



ISOTHERM AND KINETICS STUDY FOR THE ADSORPTION OF NITRATE AND PHOSPHATE IONS FROM AQUEOUS SOLUTIONS USING FUME DUST FROM ELECTRIC ARC FURNACE

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ABSTRACT

The removal of nitrate and phosphate ions from wastewater has a major concern nowadays. Excessive intake of nitrates by humans in drinking water and food can induce methemoglobinemia and stomach cancer. Therefore, it is necessary to remove nitrate and phosphate ions from wastewater. Adsorption using nano-adsorbents becomes a promising method for phosphate and nitrate removal from wastewater because of their availability, low cost, stability, large surface area to volume ratio and high adsorption capacity. In this research, an industrial waste from El Masryeen Steel factory which is Fume Dust from an Electric Arc Furnace (FD-EAF) is used for simultaneous removal of nitrate and phosphate ions from an aqueous solution. The Maximum nitrate and phosphate ions removal percents 52.74 and 92.38 %, respectively using FD-EAF waste are achieved under these conditions; pH~7, initial nitrate ion concentration = 6 mg/L, initial phosphate ion concentration = 1 mg/L, adsorbent dose = 6.5 g/L and contact time = 90 min. Simultaneous adsorption of nitrate and phosphate ions are well described by pseudo second order kinetic model ($R^2 = 0.995$) with respect to nitrate and ($R^2 = 0.955$) with respect to phosphate as they fit with the experimental results better than the pseudo first order kinetic model ($R^2 = 0.884$) with respect to nitrate and ($R^2 = 0.868$) with respect to phosphate. The rate limiting step is determined using intraparticle diffusion model and Byod plot. Isotherm models are studied for single component and multi-component adsorption systems. For two parameters isotherm model; Langmuir isotherm ($R^2 = 0.989$) fits with the experimental results in case of single phosphate adsorption. In case of single nitrate adsorption from aqueous solutions; Langmuir isotherm ($R^2 = 0.9957$) fits with the experimental results. For three parameters isotherm; Dubinin-Radushkevich isotherm and ($R^2 = 0.977$) and ($R^2 = 0.9849$) for single phosphate and single nitrate ion removal from aqueous solutions, respectively fit with the experimental results better than BET isotherm model.

Keywords: nitrate; phosphate; adsorption; isotherm; kinetics.

INTRODUCTION

The removal of nitrate and phosphate from wastewater has a major concern nowadays [1]. Excessive intake of nitrates by humans in drinking water and food can induce methemoglobinemia and stomach cancer [2], [3]. Nitrates contaminations are due to agricultural runoffs besides untreated municipal disposal, domestic and industrial wastes [4]. High levels of nitrogen are the main reason for Eutrophication of water phenomenon [5]. Eutrophication can be defined as "the excessive increase in the nutrients concentration in water which results in harmful effects to the water ecosystem due to the excessive growth of algae and aquatic plants [6], [7]. The growth of these plants leads to reduction in the amount of dissolved oxygen which results in many problems like reduction in the production of sea food also, algae growth results in taste and odor problems and fish death because of toxics that are generated by algae in water [1]. Hence, Eutrophication phenomenon has serious damage effect on human health and to the water ecological system [8]. Decreasing or limiting the concentration of nitrogen is

considered to be the most important key factor for controlling Eutrophication phenomenon [1]. Nitrate and phosphate removal from aqueous solutions can be achieved by various methods, including biological denitrification, ion exchange, chemical reduction and Reverse Osmosis (RO) process using semi-permeable membrane [7], [8]. Biological treatment usually requires biomass waste disposal which is produced in sufficient amounts. Also, it usually requires an external organic carbon source in order to reduce nitrate to nitrogen gas when organic substances in aqueous solutions are insufficient [9]. Ion exchange treatment method produces concentrated nitrate rejection and exhausted resins [10]. The RO treatment process removes many contaminants including nitrate because, membranes don't exhibit varying selectivity for any given contaminant [10]. The RO disadvantages are high operating costs, complexity during operation and production of significant waste streams [11]. Figure-1 represents a comparison between different technologies used for nitrate and phosphate removal from wastewater.

