

Pollutants Remediation by Air Stripping: A case study in Rosetta Branch

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1- Abstract

Egypt, with an arid climate, relies on 93% of the country's conventional water resources. The length of the Nile River branch (Rosetta) is 256 km from the Delta until it drains to the Mediterranean Sea, where it receives drainage from five agricultural drains that transport it from agricultural and urban areas densely populated by agriculture and the unserved by the sanitation in the Western Delta region, the water of the Rosetta branch is the primary source of irrigation, municipal and industrial uses in the western side of the Nile Delta.

Ammonia, Nitrite, Nitrate and Phosphate are the pollutants the main partnered these plants to use activation sludge technique, and they are abundantly present in the Rosetta branch due to the illegal drainage of agricultural drainage water canals. Because of the limited treatment methods inside the plants, which rely solely on alum and chlorine for treatment, there is an increased need to treat these pollutants before they reach the drinking water plants. The method of air stripping raw water at high pH is effective, inexpensive, and produces no solid or liquid waste. When the pH was raised to 11.0 and the air stripping rate was 22,000 ml/min, the efficiency of removing these pollutants was successful in treating about 90 % Ammonia, 98 % Nitrate, 100 % Nitrite, and 85 % phosphate, In the collected samples, the initial pollutant concentrations were 23.65 mg/l ammonia, 1.1 mg/l nitrite, 12.47 mg/l nitrate, and 3.31 mg/l phosphate.

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2- Introduction: Rapid population growth, agriculture, industries and domestic wastes

increased the level of pollutants. Continuously increasing rate of pollution is affecting the quality of water and converting it into wastewater.

Ammonia is an important pollutant to the water and environmental. It is affecting the oxygen transport by fish gills, high concentration of ammonia will even kill fishes ^[1]. A large amount of ammonia in drinking water resources due to wastewater discharge into the rivers and lakes, it decreases the efficiency of drinking water treatment. When the chlorine disinfection is adopted, ammonia and chlorine will produce chloramines, which increases chlorine consumption rate and further drives great demands for chlorine ^[2]. Ammonia is converted to nitric acid, nitrite, and Nitrates which directly affects human health

Nitrate (NO_3^-) is found naturally in the environment and is an important plant nutrient, it is present At varying concentrations in all plants and is a part of the nitrogen cycle.

Nitrite (NO_2^-) is not usually present in significant concentrations except in reducing environment, because nitrate is the more stable oxidation state. It can be formed by the microbial reduction of nitrate. Nitrite can also be formed chemically in distribution pipes by Nitrosomonas bacteria during stagnation of nitrate-containing and oxygen-poor drinking-water in. Galvanized steel pipes

An excess of free ammonia entering the distribution system can lead to nitrification and the potential increase of nitrate and nitrite in

drinking-water. Nitrate can reach both surface water and groundwater as a consequence of agricultural activity (including excess application of inorganic nitrogenous fertilizer sand manures), from wastewater disposal and from oxidation of nitrogenous waste products in human and other animal excreta, including Septic tanks

Phosphate is a pollutant if its concentration exceeds the permissible limit in water. The discharge of phosphate ion causes serious environmental hazards due to eutrophication in water. It is available in three forms, that is organic phosphorous, orthophosphate and polyphosphates. Orthophosphate can be precipitated through chemical methodology. While organic phosphorous and polyphosphates can be converted to orthophosphate through biological treatment. Phosphate contaminates the ground water through natural decomposition of rocks and minerals, agricultural runoff, erosion and sedimentation and direct input by animals and Sewage effluents and industrial discharges

The recommended value of phosphorous in drinking water according to EPA is 5mg/l. Beyond permissible limit it may damage kidney and causes osteoporosis ^[4]. A small amount of phosphorous may enhance the growth of algae and aquatic vegetation leading to eutrophication of the aqueous. System produces algae bloom formation in water bodies^[5]. Treatment wastewater has become a hot issue at present. Ammonia, Nitrite, Nitrate

and phosphate wastewater treatment methods are as follows: air stripping, ion exchange, chemical precipitation, membrane separation, chemical oxidation, biological method, etc. Researches mainly focus on the marterializations method, while biological methods are rarely used. It is of great practical significance to seek practical treatment technology with small investment, reliable operations and high efficiency for the processing of wastewater treatment^[3].

