Laboratory Approach for Wastewater Treatment Utilizing Chemical Addition Case study: El-Rahway Drain, Egypt

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Abstract: An examination was directed to evaluate drainage water quality parameters along El-Rahway Drain, Egypt, in regards to Law 48 of 1982 and its adjustment in 2013. Reduction of pollutants from wastewater utilizing ALUM, and disinfection via sodium hypochlorite and CuO NPs were used to investigate the removal efficiency of these chemical. Raw wastewater and treated water were analyzed after each chemical addition step to determine chemical and microbiological parameters. By the aid of jar test apparatus, we utilized assorted ALUM dosages from 0 to 250 mg/L to determine the ideal ALUM dosage for wastewater treatment. The chlorine dose must be determined via the chlorine demand strategy. CuO NPs was prepared by a quick sol-gel method, characterized utilizing X-Ray Diffraction (XRD) and Brunauer-Emmelt-Teller (BET) and different parameters were studied to decide the optimal dosage for disinfect wastewater. The outcomes shown that the drainage contains higher groupings of TP, TN, cadmium, lead, BOD, COD and *total Coliforms* (TC) higher than the permissible limits for drainage water. The results of treatment by ALUM proved that ALUM was capable of reducing TP, TN, cadmium, lead, BOD, COD and *total Coliforms* (TC) by 93%, 30%, 100%, 73%, 70%, 63% and 97%, respectively at a dose 0.2 g/L to lower than the recommended limits all pollutants except TN and TC. The chlorine dose required for purifying water treated with ALUM strategy was 10 mg/l, respectively. CuO NPs has a monoclinic and pure phase and was found to be has a surface area of about 76.3014 m^2/g, the average particle radius 1.78 nm. The dosage of CuO NPs required for disinfection was 2 g/L. The result indicated that CuO NPs was capable of replacing chlorine in order to control of chlorine toxicity. Further examinations required in situ for treating wastewater before discharge into fresh water bodies.
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1. Introduction

Chemical addition (chemical treatment) is used to reinforce the aesthetic quality of the wastewater, lessen or eliminate the rate of waterborne disease. The sorts and amounts of chemicals, extra to the water can vary greatly and will rely upon a scope of factors, including raw water quality, treatment processes utilized and their goals. Chemical treatment processes are utilized to get rid of suspended solids, turbidity and color, remove microorganisms, reduce organic matter, lessen the iron, manganese and trace element concentrations, *etc*.,. Wastewater treatment includes physical removal of solids and chemical disinfection. Treatment practices change from system to system, whilst, there are four generally accepted basic stages (Stewart *et al*., 2001).

Coagulation, flocculation & sedimentation is a universal strategy since it eliminates a considerable range of substances, of various molecular weights, at a lower price than totally different techniques (Andía, 2000; Kaewdannetra *et al*., 2009; Murillo, 2009; Rodríguez *et al*., 2007; Dotto *et al*., 2019). In the coagulation stage; various chemicals, i.e., ALUM, $FeCl_3$, $Fe_2(SO_4)_3$, and $FeSO_4$ can be utilized for coagulation. The procedures of coagulation and flocculation are aimed to create particles large enough to be isolated and expelled by resulting sedimentation. In the sedimentation procedure coagulated particles fall, by gravity, through water in a settling tank and aggregate at the base of the tank clearing the water of much of the rigid debris. Followed by filtration, in which solid particles not previously removed by sedimentation are removed via water is forced through sand, gravel, coal, or activated charcoal. In the present work, the authors determine the dose of ALUM ($Al_2(SO_4)_3$) for coagulation, fllowed by flocculation, sedimentation (clarification) and filtration.

In the Disinfection procedure, chlorine and nanoparticles is added to filtered water to demolish harmful microorganisms by killing or inactivating them, is definitely the foremost important step in a waste water treatment (Krasner *et al*., 2006). Chlorine is the most broadly utilized disinfectants for this reason by virtue of amazingly high productivity and relatively low cost (Anonymous, 1997). The unsafe of the chlorination is that chlorination of dissolved organic material by residual chlorine can produce chlorinated organic compounds that might be carcinogenic or destructive to the surroundings (Methta, 2013). So that in the present study, the authors determine the dose of chlorine required for disinfection, in addition to prepare nanoparticle has the ability to disinfect the wastewater to dispose of the disadvantage of chlorine.

An successful methodology for wastewater sanitization is that the utilization of nanoparticles to sanitize the wastewater from the distinctive pathogens. Nanomaterials, as nanoparticles, nanowires, nanotubes and thin films, are outlined as a very small aggregate of atoms with dimension less than 100 mm (Schmid *et al*., 1994; Suleiman *et al*., 2015). The significance of nanoparticles may be a result of the distinctive different physical, chemical and biological characteristics compared to the bulk scale, as an outcome of their high ratio of surface/volume (Suleiman *et al*., 2009; Suleiman *et al*., 2015).

The water quality of Rosetta branch was deteriorated as a result of the continuous release of wastewater form El-Rahway drain to Rosetta branch. Several examinations have been led to address water quality at the El-Rahawy drain. In their examination, Abdel-Satar and Elewa (2001); Abdo (2002); Badr *et al.* (2006); Elewa *et al.* (2009); Moustafa *et al.* (2010); Ezzat *et al.* (2012); Ewida and Ibrahim (2014); Mostafa (2014), the outcomes showed that elevated amounts of physicochemical parameters in the Rosetta branch at the release point of the El-Rahawy drain, the scientists presumed that the Rosetta branch water quality is adversely affected by receiving discharge from the El-Rahawy drain.