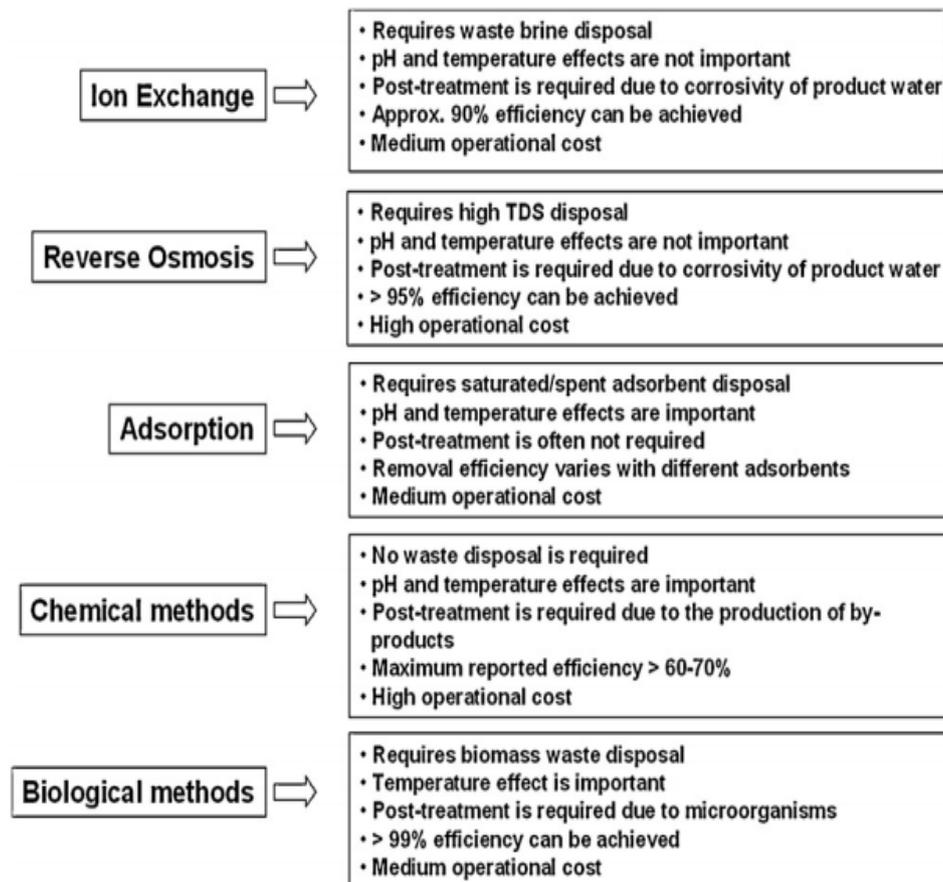


Figure-1. Comparison between different nutrients removal technologies [12].

Fume Dust is an industrial waste from El Masryeen Steel factory produced from an Electric Arc Furnace (EAF) in amount of 12 Kg per ton of steel produced. Landfill of FD-EAF waste results in harmful effects on human, animals and plants [13]. FD-EAF contains relatively high percents of hematite (Fe_2O_3) and ZnO which are almost 42 and 26 %, respectively according to the XRF analysis of FD-EAF. Therefore, Zn and Fe which are valuable metals can be recovered from this waste through two methods; the first method is the leaching method which involves chemical reaction between leachable elements in FD-EAF with acid solution. Although this method is less energy required, the process results another waste [13]. The second method is treating the FD-EAF with pyrometallurgy process which involves reaction of FD-EAF with active carbon at high temperatures [13]. This method is better than leaching because; it doesn't produce any more waste materials as happened with leaching method [13]. The main aim of this research is investigating whether Fume Dust from Electric Arc Furnace (FD-EAF) can be used for simultaneous removal of phosphate and nitrate ions from an aqueous solution.

ADSORPTION KINETICS

Adsorption kinetics plays a vital role in defining the acceptance rate of the solute and the time needed for adsorption. It is used to value and assess the adsorbent

performance and to examine the mass transfer mechanisms of adsorption. The kinetics are studied at several time intervals for adsorbing the solute by applying Pseudo First Order (PFO) and Pseudo Second Order (PSO) kinetic models [14].

Adsorption kinetics consist of curve or line which describes the rate of retention or immunity of solute molecules from an aqueous medium to solid-phase interface at constant adsorbents dose, pH, temperature and concentration. The experimental data fitted to the kinetic models PFO and PSO which are described by the following equations (1) and (2) [15], [16]:

$$\text{PFO: } \text{Log}(q_e - q) = \text{Log}(q_e) - \frac{k_1 \cdot t}{2.303} \quad (1)$$

$$\text{PSO: } \frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \left(\frac{1}{q_e}\right) \cdot t \quad (2)$$

The initial adsorption rate (mg/L.min) is described by the following equation (3) [17]:

$$h = k_2 \cdot q_e^2 \quad (3)$$

Where q_e and q_t are the amounts of nitrate adsorbed by adsorbent at equilibrium and at time (t), respectively. k_1 , k_2 are rate constants for PFO and PSO, respectively.



During adsorption, the rate controlling step is observed by applying the Intra-Particle diffusion model. For the adsorption of a solute to the adsorbent from the solution, four major steps take place [18]. Firstly, the bulk movement or the mass transfer of the solute simultaneously when the adsorbent is added to the solution. This step is too rapid and is not counted when designing the kinetic systems. Film diffusion is the second step which includes the slow drive of solute particles on the adsorbent's surface from the boundary layer. The third step (intra-particle diffusion) is the pore diffusion which includes the movement of the solute particles to the pores from the adsorbent's surface. The fourth step includes a quick solute attachment on the active sites of the pores [18]. The intraparticle diffusion model could be represented by the following equation (4) [19], [16]:

$$qt = k_{\text{diffusion}} * T^{0.5} + C_i \quad (4)$$

Where; qt is the amount of nitrate adsorbed at time (t) and C_i is the thickness of layer and $k_{\text{diffusion}}$ is the adsorption rate constant of intraparticle diffusion model.

The graph is plotted between qt and time shows a linear function. The Intra-Particle diffusion model controls the process of adsorption if the line plotted passes across the origin. However, mostly the line does not pass across the origin and is divided giving numerous linear sections [18]. These several sections resemble various mechanisms controlling the process of adsorption. If the adsorption system is described by weak mixing, low concentration, and small solute particles, film diffusion will be considered as the rate limiting step. Or else, the intraparticle diffusion model controls the adsorption process [18].

Byod plot is used to predict the actual limiting step involved in the adsorption process by plotting the B_t values vs. time (t) [20].

It is assumed that the diffusion of solute is highly affected by the boundary layer enclosing the adsorbent. This effect is determined using the following equation (5) [20]:

$$F = \frac{qt}{q_{\text{max}}} \quad (5)$$

Where; the q_{max} is the maximum adsorbed amount of nitrate and F is the fraction of the adsorbed nitrate at any time (t).