Most wastewater treatment plant in Egypt uses active sludge. This treatment method is ineffective in treating certain pollutants such as ammonia, nitrite, nitrates and phosphates; another inexpensive technology nonconsuming treatment of chemicals is needed. Also, Due to the annual maintenance of the Nile River course, the water levels of the Roseta branch many vary to reach low levels so some pollutants appear, especially ammonia. Traditional treatment plants located on Rosita branch cannot deal with this contaminant, so we had to use effective, inexpensive and easy methods to overcome this annually problem^[6].

The air stripping method was found to be the most appropriate way to overcome these contaminants no matter pollutants concentration, it does not require many constructions (just an aeration tower), inexpensive chemicals (just sodium hydroxide) and no byproducts wastes either solid or liquid are generated This study use real water

samples in the laboratory to determine the optimal treatment conditions^[7].

Our study concerned to treat high level of ammonium concentration presented along of Roseta branch and that of effluent of wastewater treatment plants which use activated sludge technique^[8].

3- Materials and Methods

3-1- Materials : Sodium hydroxide pellets (99%, from Merk company), pH 4,7,10 buffer solution (Hach pH standard solution), Ammonium Standard solution (1000 mg/l from Merk company) Nitrite Standard solution (1000 mg/l from Merk company), Nitrate Standard solution (1000 mg/l from Merk company), Phosphate Standard solution (1000 mg/l from Merk company)

3-2- Instrumentation : Ion chromatography model 881 compact IC pro Metrohm to determine Cations and Anions presents in water samples, pH meter model Sens Ion 3 Hach to adjust samples pHs, Conductivity Meter Sens Ion 7 Hach to determine samples electrical conductivity, Analytical digital balance model Mettler Toledo, Aeration pump Model Pall max air flow up to 22000ml/min.

Aeration experimental

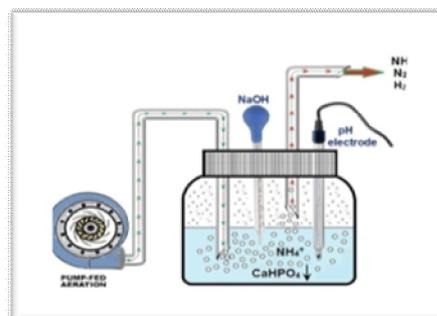


Fig. (1) Experiment diagram

The experiment was carried out using real wastewater samples withdrawn from the effluent of Abu Rewash sewage water treatment which operates under activated Sludge technology.

The concentration of contaminants (ammonia, nitrite, nitrates and phosphate) was measured in samples in order to determine the initial concentration prior to perform experiment.

Then 1000 ml of samples were taken and sodium hydroxide solution (1.0 N) was added slowly to raise the samples pH values then samples were air stripped using aeration pump,

the concentration of these pollutants were measured periodically until complete removal of pollutants is determined from the equation:

$$\text{pollutants removal \%} = \frac{C_i - C_t}{C_i} \times 100 \quad (1)$$

Where C_i is the initial concentration of pollutants (mg/l) and C_t is the remaining pollutants concentration at time t

The various effects were studied to determine the optimal conditions for the removal process within the practical application of the experiment [9]

4- Result and discussion

4-1-Effect of pH:

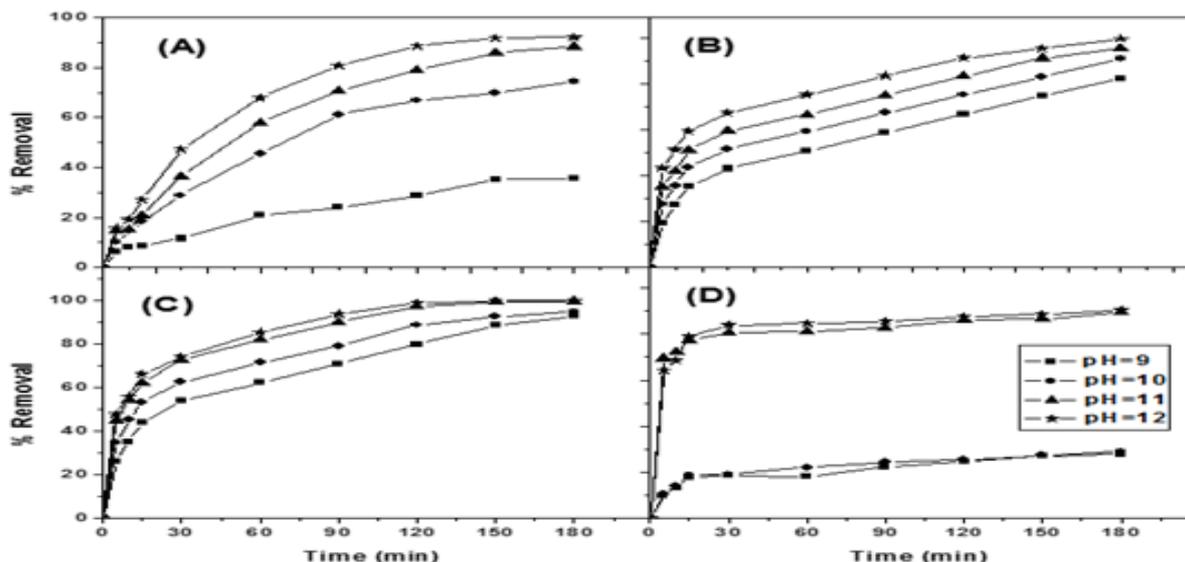


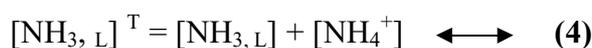
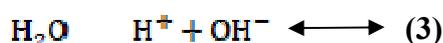
Fig. (2) Effect of pH values on removal of (a) NH₄, (B)NO₃, (C)NO₂ and (D)PO₄ from a real swage water, aeration flow rate was 22000 ml/min and initial conc. of NH₄, NO₃, NO₂ and PO₄was 23.0, 12.0, 1.1 and 4.0 mg/l respectively.

The stripping cylinder was used to perform the stripping. In the cylinder, the interface of the air bubble is the contact surface between liquid and gas; the airflow rate is constant at 22000 ml/h on 1.0 L of real sewage water; and the pH of the samples is adjusted with 1.0 N sodium hydroxide (pH range was 9–12). When conducting the experiment, it is noticed that

the pH value of samples is reduced gradually as the continuous air stripping process until it reaches the original value of the real sample pH7.5.

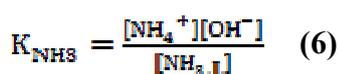
As shown in Figure 1, ammonia removal increases significantly after pH is raised to 9, with the highest removal rate appearing at pH 11. After 180 minutes of air stripping,

approximately 90% of ammonium was removed. Total ammonia exists in two forms free ammonia (NH_3) and ammonium ions (NH_4^+), as shown in Equations, and the stripping efficiency and transfer rate of ammonia were analysed as the initial concentration and pH values in the aqueous solution were changed (2-4)^[10].



Where $[\text{NH}_3, \text{L}]^T$, $[\text{NH}_3, \text{L}]$ and $[\text{NH}_4^+]$ mean the molar concentration (mol/l) of total ammonia, free ammonia, and ammonium ion, respectively.

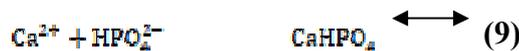
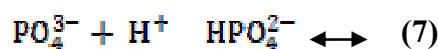
The ionization constants for water ($K_{\text{H}_2\text{O}}$) and ammonia (K_{NH_3}) are known in Equations (4) and (5), respectively.



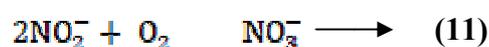
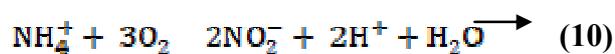
The change of pH in the ammonia solution causes a change of ammonia fraction, which means that the higher pH, the more ammonia can be removed so pH is an important parameter affecting the stripping efficiency and transfer rate.