Studies have been conducted to oversee water quality at the Rosetta branch by enhancing effluent water quality at the Abu-Rawash WWTP by Mostafa (2014); Mostafa *et al.* (2015). Results demonstrated that the aluminum chloride ($AlCl_3$) is more efficient in wastewater treatment than ferric chloride ($FeCl_3$), ferric sulphate ($Fe_2(SO_4)_3$) and ferrous sulphate ($FeSO_4$). Results moreover exhibited that a dose of 2.0 mg/L of $AlCl_3$ for wastewater was chosen and the ideal pH values for the elimination of the COD, TSS, BOD, and turbidity ranged from 6.10 to 6.20 for the $AlCl_3$.

The water qualities of El-Rahway drain require improvement to meet the prerequisite of Egyptian Law (Ministerial Decree No. 92 of 2013 changing the Ministerial Decree No. 8 of 1982 on the official rules of Law No. 48 of 1982 regarding the Protection of the Nile River and water channels from contamination). The objective of this investigation to decide the optimum dose of chemical required to treat wastewater in El-Rahway drain and make water OK for various utilizations relying upon physico-chemical and bacteriological analyses. So that the wastewater quality of El-Rahway drain was studied for one year, study the effect of addition different doses of ALUM on water characteristics, determine the dose of chlorine required for disinfection, prepare nanoparticle material has the ability to disinfect wastewater as chlorine to get rid of chlorine disadvantage. In final, comparison between ALUM & chlorineand ALUM & nanoparticle effect on water quality characteristics.

2. Materials and Methods

Study area:

El-Rahway drain is seen as one of the five agricultural drains and it gets an area of the Greater Cairo wastewater and carries the combined release from the two sewerage plants (Zenein and Abo-Rawash) and therefore the agricultural drainage system (Mohamed, 2006). The load of pollution of the drain, assessed by El Gammal and El Shazely (2008) as 400,000 m^3/day primary treated wastewater from Abo Rawash wastewater treatment plant, 600,000 m^3/dayuntreated wastewater as a detour from Abo Rawash plant, and 430,000 m^3/day of secondary treated wastewater from the Zeinen wastewater treatment plant.

Sampling: Composite wastewater samples were gathered from El-Rahway drain. Water samples were gathered in four plastic bottles, every one of them have 20 L water sample. They were quickly transported in a water cooler at 4°C to the laboratory.

Water analyses:

The following physico-chemical characteristics have been analyzed & estimated according to standard strategies for testing fresh water and wastewater (APHA, 2005). pH was estimated utilizing an Info Lab meter. Alkalinity was determined titrimetrically against 0.2 N–H_2SO_4, utilizing phenolphthalein and methyl orange indicators. True color was estimated for filtered water sample with a 0.45 micron (µ) filter paper through visual examination of the sample with known colored solutions of (platinum-cobalt) concentrations. Turbidimeter Thermo Orion AQ 4500 was utilized to quantify the turbidity of the water samples utilizing purchased calibration solutions of 0.1, 15 and 100 NTU. Total nitrogen (TN) concentration was determined applying Kjeldahl Method. Total phosphorous (TP) was determined colorimetric detection utilizing continuous flow analysis after digestion with alkaline persulphate (Patton and Kryskalla, 2003). Total dissolved solids (TDS) were determined by weighing the solid residue gotten by evaporating a measured volume of filtered water sample to dryness at 103-105 ^oC. Total suspended salt (TSS) was the distinction between the total solid (TS) and total dissolved solid (TDS) determined gravimetrically at 105 ^{o}C. Major anions; chloride (Cl^-), sulfate (SO_4^{2-}) and nitrate (NO_3^-) were estimated utilizing Ion Chromatography (IC). Major cations; (calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}), and sodium (Na^+)) and heavy & trace metals (Cd, Cu, Fe, Mn and Zn) were estimated in water by utilizing Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) Dual View.

Biological Oxygen Demand (BOD) was estimated utilizing BOD fast respirometry system model TS606/2 at 20ºC incubation in a thermostatic incubator chamber model WTW for 5-day. The Chemical Oxygen Demand (COD) was estimated calorimetrically using a strong chemical oxidant (potassium dichromate) in acid medium, then heated to oxidize organic carbon. COD Reactor (block heater operates at 150±2°C) and Spectrophotometer Huch-DR-2010 was utilized to measure the amount of dichromate consumed in the breakdown of organic matter.

Bacteriological Analyses: Collected raw wastewater and treated water samples were examined through 6 hours subsequent gathering and treatment, respectively. Membrane filter strategy was utilized using a filtration system finished with stainless steel autoclavable manifold and oil-free" vacuum/pressure pump for *total Coliforms* enumeration. The fiteration of samples were done through sterile (the membrane has a diameter of 47 mm & a pore size of 0.45 µm). The information was recorded as Colony Forming Unit (CFU/100 ml) utilizing the nextequation:

$$\frac{Colonies}{100\ ml} = \frac{Counted\ colonies}{ml\ of\ sample\ filtered} \times 100$$

Treatment methods:

*Jar test procedure:*5 beakers were utilized in this investigation. Each beaker filled with composite raw wastewater gathered from El-Rahway drain. The stirrer device turned on, and the paddles were running at maximum speed, with the reason for homogenizing the sample for one min. Then, the coagulant was added with the doses 0.025, 0.1, 0.15, 0.2, 0.25 g of ALUM at the center of the pallet where the vortex is formed for 20 min at the maximum speed for coagulation occurs. Thereafter, the mixing speed was slowed for flocculation occurs for 20 min. Each of the beakers was carefully removed, left to sit for 1 hour before filtration through cotton. The treated water samples were subject for complete analyses as appeared in the section before to determine the removal efficiency for coagulant according to the next equation:

$$\text{Removal efficiency } (\%) = [\frac{(Ci - Cf)}{Ci}] \times 100$$

Where *Ci* and *Cf* are the initial and final concentrations of the element, respectively.