The B_t values could be calculated at different contact times through the following equation (6) [20]:

$$Bt = -0.4977 - \ln(1 - F) \quad (6)$$

Where; Bt is the mathematical function of F .

SINGLE COMPONENT ADSORPTION ISOTHERM MODELS

The adsorption isotherm is a curve that relates the equilibrium solute concentration on the adsorbent's surface (q_e) to the contacted solute concentration in the

liquid (C_e) [21]. It is usually used to characterize of porous solid, design process of adsorption and calculate the specific surface area of adsorbent [21].

Single component adsorption isotherm models consists of five types based on the number of constants in each isotherm model; One-Parameter Isotherm such as Henry's Isotherm, Two-Parameter Isotherm such as Langmuir Isotherm, Freundlich Isotherm, Halsey isotherm and Dubinin-Radushkevich Isotherm, Three-Parameter Isotherms such as Koble-Carrigan Isotherm and Langmuir-Freundlich Isotherm, Four-Parameter Isotherms such as Fritz-Schlunder Isotherm and Five-Parameter isotherm [22].

One-Parameter Isotherm

Henry's Isotherm

This is the simplest adsorption isotherm in which the amount of surface adsorbate is proportional to the partial pressure of the adsorptive gas [4]. This isotherm model describes an appropriate fit to the adsorption of adsorbate at relatively low concentrations such that all adsorbate molecules are secluded from their nearest neighbours [22]. Thus, the equilibrium adsorbate concentrations in the liquid and adsorbed phases are related to the linear expression as represented in equation (7):

$$q_e = K_{HE} * C_e \quad (7)$$

Where; " q_e " is amount of the adsorbate at equilibrium (mg/g), " K_{HE} " is Henry's adsorption constant, and " C_e " is equilibrium concentration of the adsorbate on the adsorbent.

Two-Parameter Isotherm Models

Langmuir

Langmuir isotherm model is concept of the monomolecular adsorption on homogeneous surfaces. It is represented by the following equation (8) [23] [14]:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m}\right) * C_e + \frac{1}{q_m * K_L} \quad (8)$$

Where C_e and q_e represent the concentrations of nitrate at equilibrium (mg/L) in solution and in solid phase, respectively. q_m is the maximum monolayer adsorption capacity (mg/g) and K_L is the Langmuir constant which indicates the adsorption energy (L/mg). The values of q_m and K_L can be determined from the linear plot of C_e/q_e versus C_e .

Freundlich

This model is used to give information of the adsorption characteristics for the heterogeneous surface. Freundlich isotherm is a two-parameter isotherm model and it is represented by the following equation (9) [23] [14]:



$$\text{Log } q_e = \text{Log } KF + \frac{1}{n} * \text{Log } C_e \quad (9)$$

Where K_F (L/mg) and n are the Freundlich constants that indicate the adsorption capacity and adsorption intensity, respectively.

Halsey

Halsey isotherm is used for multilayer adsorption system and heterogeneous surfaces for adsorption of metal ions at a relatively large distance from the surface [25]. Halsey isotherm is a two-parameter isotherm model and it is represented by the following equation (10) [23] [14]:

$$\text{Ln } q_e = \frac{1}{n_H} * \text{Ln } K_H - \frac{1}{n} * \ln \frac{1}{C_e} \quad (10)$$

Where K_H and n_H are the Halsey constants.

Dubinin-Radushkevich

This model uses Gaussian energy distribution to represent the adsorption mechanism onto heterogeneous surfaces. This model is applicable for physical adsorption and it is a temperature dependent model. This model is only applicable for intermediate concentration range of pollutant. Dubinin-Radushkevich isotherm model is represented by the following equations (11) and (12) [23], [14]:

$$\text{Ln } q = \text{Ln } q_{\max} - \beta R^2 T^2 \text{Ln}^2 \left(1 + \frac{1}{C}\right) \quad (11)$$

$$E = \frac{1}{\sqrt{2\beta}} \quad (12)$$

Where; q_{\max} (mg/g) is the maximum adsorption capacity, β (mol^2/kJ^2) is a constant related to adsorption energy and E is the free energy per molecule of adsorbate (kJ). The value of E can be used to differentiate between types of adsorption processes as follows [23], [14];

- If the value of E is less than 8 kJ/mol so, this will be a physical adsorption.
- If the value of E is greater than 8 kJ/mol and less than 16 kJ/mol so, this will be a chemical adsorption or ion exchange.
- If the value of E is greater than 16 kJ/mol so, this will indicate that particle diffusion governs the reaction.

Brunauer-Emmett-Teller (BET)

This isotherm model is used to represent the multilayer adsorption mechanism. BET isotherm model for liquids is represented by the following equation (13) [23], [14];

$$q_e = \frac{q_s \cdot C_{BET} \cdot C_e}{(C_s - C_e) * [1 + (C_{BET} - \frac{C_e}{C_s})]} \quad (13)$$

Where; C_{BET} (L/mg) is the BET adsorption isotherm constant, C_s (mg/L) is the contaminant saturation

concentration and q_s (mg/g) is the theoretical isotherm saturation capacity.

Three-Parameter Isotherm Models

Koble-Carrigan

The Koble-Carrigan isotherm model is a combination of Langmuir and Freundlich isotherms which is used to represent the equilibrium adsorption data. Koble-Carrigan isotherm is a three-parameter isotherm model and it is expressed by the following equation (14) [23], [14];

$$q_e = A \cdot C_e \frac{A \cdot C_e}{1 + B \cdot C_e^2} \quad (14)$$

Where A ($\text{L}^n \cdot \text{mg}^{1-n}/\text{g}$), B (L/mg) ^{n} and n are the Koble-Carrigan constants, n is exponent that lies between 0 and 1 and q_e is the amount of pollutant which is adsorbed on the sorbent at equilibrium (mg/g).