Phosphate removal increases significantly after pH 10, with the highest removal rate appearing at pH 11, where approximately 90% of Phosphate was removed after 30 minutes of air stripping. Phosphate was presented in

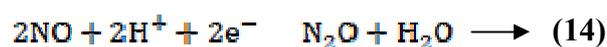
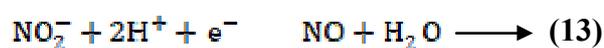
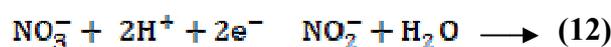
aqueous solution as orthophosphate at lower pH; increasing the pH affected the concentration of orthophosphate; increasing the pH lowered the overall concentration of orthophosphate; after pH 10.0, a significant difference in PO₄ concentrations from the pH range was detected due to an increase in the formation of insoluble calcium phosphate species that precipitated from solution.

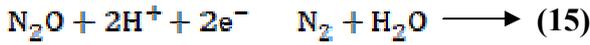


Ammonia is oxidized to nitrite, which is then oxidized to nitrate by biological processes in real sewage water, a process known as nitrification. Increasing the initial pH values has little effect on biological activity, as shown in Fig 1, and the removal percentage of Nitrite and Nitrate increases slightly between pH 9 and pH 12. (About 95 % of nitrite and nitrate removed after 180 min at pH 11)^[11]



Nitrification is always followed by denitrification, in which nitrate is reduced to nitrite, which is then reduced to nitrogen gas, resulting in the removal of nitrogen gas from The atmosphere





Aerobic denitrification process removal the nitrate and nitrate efficiencies up to 100%, the efficiency increased for $pH \geq 7$ due to presence

of some types of microorganisms called *Pseudomonastaiwanensis*

4-2- Effect of air stripping:

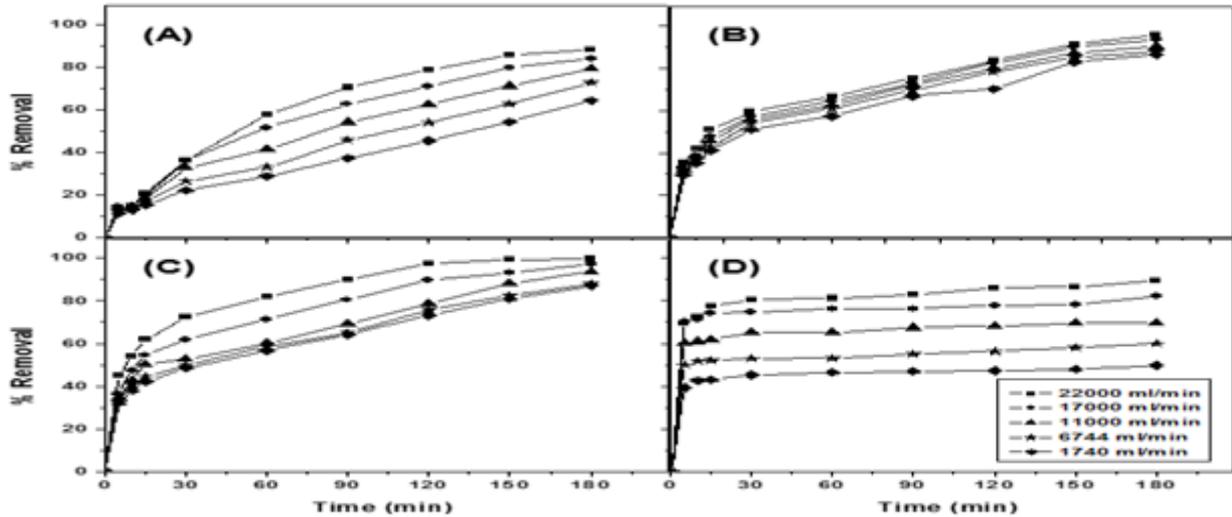


Fig. (3) Effect of air stripping on the removal of (NH₄, NO₃, NO₂, PO₄) from real swage water, pH value was 11, and initial conc. of NH₄, NO₃, NO₂ and PO₄ was 23.0, 12.0, 1.1 and 4.0 mg/l respectively.