Disinfection: Disinfection was completed utilizing two materials, sodium hypochlorite (NaClO) and CuO nanoparticles (CuO NPs) for comparison. Wastewater samples disinfection utilizing sodium hypochlorite (NaClO) and CuO NPs antibacterial activity were considered .

Chlorine demand procedure: Chlorine demand was determined according to the DPD (N, N-diethyl-p-phenylenediamine) method (Environmental Protection Agency of China, 2002; Ibrahim *et al*., 2017). Ten chlorine demand-free bottles labeled from one to ten were prepared and each bottle rinsed with sample and filled with 100 mL of the sample to be tested. A stir bar magnet was inserted into each bottle and stir gently. A small vortex should be visible on the surface of the liquid. Different chlorine doses of 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 mg/l were added to each bottle while stirring. The stirrer was turned and the bottle was filled with sample until it overflows. The bottles were capped and inverted to mix (the time recorded as a start point). The bottles were put in the dark until 15 minutes and the chlorine residual was measured at this time by the DPD method (Environmental Protection Agency of China, 2002). The concentration of chlorine added was calculated from the next equation:

$$mg/L\ Cl_2 = \frac{Volume\ of\ chlorine\ added \times concentraton\ of\ chlorine\ added}{ml\ of\ sample}$$

Preparation of copper oxide nanoparticles (CuO NPs): Sol-Gel methods (Suleiman et al., 2015) were utilized for preparation of CuO Nano powders. 0.2 M of $CuCl_2.6H_2O$ was prepared in cleaned flask. 1 mL of glacial acetic acid is added to the above aqueous solution and then heated to 1000 ^{o}C with consistent blending. NaOH (8 M) was added with vigorous stirring to adjust pH to 7. At this point, black precipitate is formed instantly and washed 3-4 times by deionized water. The got precipitate was dried for 24 h in air. This powder is additionally utilized for the characterization of CuO nanoparticles.

X-Ray diffractorometer (XRD, Bruker D8 Advance, Germany) was utilized to determine the crystalline phases of CuO Nano particle, utilizing CuKα as a radiation source (40 Kiev, Step Size 0.020, scan rate 0.50 min-1, 200≤700). The surface area analysis & pore size distribution of the prepared nanoparticle particle were calculated by Brunauer-Emmelt-Teller (BET, HitachiVP-SEM S-3400N, Germany).

Diverse parameters impact on copper nanoparticle, which are nanoparticle concentrations, contact time, shaking and pH of wastewater effect.

- Concentration impact: The antibacterial activity of various CuO NPs concentrations 0.1, 1, 2, 3, 5 and 7 mg/L was studied. All samples, in addition to control sample were shaken at 150 rpm for 2 h at 25 °C (Suleiman *et al*., 2015).
- Contact time impact: The investigation did with concentrations 1 and 2mg/L of CuO NPs. All samples, in addition to control sample were shaken at 150 rpm for 1, 2 and 24 h at 25 °C (Suleiman *et al*., 2015).
- pH impact: 1 and 2 mg/L of CuO NPs were utilized in various pH; 6.0, 7.0 and 8.0, of wastewater were researched. Phosphate-citrate buffer solution was utilized to modify the pH values of wastewater samples. All samples, in addition to control sample were shaken at 150 rpm for 2 h at 25 °C (Suleiman *et al*., 2015).
- Shaking impact: As in the above analyses; 1 and 2 mg/L of CuO NPs were utilized to investigate the shaking impact at 0 and 150 rpm for 2 h at 25 °C (Suleiman *et al*., 2015).

Comparison between two treatment wastewater techniques

- Technique I: Three liters of the samples were treated with a 0.6 g of ALUM followed sodium hypochlorite. After that the samples were subject to complete analyses.
- Technique II: Three liters of the samples were treated with 0.6 g of ALUM followed CuO NPs. After that the samples were subject to complete analyses.

Statistical analysis: The data are investigated utilizing Statistical Package for Social Science (SPSS). The data are analyzed and exhibited as mean ± standard deviation.

3. Result and Discussion

Samples gathered from the outlet of El-Rahway drain were analyzed in triplicates and the standard deviation was ascertained. The statistical examinations of chemical and microbiological variables of samples were exhibited in table 1. The results of the treatment process were organized in table 2 and portrayed in figures 2 & 3.

Wastewater quality of El-Rahway drain

El-Rahway drainis one of most dirtied water bodies in Egypt. It suggests one of the biggest environmental problems there, gets primary treated wastewater from the Abu-Rawash Wastewater Treatment Plant (WWTP). The wastewater characteristics were assessed relying upon the Law of Ministry of Irrigation and Water Resources (48/1982) by decision Number 92, 2013; article sets the guideline must be available in the drainage water before they are submitted to the freshwater bodies. The outcomes exhibited that the drain contains TN, TP, BOD, COD, *total Coliforms* (TC) higher than the Egyptian license. The results of the physico-chemical analysis of El-Rahway drainwater samples are appeared in table1.

In the present investigation, three species of nitrogen are measured in water bodies which are ammonia, nitrates and nitrites. Total Kjeldahl nitrogen is the whole of [ammonia, organic (i.e. Amino acids, humic acids, proteins & urea) and reduced nitrogen] and nitrate. The mean concentration of total nitrogen (TN) was 18.11 mg/L exceeded acceptable limits by Egyptian governmental law No. 48. Ammonia concentration was 13.21 mg/L, while nitrate concentration was 2.07 mg/L and nitrite concentration was less than 0.2 mg/L. These discoveries are agreed with Gaber *et al.* (2013) who acquired the most elevated amount of ammonia. The highest concentrations might be ascribed to the increased denitrification ($NO_2^- \rightarrow NO_3^- \rightarrow NH_3$) in water, when dissolved oxygen concentration is low. The increase of ammonia level is an indicator of the existence of pollutants of high activity *viz:* sewage discharge, industrial effluents and agriculture – runoff and could be ascribed to the increment in the oxygen consumption of the deteriorating organic matter and oxidation of chemical constitutes (Gaber *et al*., 2013).