Langmuir-Freundlich

Langmuir-Freundlich isotherm includes the knowledge of adsorption heterogeneous surfaces. It describes the distribution of adsorption energy onto heterogeneous surface of the adsorbent. At low adsorbate concentration this model becomes the Freundlich isotherm model, while at high adsorbate concentration it becomes the Langmuir isotherm. Langmuir-Freundlich isotherm can be expressed as follows in equation (15) [23], [14]:

$$q_e = \frac{q_{MLF} (K_{LF} \cdot C_e)^{M_{LF}}}{1 + (K_{LF} \cdot C_e)^{M_{LF}}} \quad (15)$$

Where; " q_{MLF} " is Langmuir-Freundlich maximum adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$), " K_{LF} " is equilibrium constant for heterogeneous solid, and " M_{LF} " is heterogeneous parameter and it lies between 0 and 1. These parameters can be obtained by using the nonlinear regression techniques [22].

Four-Parameter Isotherm Models

Fritz-Schlunder Isotherm

Fritz and Schlunder derived an empirical equation which can fit a wide range of experimental results because of the large number of coefficients in the isotherm [14], [18]. This isotherm model has the following equation (16) [22]:

$$q_e = \frac{q_{mFS} \cdot (K_{FS} \cdot C_e)}{1 + q_m \cdot C_e^{M_{FS}}} \quad (16)$$

Where; " q_{mFS} " is Fritz-Schlunder maximum adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$), " K_{FS} " is Fritz-Schlunder equilibrium constant ($\text{mg} \cdot \text{g}^{-1}$), and " M_{FS} " is Fritz-Schlunder model exponent.

If $M_{FS} = 1$, then the Fritz-Schlunder model becomes the Langmuir model, but, for high adsorbate concentrations, the model reduces to Freundlich model.



Fritz-Schlunder isotherm parameters can be determined by nonlinear regression analysis [22].

Five-Parameter Isotherm Model

Fritz and Schlunder developed a five-parameter empirical model that is capable of simulating the model variations more precisely for application over a wide range of equilibrium data [22]. The isotherm model has the following equation (17) [22]:

$$q_e = \frac{1m.FSs.K1.Ce^{\alpha FS}}{1+K2.Ce^{\beta FS}} \quad (17)$$

Where; “ q_{mFS} ” is Fritz-Schlunder maximum adsorption capacity (mg g^{-1}) and K_1 , K_2 , α_{FS} and β_{FS} are Fritz-Schlunder parameters.

This isotherm is valid only in the range of L_{FS} value less than or equal to 1.

This model approaches Langmuir model while the value of both exponents α_{FS} and β_{FS} equals 1 and for higher adsorbate concentrations it reduces to Freundlich model [22].

MULTI-COMPONENT ADSORPTION ISOTHERM MODELS

Due to the presence of high concentrations of multi-pollutants in wastewater, the multi-component adsorption concept has a great importance in wastewater treatment processes nowadays. This is because, the competitive interactions occurred between the pollutants present in the wastewater can't be represented by single component isotherm models. Also, competitive interactions among pollutant molecules have a large effect on the overall adsorption process. Extended Langmuir isotherm, Extended Freundlich isotherm and Modified Langmuir isotherm models can be used to illustrate multi-component adsorption systems [26].

Extended Freundlich

This model is used to represent multilayer adsorption processes on heterogeneous surfaces in case of interaction occurrence between adsorbed pollutant molecules. Extended Freundlich isotherm model is represented by the following equations (18) and (19) [26]

$$q_{e,1} = \frac{K_{F,1} \cdot C_{e,1}^{\left(\frac{1}{n_1}\right)+X_1}}{C_{e,1}^{X_1} + y_1 \cdot C_{e,2}^{Z_1}} \quad (18)$$

$$q_{e,2} = \frac{K_{F,2} \cdot C_{e,2}^{\left(\frac{1}{n_2}\right)+X_2}}{C_{e,2}^{X_2} + y_2 \cdot C_{e,1}^{Z_2}} \quad (19)$$

Where $q_{e,1}$ and $q_{e,2}$ in (mg/g) are the equilibrium adsorption capacity for components 1 and 2, respectively. $C_{e,1}$ and $C_{e,2}$ in (mg/L) are the equilibrium concentrations of components 1 and 2, respectively. $K_{F,1}$ and $K_{F,2}$ are the Freundlich constants for components 1 and 2, respectively. n_1 and n_2 are the adsorption intensities for components 1 and 2 obtained from the experimental data of individual Freundlich isotherms.

Extended Langmuir

This model is developed according to the following assumptions; Equal availability of sites to all adsorbates, the adsorbent has uniform active sites which have uniform adsorption energy, no competitive interaction occurred among pollutants in the multi-component system and the adsorbent adsorbs all pollutant molecules on identical active sites. Extended Langmuir isotherm model for multi-component system is represented by the following equation (20) [26];

$$q_{e,i} = \frac{q_{m,i} \cdot b_{L,i} \cdot C_{e,i}}{1 + \sum_{j=1}^N (b_{L,j} \cdot C_{e,j})} \quad (20)$$

Where; $q_{e,i}$ (mg/g) is the adsorption capacity of component i at Equilibrium, $C_{e,i}$ (mg/L) is the concentration of component i at Equilibrium, $b_{L,i}$ (L/mg) is the Langmuir constant for component i , $q_{m,i}$ (mg/g) is the monolayer adsorption capacity for component i and N is the total number of components in the solution.