As shown in Figure 3, the percentage removal of ammonia, nitrate, nitrite and phosphate are increasing by increasing air stripping rate

In the case of ammonia, air stripping rate is an important parameter to remove ammonia out from water, the removal efficiency increases at high-rate flow of air stripping due to increase the transfer of ammonia into the air phase

In aqueous solution, the free ammonia can be stripped through transfer from liquid to gas. Thus, the concentration ratio of the free ammonia to total ammonia is a major factor in stripping and is defined as the ammonia fraction (f_{NH_3}) in Equation (16). [12]

$$f_{NH_3} = \frac{[NH_{3,L}]}{[NH_{3,L}] + [NH_4^+]_L} \quad (16)$$

The ammonia fraction is also expressed by Equation (17) from Equations (5) and (6)

$$f_{NH_3} = \frac{K_{H_2O}}{K_{H_2O} + K_{NH_3}^+ [H^+]} = \frac{1}{1 + \left(\frac{K_{NH_3}^+}{K_{H_2O}}\right) 10^{-pH}} \quad (17)$$

The percentage of ammonia removal (NH₃ R%) is calculated as the amount of ammonia removed compared to the initial ammonia and is expressed as Equation (18):

$$(NH_3 \text{ R}\%) = \frac{[NH_{3,L}]_0^T - [NH_{3,L}]_t^T}{[NH_{3,L}]_0^T} \times 100 \quad (18)$$

In the case of phosphates, the percentage of removal increases as the air flow rate increases due to increase the proportion of potential collisions rate between phosphate ions and calcium ions, which helps to form Precipitate of calcium phosphate. Equation(9)

In the case of nitrite and nitrates by increasing the rate of air stripping increases the concentration of dissolved oxygen in the

water, which helps to increase the speed of the oxidation of nitrite and turn it into nitrates, that in the nitrification process also helps in increasing of the activity of aerobic bacteria, which leads to increased effectiveness in converting formed nitrate into nitrogen gas, the stripped air kicked out nitrogen gas from the water. Equations (10-15)^[13]

4-3- Kinetics measurements

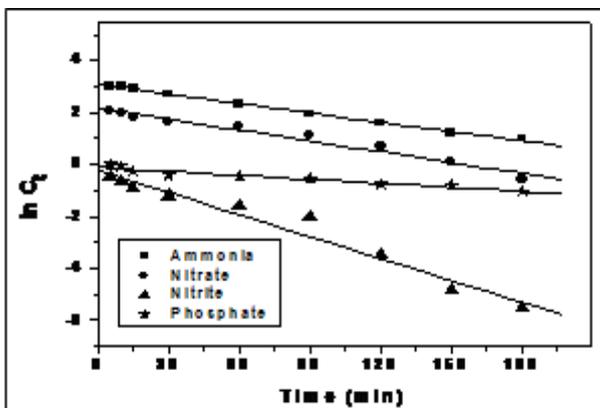


Fig. (4) Pseudo first order plots for the removal of different pollutants from a real swage water, at pH 11, and aeration flow rate of 22000 ml/min.

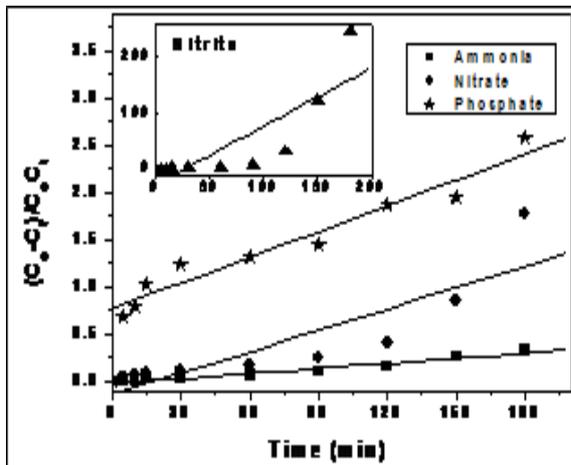


Fig. (5): Pseudo second order plots for the removal of different pollutants from a real swage water, at pH = 11, and aeration flow rate of 22000 ml/min.