The mean and median values of the trace and heavy metals in this examination indicated that manganese to be the most abundant element in water whilst cadmium got the least concentration. The outcomes of heavy or trace elements were less than the prescribed limits of articles 51 with the exception of cadmium and lead. The outcomes therefore acquired are perfect with study conducted by Gaber *et al*., (2013) on El-Rahway drain. They found that cadmium and lead concentrations ranged from 0.007 t0 0.009 mg/L and 0.042 to 0.071 mg/L, respectively.

The mean of COD and BOD values are higher than the breaking point suggested of article 51, which could be ascribed to heavy organic and inorganic stacking in addition to low oxygen demand values. The COD/BOD proportion are somewhere in the range of 1.3 and 1.7, which demonstrates that these wastes are readily biodegradable as shown in the investigation of Chatoui *et al.* (2016).

Total Coliforms counts in the composite samples were higher than the permissible limits of articles 51. Bacterial contamination recorded in this study could be credited for the most part to domestic sewage contamination and agriculture overflow (Zaghloul and Elwan, 2011).

Treatment process

In order to enhance water quality of El-Rahway drain, it would be essential to treat water to less than the permissible limit. This would be possible, if the purification efficiency of the present wastewater plants such as Zeinen and Abo Rawash is improved. The outcomes of the previous section of the present examination demonstrated that the wastewater contains high groupings of TP, TN, cadmium, lead, BOD, COD and TC. Moreover, investigated the adequacy of ALUM and disinfection (*via* chlorine and CuO NPs) to diminish these contaminations from wastewater. Two methodologies utilizing ALUM were carried on wastewater, followed by a sterilization utilizing chlorination process and nanoparticle was utilized to treat blended wastewater.

The impact of ALUM: A total of 5 jar test experiments was conducted by varying parameters, for example, ALUM dose. The fundamental goals of the examinations were to decide the ideal ALUM dosage which was efficient for removal TP, TN, cadmium, lead, BOD, COD and *total coliforms* bacteria. The impacts of ALUM on different parameters, for example, changes in pH, color, turbidity, TSS, TDS and trace elements were additionally noted and studied. The treatment train was; Sedimentation → Coagulation → Flocculation → Sedimentation→ filtration.

Table 1: The average and median for composite wastewater quality parameters collected along El-Rahway drain (n=20).

Parameter	Unit	Average	Median	Article 51-Decree 92 of Law 48 in 2013	Parameter	Unit	Average	Median	Article 51-Decree 92 of Law 48 in 2013
pH	Unitless	7.54±0.29	7.45	6.5-8.5	Chloride	mg/L	192.41±70	146.7	-
Alkalinity	mg/L	296.16±54	295.85	-	Nitrate	mg/L	2.07±2.3	1.27	-
Color	Pt/Co	95±57	60	-	Sulfate	mg/L	99.2±49	112.5	-
TDS	mg/L	753.33±150	646	1000	Aluminum	mg/L	0.128±0.102	0.1	-
TSS	mg/L	214.51±117	266	-	Cadmium	mg/L	0.007±0.0002	0.005	0.003
Turbidity	NTU	40.64±42	14.5	-	Copper	mg/L	0.066±0.005	0.064	1
T.N	mg/L	18.11±3.5	18.44	15	Iron	mg/L	0.265±0.131	0.196	3
Ammonia	mg/L	13.21±2.5	13.55	-	Manganese	mg/L	0.270±0.05	0.216	2
T.P	mg/L	5.51±0.96	5.47	3	Lead	mg/L	0.03±0.003	0.02	0.01
Calcium	mg/L	41.01±10.8	37.75	-	Zinc	mg/L	0.037±0.03	0.05	2
Magnesium	mg/L	20.09±3.7	20.15	-	BOD	mg/L	87.83±30.3	80	30
Potassium	mg/L	16.21±5.6	15	-	COD	mg/L	118.44±31.1	107	50
Sodium	mg/L	121.84±52	120	-	*Total Coliforms*	CFU/100ml	278×10^5	282×10^5	5000

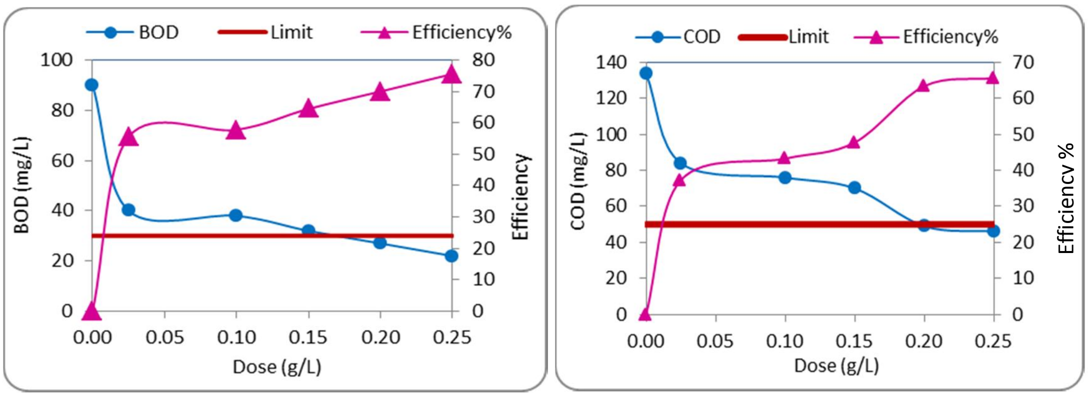

Figure 1: Variation of BOD and COD concentrations and their removal efficiencies with the dose of ALUM added to raw wastewater from El-Rahway drain ((R^2= 0.62 and 0.79, respectively).