Extended Langmuir isotherm model for binary system is represented by the following equations (21) and (22) [26];

$$q_{e,1} = \frac{q_{m,1} \cdot b_{L,1} \cdot C_{e,1}}{1 + b_{L,1} C_{e,1} + b_{L,2} C_{e,2}} \quad (21)$$

$$q_{e,2} = \frac{q_{m,2} \cdot b_{L,2} \cdot C_{e,2}}{1 + b_{L,1} C_{e,1} + b_{L,2} C_{e,2}} \quad (22)$$

Where the values of $q_{m,1}$, $b_{L,1}$, $q_{m,2}$ and $b_{L,2}$ parameters can be calculated using solver function of non-linear regression in Microsoft Excel program.

Modified Langmuir

This model explains how the interaction among pollutant molecules occurs in a solution. Therefore, this model includes the interaction factor which describes the adsorption process nature and illustrates the competitive influence of pollutant molecules in the solution. Modified Langmuir isotherm model is represented by the following equation (23) [26];

$$q_{e,i} = \frac{q_{m,i} \cdot b_{L,i} \cdot \left(\frac{C_{e,i}}{\eta_{L,i}}\right)}{1 + \sum_{j=1}^N (b_{L,j} \cdot \left(\frac{C_{e,j}}{\eta_{L,j}}\right))} \quad (23)$$

Where; $q_{e,i}$ (mg/g) is the adsorption capacity of component i at equilibrium, $C_{e,i}$ (mg/L) is the concentration of component i at equilibrium, $b_{L,i}$ (L/mg) is the Langmuir constant for component i which is obtained from experimental data of single Langmuir isotherms, $q_{m,i}$ (mg/g) is the monolayer adsorption capacity for component i , N is the total number of components in the solution and $\eta_{L,i}$ is the interaction factor which depends on the other component concentration. The values of interaction factors $\eta_{L,i}$ and $\eta_{L,j}$ were calculated by using solver function for non-linear regression on Microsoft Excel program.



MATERIALS

Fume Dust from Electric Arc Furnace (FD-EAF) is a waste from El Masryeen Steel factory with amount of 12 Kg per ton of steel. All chemicals used in this study are analytical grade reagents including, Sodium Hydroxide (NaOH) and Hydrochloric acid (HCl). All of these reagents are purchased from Alahram Laboratory Chemicals Company, Egypt except Magnesium Nitrate Hexahydrate $[Mg(NO_3)_2 \cdot 6H_2O]$ and Sodium Phosphate Mono Basic (Na_2HPO_4) are purchased from Alpha Chemika Company, India. Preparation of all solutions is performed using distilled water.

BATCH EXPERIMENTS

Batch experiments are performed for nitrate ion removal using pH from 2.8 to 12 which is adjusted by using 0.1 M NaOH and 0.1 M HCl solutions. Initial nitrate ion concentration is prepared using $Mg(NO_3)_2 \cdot 6H_2O$ while initial phosphate ion concentration is prepared using Na_2HPO_4 . Experiments are performed in glass conical flasks which are shaken vigorously at 180 rpm using laboratory shaker. The concentration of nitrate ion is measured using a UV/VIS spectrophotometer (UV-5100, Shanghai Metash Instruments Company) and phosphate ion is measured by Water Conditioning Photometer device with kits. The removal efficiency is calculated by the following equation (24):

$$RE\% = [(C_0 - C) / C_0] * 100 \quad (24)$$

Where C_0 and C are initial and final concentrations in mg/L, respectively.

PARAMETERS OF BATCH EXPERIMENTS FOR FD-EAF INDUSTRIAL WASTE

The parameters of the batch adsorption experiments using AARS-nZVI synthesized adsorbent and FD-EAF waste are chosen based on certain criteria as represented in this section.

Initial pH of Solution

Initial pH is chosen between 2 to 12 in order to study the effect of pH on the nitrate and phosphate removal percentages at a wide range of pH.

Initial Nitrate and Phosphate Ions Concentrations

Initial nitrate and phosphate ions concentration are chosen in range from 6 - 40 mg/L and from 1-10 mg/L, respectively based on the maximum limits of wastewater discharge into the Nile River which are mentioned in the Egyptian Environmental Law number 4 of year 1994. $Mg(NO_3)_2 \cdot 6H_2O$ is used to prepare nitrate ion concentrations and NaH_2PO_4 is used to prepare phosphate ion concentrations.

Adsorbent Dose for FD-EAF Waste

Preliminary experiments have been conducted to check the effect of adsorbent dose on simultaneous phosphate and nitrate ions removal efficiency. The experiments are conducted at adsorbent doses ranging from 0.5 - 6.5 g/L, at fixed initial nitrate ion concentration of 6 mg/L, initial phosphate ion concentration of 1 mg/L, contact time of 90 min and pH ~ 7. The adsorbent dose from 0.5-6.5 g/L gives better nutrients removal efficiency and beyond this range the nutrient residual concentration in aqueous solution increases leading to decrease in the nutrient removal percents as represented in Table-1. The reason for this can be attributed to the accumulation of adsorbent when the adsorbent dose exceeds 6.5 g/L which results in decreasing in its specific surface area and thus, decreasing in the efficiency of the simultaneous removal of phosphate and nitrate ions from an aqueous solution.

Table-1. Simultaneous phosphate and nitrate ions removal percents versus adsorbent dose.