From Differential rate laws are used to describe the occurrence of molecular level during a reaction, to determining the reaction order and the value of the rate constant from experimental measurements. The order of

reaction is First order reaction due to rate that depends linearly on only one reactant concentration

$$Rate = -\frac{d[C]}{dt} = k[C] \quad (19)$$

Where the "rate" is the reaction rate (in units of molar/time) and k is the reaction rate coefficient (in units of 1/time)

Rearrange to give^[14]

$$\frac{d[C]}{[C]} = -k dt \quad (20)$$

Integration

$$\ln[C_t] = -kt + \ln [C_0] \quad (21)$$

Where slope is -kt and intercept is $\ln [C_0]$

As shown in figure 3 Pseudo-firstorder model is well fitted with the experimental data with a correlation coefficient (0.997,0.985, 0.983,0.950) for NH₄, NO₃, NO₂ and PO₄respectively table (1)^[15]

Second order reaction where rate is proportional to the square of the concentration of one reactant

$$Rate = -\frac{\Delta[C]}{2 \Delta t} = k[C]^2 \quad (22)$$

Integrated rate law describes the concentration of the reactant at a given time

$$\frac{1}{[C_t]} = \frac{1}{[C_0]} + kt \quad (23)$$

Where slope is k and intercept are $\frac{1}{[C_0]}$

As shown in figure 4Pseudo-second order model isn't well fitted with the experimental data with a correlation coefficient (0.980,0.872, 0.910,0.835) for NH₄, NO₃,

NO₂ and PO₄ respectively table(1)

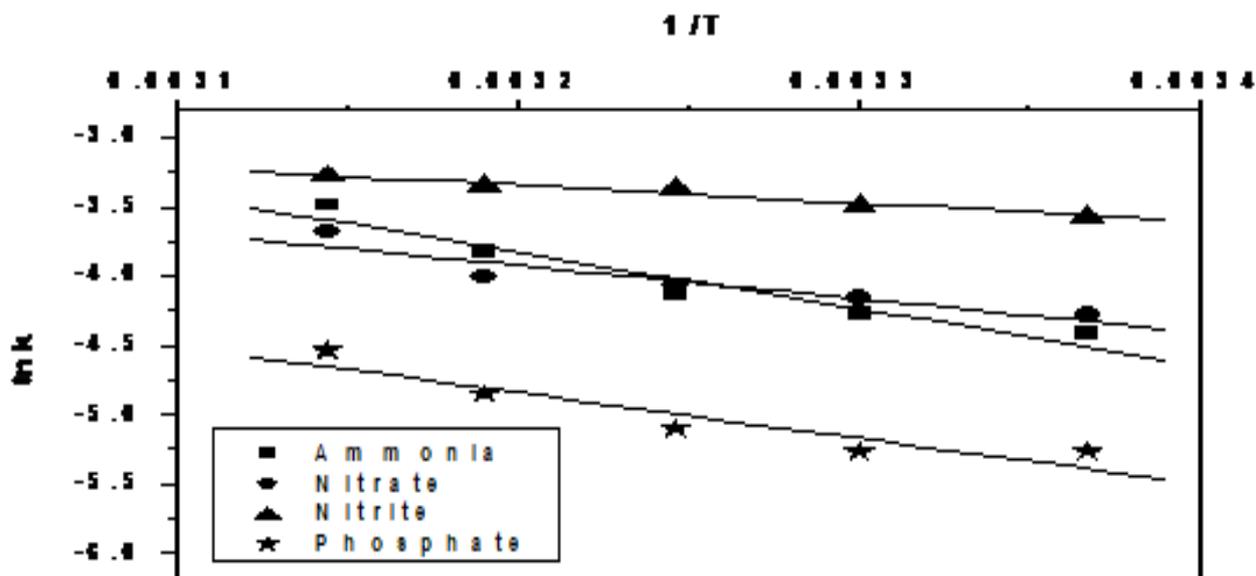


Fig. (6) Arrhenius plots for the determination of the activation energy, for the removal of different pollutants from a real swage water.

We can graphically determine the activation energy by manipulating the Arrhenius equation to put it into the form of a straight line [16]

$$\ln k = \ln A - \frac{E_a}{RT} \quad (24)$$

Where (k) is the rate constant for the reaction, slope equal to $(-E_a/R)$ and intercept equal $(\ln A)$.