The dose required for the contaminated parameters:

Organic removal: Humic and fulvic acids are coagulated by aluminum salts. Figure 1 delineated the removal of BOD and COD using various dosage 0, 0.025, 0.10, 0.15, 0.20 and 0.25 g/L of ALUM. The highest BOD and COD removal (%) was observed to be 70 % and 63.4% at 0.20 g/L of ALUM. The outcomes additionally demonstrated that the ALUM removal efficiency at 0.2 and 0.25 g/L were less than the recommended limit for BOD and COD. Dissolved organic can be expelled by adsorption on aluminum precipitation (Benschoten, 1990). The past investigation directed by Abdel-Kader *et al*., (2013) demonstrated that the COD removal efficiency by ALUM doses 0.15 to 0.35 g/L was extended from 25% to 69%, or, in other words, which is less than the efficiency in the present study. This distinction could be induced to the nature of raw wastewater, laboratory environment, purity of chemical used and time of experiment.

Total nitrogen (TN) removal: The reduction of total nitrogen by ALUM is delineated in Figure 2. Examination of the figure showed that the removal of total nitrogen with an ALUM dose of 0.2 g/L was 30.7%. While at ALUM dose 0.25 g/L have demonstrated that the removal efficiency was 28% shown that the highest removal was achieved at 0.2 g/L dosage.

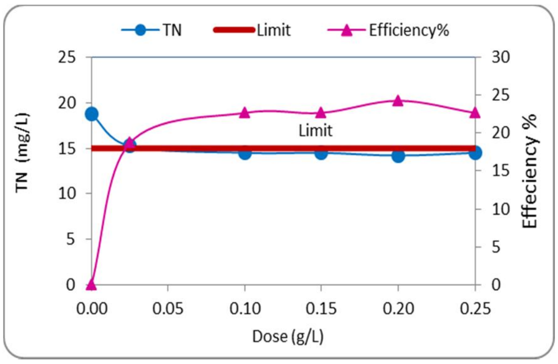

Figure 2: Effect of ALUM doses on total nitrogen (TN) concentration and removal efficiency (R^2= 0.69).

ALUM is extremely outstanding as an enhancer of phosphorus removal in aerobic biological systems (Ebelling *et al*., 2003). In this investigation, the raw composite wastewater samples were tested by ALUM doses of 0.025, 0.1, 0.15, 0.2 and 0.25 g/L resulted in removal efficiency 52%, 75%, 91%, 93% and 92%, respectively in concentrations less than the recommended limit, Figure 3. The removal of phosphorus by ALUM is illustrated by the accompanying precipitation reaction; aluminum is supplied by ALUM:

$$Al^{3+} + PO_4^{3-} \rightarrow AlPO_4 \downarrow$$

The outcome of the present work for TP removal are in a similar scope of the outcome acquired by Malhotra *et al.,* (1964) and higher than the percent got in an investigation led by Abdel-Kader *et al*., (2013).

ALUM did indicated high lessening impact on the counts of TC bacteria under scrutiny. The counts of TC before treatment was 4000000 CFU/100 ml and become 80000 CFU/ml after treatment with 0.2 g/L ALUM removing percentages of 98%. That might be explained to the capacity of $Al_2(SO_4)_3$ to form huge sized flocs in drain water because to its high content of natural organic matters and other chemical contaminants. Thus, most bacterial cells during stirring step be adsorped on these flocs, that generally removed during filtration. Similar outcomes accomplished by Bulson *et al.* (1984) who consider the impact of ALUM to remove some bacterial groups from Liberty lake water, USA. They established that 90% for each of *E. coli* and *fecal coliform* were reduced from the water samples and concentrated in the flocs. Another study by Ewida and Ibrahim (2014) indicated that 99.8% of *total coliforms* were treated or reduced from raw wastewater collected from El-Rahway drain.

Impact of ALUM on other parameters:

The addition of ALUM to water tested with various doses resulted in the decrease of pH from 7.46 for raw wastewater to 7.36, 7.34, 7.10, 6.99 and 6.82 for samples treated with dosages 0.025, 0.1, 0.15,0.2 and 0.25 g/L of ALUM, respectively. This implies that the higher the dose the lower the pH becomes. ALUM reduced the pHscale, since aluminum sulfate was hydrolyzed to form a colloidal aluminum hydroxide and an equal amount of sulfuric acid in accordance with the accompanying chemical reaction (1):

$$Al_2(SO_4)_3.18H_2O \leftrightarrow 2Al(OH)_3.3H_2O(s) + 3H_2SO_4 + 6H_2O \quad (1)$$

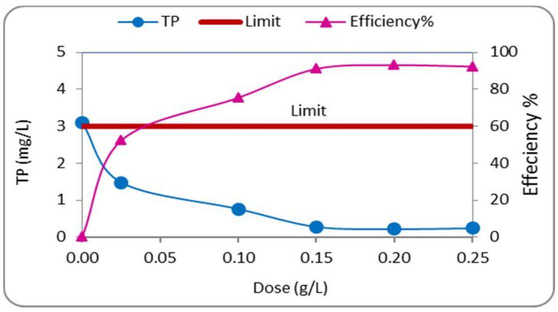

Figure 3: Variation of Total phosphorous (TP) concentration and its removal efficiency with the dose of ALUM (R^2= 0.73) added to raw wastewater from El-Rahway drain.

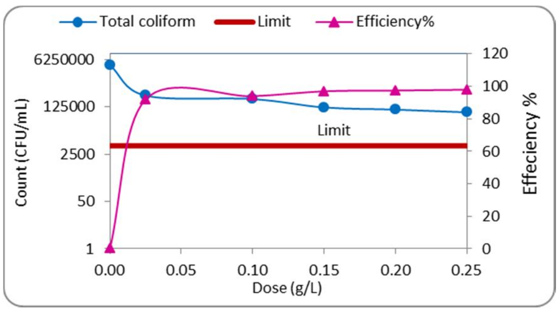

Figure 4: Variation of Total bacteria count (TBC) concentration and its removal efficiency with the dose of ALUM added to raw wastewater from El-Rahway drain (R^2= 0.47).