Adsorbent dose (g/L)	3.5	4	6.5	7	8	10
Nitrate ion concentration after adsorption (mg/L)	3.4	3.3	2.9	3.1	3.36	3.4
Phosphate ion concentration after adsorption (mg/L)	0.14	0.1	0.075	0.089	0.11	0.12
% Nitrate removal	43.4	44.5	50.5	48.3	44	43.5
% Phosphate removal	86	89.2	92.5	91.1	88.6	87.8

Contact Time of FD-EAF Waste

The contact time range 6 - 90 min is chosen based on experiments that are performed at pH ~ 7, adsorbent dose = 3.5 g/L, initial phosphate ion concentrations that ranged from 1 - 10 mg/L and initial nitrate ion concentrations that ranged from 6 - 40 mg/L. Through these experiments, equilibrium time of FD-EAF adsorbent is measured and it is found to be achieved at 90 min.

ADSORPTION KINETICS STUDY

The adsorption kinetics of nitrate and phosphate ions by the FD-EAF waste is studied at the following conditions; pH ~ 7, initial nitrate ion concentration = 40 mg/L, initial phosphate ion concentration = 5.5 mg/L, temperature = 25 °C, contact time = 90 min and adsorbent dose = 3.5 g/L. The experimental data are fitted to the kinetic models PFO and PSO. Table-2 represents the parameters of kinetic models, the correlation coefficients (R^2), k_1 and k_2 are rate constants for Pseudo-First Order (PFO) and Pseudo-Second Order (PSO) models, respectively.

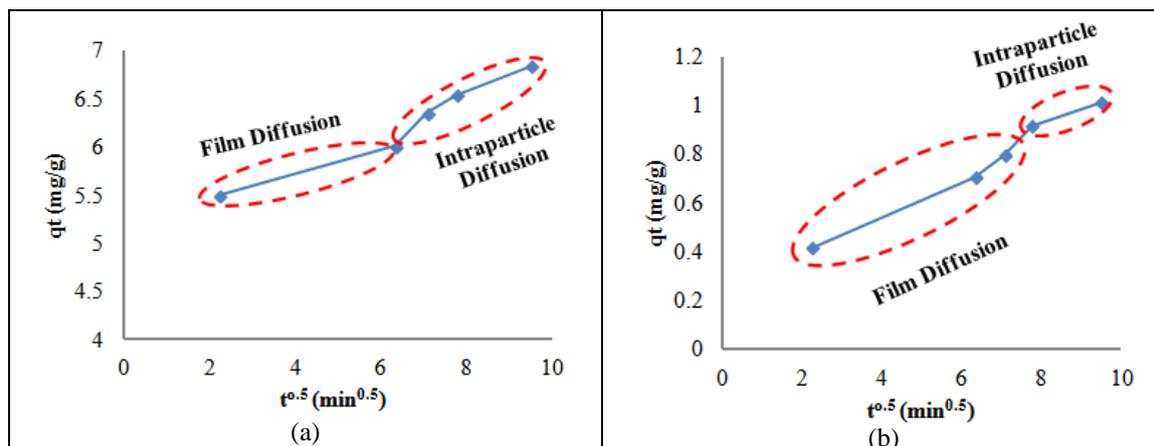
**Table-2.** Parameters of PFO and PSO models.

Kinetic model	Parameters	With Respect to Nitrate	With Respect to Phosphate
PFO	q_e (exp) (mg/g)	6.56	0.91
	q_e (calculated) (mg/g)	1.48	1.18
	k_1 (min^{-1})	0.035	0.038
	R^2	0.884	0.868
PSO	q_e (exp) (mg/g)	6.83	1.01
	q_e (calculated) (mg/g)	6.95	1.12
	k_2 (mg/g.min)	0.04	0.057
	R^2	0.995	0.955

Table-2 shows that the PFO model is not suitable for the adsorption of phosphate and nitrate ions simultaneously by the FD-EAF waste as the PFO model showed lower ($R^2 = 0.884$) with respect to nitrate ion adsorption than the PSO model ($R^2 = 0.995$). And the PFO model shows lower ($R^2 = 0.868$) with respect to phosphate ion adsorption than the PSO model R^2 (0.955). Also, it is noticed in PFO model that the difference between the q_e (theoretical) and q_e (experimental) for phosphate and nitrate ions is higher than the difference in PSO model. Therefore, the simultaneously nitrate and phosphate ions adsorption from an aqueous solution using FD-EAF waste is well represented by the PSO kinetic model. It is observed that adsorption rate constant k_2 values in PSO model 0.04 and 0.057 mg/g.min for nitrate and phosphate,

respectively are higher than that of PFO model 0.035 and 0.038 min^{-1} for nitrate and phosphate, respectively. This also ensures that the best fit model is PSO model due to the higher rate of nitrate and phosphate ions adsorption from an aqueous solution using FD-EAF waste.

The rate controlling steps of this adsorption system are determined using the intraparticle diffusion model and the actual rate controlling step is determined using the Byod plot. Figure-2a and Figure-2b represent the intraparticle diffusion model plot with respect to nitrate and phosphate where the first linear portion represents the occurrence of film diffusion mass transfer step followed by another linear portion which represents the occurrence of intraparticle diffusion mass transfer step.

**Figure-2.** Intra-particle diffusion models "a" with respect to nitrate and "b" with respect to phosphate.

Byod plot is used to predict the actual limiting step is involved in the adsorption process by plotting the B_t values vs. time (t) with respect to nitrate and phosphate. In Figure-3a and Figure-3b; Byod plot doesn't pass

through the origin point referring to the rate limiting step is the film diffusion with respect to nitrate and phosphate [23].

