with the experimental data as compared to Freundlich and Temkin models
- Kinetics data were best modeled by a pseudo second order kinetics equation since the second order constant k_2 is very less when compared to the first order constant k_1 .
- Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants

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