ALUM decreased alkalinity of the treated water tests in light of the fact that the metal ion is hydrolyzed to form hydrogen ions and floc from aluminum hydroxide. This hydrogen ions will react with the alkalinity of the water and the accompanying reaction (2) occurs:

$$Al_2(SO_4)_3.18H_2O + 6HCO_3^- \leftrightarrow 2Al\,(OH)_3.3H_2O\,(s) + 6CO_2 + 3SO_4^{2-} + 12H_2O \quad (2)$$

Color in water is obvious color and true color. Apparent (obvious) color came about because of colloid and suspended matters that can be secluded by filtration, while true color resulted from soluble chemical substances that cannot be isolated by filtration. Color in water may result from iron, manganese, ferric & sulfuric bacteria, humic and fulvic acids, lignin, algae, planktons, tannin and trade waste matters (Chermisinoff, 2002; Spellman, 2008). In this investigation distinctive doses of ALUM were applied wastewater tests resulted in the reduction of color of water with respect to raw wastewater sample. The samples treated with doses 0.2 and 0.25 g/L, the color strength reduced with removal efficiency 80%.

In this examination, the utilization of coagulation, flocculation, sedimentation and filtration on raw wastewater samples resulted in removal efficiency 55.5% for turbidity and 72% for suspended solids. The higher removal efficiency utilizing coagulants (ALUM) could be assigned by charge neutralization of negatively charged colloidal particles adsorb of positively charged species coagulant, and trap of the colloids in precipitating $Al(OH)_3$ solids (Amirtharajah and Mills 1982; Lartiges *et al*., 1997; Bache *et al*., 1999; Pernitsky and Edzwald 2006).

ALUM reduced the concentration of TDS by 0.2%, somewhat increased potassium, magnesium and chloride, for the most part increased in the form of sulfate concentration. ALUM increased lead and zinc. ALUM success to reduce cadmium, copper, iron, manganese, lead and zinc with removal efficiency 100%, 33%, 35%, 62%, 73% and 78%.

Table 2: Reduction of the water quality parameters after coagulation, flocculation, sedimentation and filtration and their removal efficiency.

Parameters	Unit	Raw wastewater	Characteristics after coagulation, flocculation, sedimentation and filtration	**% Removal efficiency**	Article 51-Decree 92 of the Law of 48 in 2013
pH	Unitless	7.455±0.01	6.905±0.12	**7.4**	6.5-8.5
Alkalinity	mg/L	363.65±2.33	249.5±9.20	**31.4**	-
Color	Pt/Co	150±16.7	30±16.7	**80.2**	-
TDS	mg/L	944.5±34.65	943±11.31	**0.2**	1000
Turbidity	NTU	71.75±25.53	31.9±2.40	**55.5**	-
TSS	mg/L	174.5±19.21	48.5±12.02	**72.2**	-
Calcium	mg/L	62.55±	60.545±3.51	**3.2**	-
Potassium	mg/L	15.5±0.71	16±0.84	**-3.2**	-
Magnesium	mg/L	25.75±1.54	28.57±2.33	**-11.2**	-
Sodium	mg/L	140±12.1	140±13.5	**0.0**	-
Chloride	mg/L	259.25±37.69	282.9±4.67	**-9.1**	-
Sulfate	mg/L	150.4±26.16	303.5±23.76	**-101.8**	-
Cadmium	mg/L	0.007±0.0002	<0.001	**100.0**	0.003
Copper	mg/L	0.066±0.005	0.044±0.002	**33.3**	1
Iron	mg/L	0.266±0.10	0.029±0.06	**89.5**	3
Manganese	mg/L	0.270±0.05	0.103±0.01	**61.9**	2
Lead	mg/L	0.03±0.003	0.008±0.002	**73.3**	0.01
Zinc	mg/L	0.037±0.03	0.008±0.01	**78.4**	2

Negative values represent byproducts of the treatment process or increase the concentration after application of treatment.

Disinfection by chlorination

A 100 mL test wastewater sample was taken for every chlorine dosage applied in various concentrations utilizing NaOCl dozing. The relation between the chlorine dose and chlorine residual are figured in Figure 6 to build up a break point chlorination for an ideal dosage of chlorine. Various chlorine dosages were applied to raw wastewater and treated water to decide the ideal dosage of chlorine required. The outcomes proved that 35 mg/L and 10 mg/L was the ideal dosage for disinfection of raw and treated water, respectively.

Disinfection by copper oxide nano particles (CuONPs)

Bacterial sterilization by CuO NPs was elucidated by numerous writers to the released Cu ions from the NPs come in contact with the bacteria cell membrane that harm to cell membrane (Ruparelia *et al*., 2008). Since the released Cu ions may lead to disorder in the DNA helical structure by the interaction of the ions with DNA molecules. Another elucidation was accounted for by Heinlaan *et al.* (2008) to "nano-effect" that is the size of nano-copper oxide plays an essential role in the toxicity and hence, in the disinfection efficiency. The most recent proposed mechanism is the oxidative stress reported by Ivask *et al.* (2010) that is reactive oxygen species (ROS) might be actuated by CuO NPs, relying upon CuO NPs dissolution rate, where ROS may do damage to the bacterial cell structure. Nonetheless, the mechanism was applied to *E. coli* bacteria only Heinlaan *et al.* (2008).