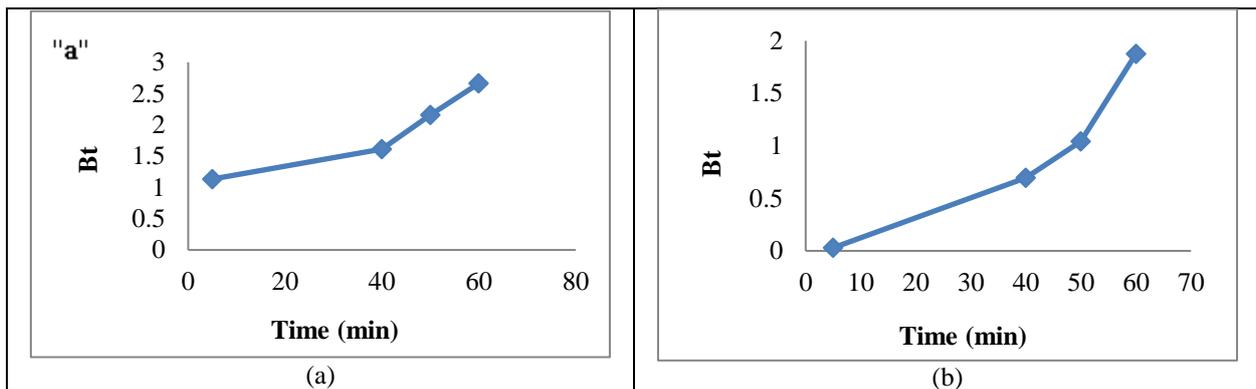


Figure-3. Byod plots; "a" with respect to nitrate and "b" with respect to phosphate.

Single Component Adsorption Isotherm Study

Single component isotherm models including Langmuir, Freundlich, Dubinin-Radushkevich and BET isotherm models are studied at the following fixed conditions; adsorbent dose = 3.5 g/L, contact time = 90 min, pH ~ 7 and at different initial nitrate ion concentrations from 6 - 40 mg/L and initial phosphate ion concentrations from 1 - 10 mg/L.

Table-3. Isotherm parameters for single nitrate component.

Isotherm Models	Parameters	Values
Langmuir	R ²	0.9957
	q _{max} (mg/g)	0.176
	K _L (L/mg)	10.77
	R _L (Separation factor)	0.001
Freundlich	R ²	0.81
	1/n	0.16
	n	6.23
	K _F (L/mg)	3.56
Dubinin-Radushkevich	R ²	0.9849
	B (mol ² /kJ ²)	0.078
	E (kJ/mol)	2.52 < 8 kJ/mol
	q _{max} (mg/g)	5.91
BET	R ²	0.8311
	b	10.92
	q _{max} (mg/g)	1.55

Table-3 shows that Langmuir and Dubinin-Radushkevich isotherm models are the best fitted models with the experimental data comparing with Freundlich and BET isotherm models. Both of them have the greatest values of R²; 0.9957 and 0.9849, respectively. While the R² values for Freundlich and BET isotherm models are 0.889 and 0.8311, respectively. Therefore, the adsorption type of nitrate ion using the FD-EAF waste is a monolayer adsorption process. In Dubinin-Radushkevich isotherm

model the value of E = 2.52 kJ/mol is less than 8 kJ/mol which indicates that the adsorption type of nitrate using the FD-EAF is a physical adsorption process where the nitrate ions particles are attached to the surface of FD-EAF with van der waals forces. BET isotherm model is used to represent the multilayer adsorption systems [24] and due to its lower R² (0.8311) comparing with Langmuir and Dubinin-Radushkevich isotherms, the nitrate ion adsorption system using the FD-EAF waste is not a multilayer adsorption system but, it is a monolayer adsorption system.

Table-4. Isotherm models for single phosphate component.

Isotherm Models	Parameters	Values
Langmuir	R ²	0.989
	q _{max} (mg/g)	2.76
	K _L (L/mg)	1.025
	R _L	0.088
Freundlich	R ²	0.9683
	1/n	0.627
	n	1.59
	K _F (L/mg)	4.25
Dubinin-Radushkevich	R ²	0.977
	B (mol ² /kJ ²)	0.053
	E (kJ/mol)	3.068 < 8 kJ/mol
	q _{max} (mg/g)	1.75
BET	R ²	0.9134
	b	10.34
	q _{max} (mg/g)	0.375

Table-4 shows that Langmuir and Dubinin-Radushkevich isotherm models are the best fitted models with the experimental data comparing with the Freundlich and BET isotherm models. Both of them have the greatest values of R² equals to 0.989 and 0.977, respectively. While R² values for the Freundlich and BET isotherm models equal to 0.9683 and 0.9134, respectively.



Therefore, the adsorption type of phosphate using the FD-EAF is a monolayer adsorption process. In Dubinin-Radushkevich isotherm model the value of $E = 3.068$ kJ/mol is less than 8 kJ/mol which indicates that the adsorption type of phosphate using the FD-EAF is a physical adsorption process where the phosphate ions particles are attached to the surface of FD-EAF with van der Waals forces. The value of Freundlich constant " $1/n$ " should be in a range from 0 to 1 [17]. In both nitrate and phosphate single isotherm models; the values of Freundlich constant " $1/n$ " for single adsorption of nitrate and phosphate ions are 0.16 and 0.627, respectively which indicates that a successful adsorption process is occurred for both species using the FD-EAF waste as an adsorbent. Also, the higher value of " n " indicates a great heterogeneity of the adsorbent sites.