The predicted activation energy to remove ammonia, nitrite, nitrates, and phosphorus has a positive sign in table (1), suggesting that the

removal process is completely dependent on the reaction temperature [17,18]

Table (1). Kinetics parameters of pseudo-first and second order models for the removal of different pollutants from a real swage water, at pH 11, and aeration flow rate of 22000 ml/min

Pollutant species removed	1 st order			2 nd order	
	k (min ⁻¹)	R ²	E _a kJ/mol	k (mg ⁻¹ L. min ⁻¹)	R ²
Ammonia	0.012	0.997	34.0	0.00173	0.980
Nitrate	0.0138	0.985	20.0	0.007	0.872
Nitrite	0.0282	0.983	10.8	0.010	0.910
Phosphate	0.0051	0.960	27.5	1.046	0.835

5- Applied Methodology

drinking water plants located on Rosetta branch suffer from the high concentrations of ammonia in raw water before entering the

main stages of treatment plants, this affect the first and final disinfection of chlorine, the study was conducted to use new method of

removing ammonia using aeration towers to displace ammonia after raising the pH of raw water up to 11 by dietary caustic soda and after all treatment process are completed the pH of water is returned by dietary

hydrochloric acid as well and we noticed that the amount consumed from these chemicals is very low and the expected increase in the value of dissolved total solids does not exceed 100 mg/l

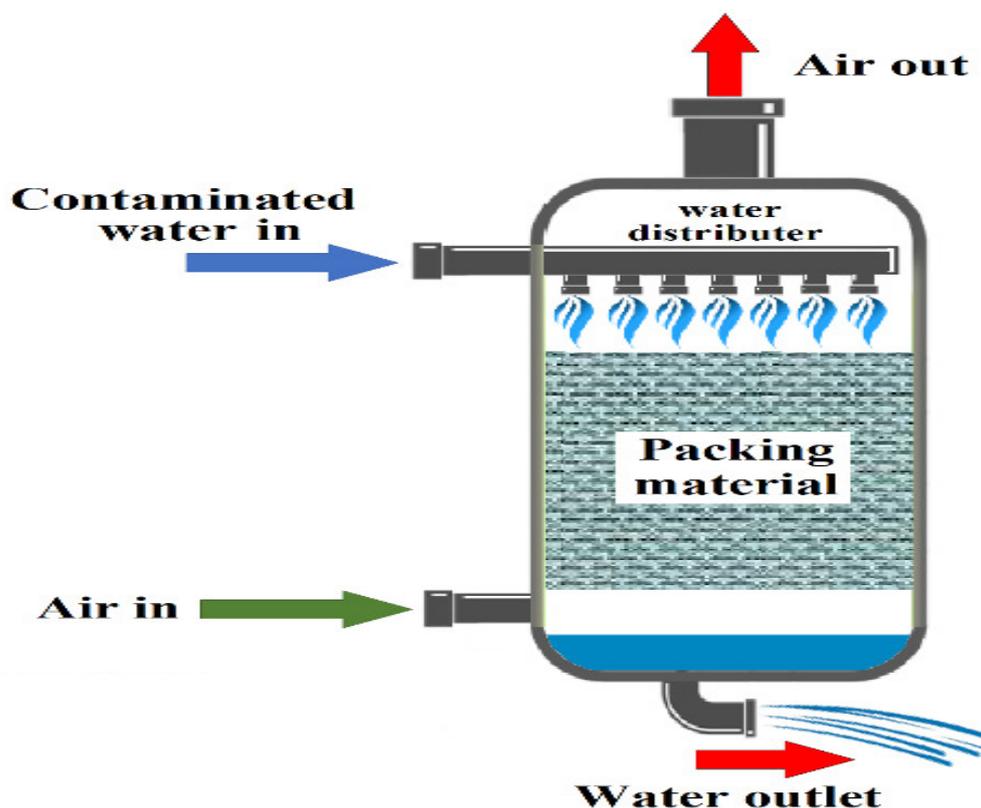


Fig. (7): The schematic shape of the aeration tower used to remove of ammonia before entering the traditional treatment stages of drinking water plants located on the Rosetta branch

6- Conclusion

*Efficiency of ammonium, organic pollutants and phosphate removal increases electively by increasing aeration power, helping to shorten water treatment time if aeration rates increase

*Air stripping is easy to use to remove ammonia, organic pollutants and phosphates presented in high concentration at Rosetta branch.

*Air stripping is a mechanical process that does not require any backwashing or

regeneration.

*Toxic chemicals that may impede the operation of the air stripping process are unaffected.

*Air stripping is a straightforward process that is unaffected by changes in water contaminants

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