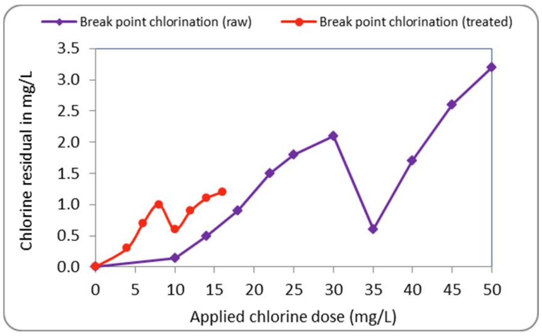

Figure5: Residual chlorine versus applied chlorine dose for composite wastewater collected from El-Rahway drain and treated water samples by ALUM.

In this investigation, the sol-gel process includes the formation of CuO nanoparticles by these chemical reactions:

$$CuCl_2 + 2NaOH \rightarrow 2NaCl + Cu(OH)_2$$

$Cu\ (OH)_2$ decomposes on heating into CuO:

$$Cu\ (OH)_2 \rightarrow CuO + H_2O$$

Particular CuO NPs sizes acquired utilizing the sol-gel strategy. By applying Debye–Scherrer equation to the obtained XRD pattern of the CuO-NPs, The BET Surface area was found to be 76.3014 m^2/g and the average particle radius was seen to be 1.78 nm. The X-ray diffraction (XRD) pattern of the CuO samples prepared is portrayed in Figure 6 and showed CuO with a monoclinic phase. No characteristic peaks of any other impurities such as Cu $(OH)_2$, Cu_2O, or precursors used are watched, indicating the formation of a pure phase CuO. The peaks were matched utilizing JCPDS (Joint Committee on Powder Diffraction Standards) software and it was well matched with the CuO of file No "Pdf # 892531".

Diverse parameters impact on copper nanoparticle

Antibacterial activity of various CuO NPs concentrations: The antibacterial activity of the diverse concentrations of CuO NPs was analyzed against TC bacterial indicators. The results of TC bacterial degradation by various concentrations CuO treated wastewater are recorded in Figure 7. At a concentration of 0.1 and 1 mg/L CuO NPs, TC degradation was 10% and 83%, respectively. While at higher concentrations 2, 3, 5 and 7 mg/L, TC degradation achieved more than 99%. Finally, the ideal concentration of CuO NPs for TC antibacterial removal was 2 g/L.

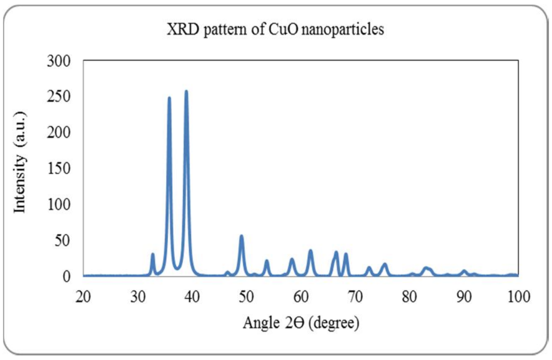

Figure 6: XRD pattern of prepared CuOnanoparticles by sol - gel method.

Impact of pH: To decide the ideal pH for TC antibacterial activity utilized CuO NPs. To prepare 6, 7 and 8 (acidic, neutral ad basic media) pH values phosphate –citrate was utilized. This ranged was chosen in perspective on that represent the ideal range for bacterial growth and were utilized as the test medium for the bacterial degradation percentage. CuO NPs at examined pH medium demonstrated a slight difference in the TC indicator. The outcomes demonstrated increasing degradation percentage of TC bacteria with decreasing pH values by 5% and 1 % maximum impact for 1 mg/L and 2 mg/L CuO NPs, respectively, as appearedin Figure (8). For Raw wastewater, the ideal pH was 6 for TC antibacterial removal at 1 and 2 g/L CuO NPs.

Impact of shaking time: The TC antibacterial inhibition growth rate utilizing 1 mg/L CuO NPs after shaking time 0, 1, 2 and 24 hours was 54%, 80%, 82% and 95%, respectively. While at 2 mg/L CuO NPs, the TC antibacterial inhibition was 63.6%, 98.2%, 99.6% and 99.9 % at shaking time 0, 1, 2 and 24 hours, respectively. For TC antibacterial removal, the perfect shaking time was 24 and 2 hours for 1 and 2 g/L CuO NPs, respectively. These results proved that the antibacterial activity of CuO NPs ascended with shaking time. In conclusion, shaking may give a higher chance for bacterial contact impact with the CuO NPs as indicated in Figure (9).

Finally, the ideal concentration of CuO NPs for TC antibacterial removal was 2 g/L at pH 6 and shaking time 2 hours.

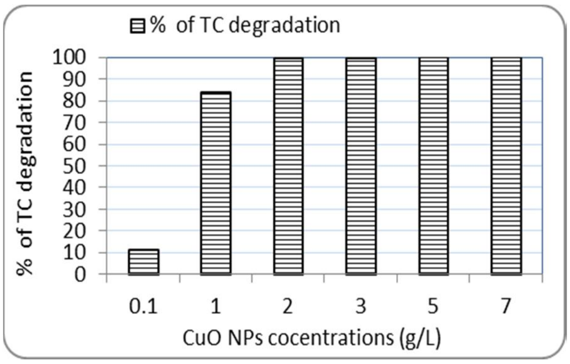

Figure 7: Effect of CuONPs different concentrations on TC bacterial degradation percentage.

Comparison between the two treatment Techniques:

Technique 1: Sedimentation → Coagulation→ Flocculation (ALUM)→ Sedimentation→ Filtration→ Disinfection (sodium hypochlorite).

Technique 2: Sedimentation → Coagulation (ALUM) → Flocculation → Sedimentation → Filtration → Disinfection (CuO NPs).

The obtained results of the treated water were in comparison to the permissible limits of article 51 concerning the license criteria of releasing the drainage water before throwing to the freshwater bodies as appeared in table 3. The influence of chemical additions on the physical, chemical and microbiological water quality is well examined as a appeared in Table 3.