The higher value of K_F for phosphate 4.251 L/mg than that of nitrate 3.564 L/mg indicates that the FD-EAF waste adsorbs phosphate amounts higher than nitrate. The values of q_{max} for nitrate and phosphate 0.176 mg/g and 2.766 mg/g, respectively indicates that the FD-EAF waste adsorbs higher phosphate amounts than nitrate and this result is consistent with the values of the Freundlich constant K_F for nitrate and phosphate. Additionally, BET isotherm model is used to represent the multilayer adsorption systems [24] and due to its lower value of R^2

(0.9134) comparing with R^2 values of Dubinin-Radushkevich and Langmuir isotherms so, this ensures that the phosphate ion adsorption system using the FD-EAF is not a multilayer adsorption system but, it is a monolayer adsorption system.

Simultaneous Adsorption of Nitrate and Phosphate from Aqueous Solutions Using FD-EAF Waste and Other Adsorbents

As represented in Table-5, the optimum adsorption capacity for nitrate and phosphate ions using Solid Waste Residue generated from Awash Melkassa Aluminum Sulphate and Sulphuric Acid Factory (SWR) is 13.15 mg/g for phosphate and 0.065 mg/g for nitrate. Also, the maximum adsorption capacities for phosphate and nitrate using Calcined Magnesium-Aluminum Layered Double Hydroxides (Mg-Al CLDHs) are 2.49 mg/g and 15.25, respectively. In case of using Dolochar; the maximum adsorption capacities for phosphate and nitrate are 327.7 mg/g and 6.51 mg/g, respectively. The maximum adsorption capacities for phosphate and nitrate using Solid Waste containing Boron (SWB) are 52.51 mg/g and 63.16 mg/g, respectively. This present study reflects that the maximum capacities for phosphate and nitrate removal using FD-EAF waste are 2.76 mg/g and 0.176 mg/g, respectively.

Table-5. Optimum simultaneous adsorption capacities of nitrate and phosphate ions using various adsorbents.

Adsorbent	Dose (g/L)	pH	time (hr)	Temp (°C)	Initial Conc. PO_4^{3-} (mg/L)	Initial Conc. NO_3^- (mg/L)	$Q_{max} PO_4^{3-}$ (mg/g)	$Q_{max} NO_3^-$ (mg/g)	Ref.
SWR	32	7	2	25	0.2-260	3- 19	13.15	0.065	[27]
Mg-Al CLDHs	2	4	2	40	5 -100	30-100	2.49	15.25	[2]
Dolochar	5	7	1.5	25	4 - 16	5 - 65	327.7	6.51	[10]
SWB	2	4	1.5	25	50-120	50-140	52.51	63.16	[28]
FD-EAF	3.5	7	1.5	25	1 - 10	6 - 40	2.76	0.176	This work

Multi-component Adsorption Isotherm Study

Table-6 represents the parameters of different isotherm models for binary system of (nitrate and

phosphate) ions removal from an aqueous solution using the FD-EAF waste.

**Table-6.** Binary isotherm parameters for simultaneous nitrate and phosphate ions removal using FD-EAF waste.

Isotherm Models	Parameters	x_1	y_1	z_1	SSE
Extended Freundlich	Nitrate Removal	1.34	1.56	1.64	0.001
	Phosphate Removal	-7.18	164.6	-9.53	
Extended Langmuir	Parameters	K_L (L/mg)	q_{max} NO ₃ & PO ₄ (mg/g)	SSE	2.367
	Nitrate Removal	0.335	2.049	2.367	
	Phosphate Removal	0.949			
Modified Langmuir	Parameters	n	SSE	5.452	
	Nitrate Removal	0.455			
	Phosphate Removal	1.601			

As per the results represented in Table-6, in the Extended Langmuir isotherm model, the higher value of the equilibrium constant ($K_L = 0.949$ L/mg) for phosphate than the value of K_L for nitrate = 0.335 L/mg indicates that there is a stronger bonding between phosphate and the FD-EAF adsorbent than nitrate ion. The maximum simultaneous uptake (2.049 mg/g) for nitrate and phosphate ions by the FD-EAF waste is less than the sum of individual q_{max} for nitrate and phosphate ions which is obtained from the results of single component adsorption isotherms. The reason can be attributed to either partial overlying of adsorption active sites for phosphate and nitrate in binary system or can be due to occurrence of diverse binding sites on the surface of the FD-EAF waste with different degree of specificity toward the individual nitrate and phosphate ions.

In Table-6, the lowest Sum of Squared Errors (SSE) value of 0.001 is for the Extended Freundlich isotherm model comparing with the Extended Langmuir and the Modified Langmuir isotherm models with SSE values of 2.367 and 5.452, respectively. Therefore, the adsorbent surface of the FD-EAF is heterogeneous and there are competitive interactions among the single nitrate and phosphate molecules, between the nutrients and the adsorbent as well.

CONCLUSIONS

Pseudo second order kinetic model is the best model to describe the simultaneous nitrate and phosphate ions removal by FD-EAF waste where the rate limiting step is the film diffusion. Langmuir and Dubinin-Radushkevich isotherms are the best fitted models for single nitrate and phosphate ions adsorption from an aqueous solution using FD-EAF waste. Multi-component isotherms are investigated where the Extended Freundlich isotherm is the best fitted isotherm model for simultaneous nitrate and phosphate ions removal using FD-EAF waste. The Maximum nitrate and phosphate ions removal percents 52.74 % and 92.38 %, respectively using FD-EAF waste are achieved under these conditions; pH~7, initial nitrate ion concentration = 6 mg/L, initial phosphate ion concentration = 1 mg/L, adsorbent dose = 6.5 g/L and contact time = 90 min.

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