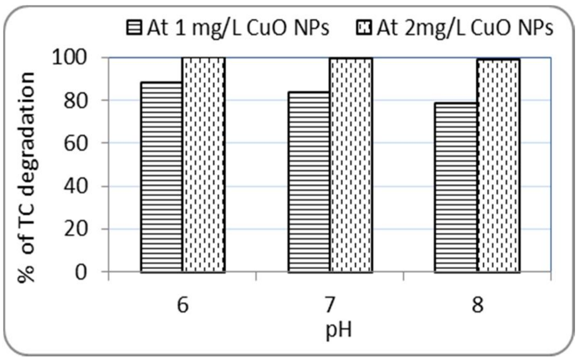

Figure 8: Antibacterial of CuO NPs on TC bacterial degradation percentage with different pH (6,7 and 8).

Statistically, the results of table 3demonstrated that the comparison between the results of the two techniques to treat of composite wastewater samples from El-Rahway drain and Raw wastewater showed significant difference (<0.05) for all studied water quality parameters except TDS, potassium, chloride, iron and zinc. In order that the effect of the two techniques on pH, alkalinity, color, turbidity, TSS, TP, TN, BOD, COD, calcium, sodium, magnesium, sulphate, cadmium, copper, lead, manganese, TC, is unmatched.

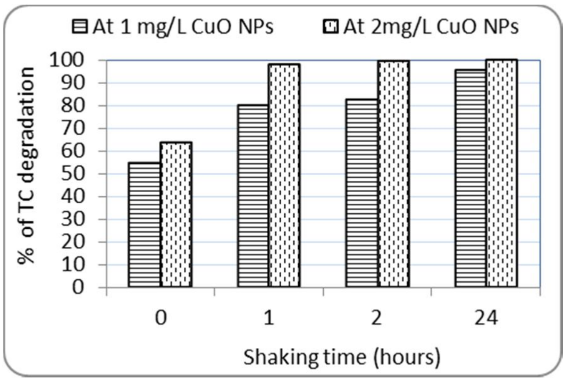

Figure 9: Antibacterial of CuO NPs on TC bacterial degradation percentage with shaking time (0, 1,2 and 24).

The outcome of the techniqueI indicated that the chemical added (0.25 g/L ALUM & 35 mg/L chlorine) reduced pH, alkalinity, color, turbidity, TSS, TP, TN, BOD, COD, calcium, magnesium, sodium, chloride, cadmium, copper, iron, manganese, lead, zinc & *total coliform* (TC). While the concentration of TDS was raised by 1 % as a result of increase potassium and sulfate concentrations. The high removal efficiency of these chemicals may be ascribed to the sedimentation. Coagulation, formation of floc, filtration and chlorination steps.

The data of technique II indicated that the chemical added (0.25 g/L ALUM & 2 mg/L CuO NPs) reduced pH, alkalinity, color, turbidity, TSS, TP, TN, BOD, COD, calcium, potassium, magnesium, sodium, chloride, cadmium, copper, iron, manganese, lead, zinc & *total coliform* (TC). While the concentration of TDS was raised by 1% as a result of increase sulfate concentration.

The results proved that technique I and technique II removed the studied parameter by approximately the same percentage except that alkalinity, potassium, sulfate, copper, manganese, lead & zinc were removed in higher percentages by procedure II than the procedure I. The CuO NPs showed the higher adsorption capacity of the aforementioned parameters could be ascribed by its nano-scale particle size giving access to a larger surface area. For cadmium and iron agree with the finding of Taman *et al.,* (2015).

Conclusion

The present examination accomplished that, composite wastewater collected from El-Rahawy drain were mostly suffering from quality disorders concerning physico-chemical and bacteriological qualities. The drainage water contains higher groupings of TP, TN, cadmium, lead, BOD, COD and *total Coliforms* (TC) higher than the permissible limits for drainage water. The outcomes of utilizing ALUM for wastewater treatment showed that the removal efficiencies of TP, TN, cadmium, lead, BOD, COD and *total coliforms* (TC) were increased with increasing the ALUM doses. ALUM was capable of reducing TP, TN, cadmium, lead, BOD, COD and *total Coliforms* (TC) by 93%, 30%, 100%, 73%, 70%, 63% and 97%, respectively at a dose 0.2 g/L to lower than the recommended limits of all pollutants except TN and TC. The chlorine dosage required for sanitizing raw wastewater and water treated by ALUM were 35 and 10 mg/L, respectively. CuO NPs were prepared by a sol-gel method has a monoclinic pure phase, has a surface area of about 76.3014 m²/g and the average particle radius 1.78 nm. The dosage of CuO NPs required for disinfection was 2 g/L at pH 6 and shaking time two hours. The outcome demonstrated that both techniques applied have the ability to treat wastewater to less than the limits and CuO NPs was capable of to replace chlorine in order to control of chlorine toxicity. Further research needs attention on these technique for utilization in a better way in situ for treating wastewater before release into fresh water bodies.

Table 3. Comparison between raw wastewater, water treated by technique I (ALUM+chlorination) and water treated by technique II (ALUM+CuO NPs) on chemical and microbiological parameters of El-Rahway wastewater drain (average n=3).

Sample code	**Unit**	**Raw wastewater**	**Characteristics after coagulation, flocculation, sedimentation, filtration and chlorination**	**% Removal efficiency**	**Characteristics after coagulation, flocculation, sedimentation, filtration and CuO NPs**	**% Removal efficiency**	**Article 51-Decree 92 of the Law of 48 in 2013**
			Technique I		**Technique II**		
pH	Unitless	7.59^{A}±0.01	7.12^{B}±0.02	**6**	7.53^{A}±0.01	**1**	6.5-8.5
Alkalinity	mg/L	333.65^{A}±2.33	233.80^{B}±1.68	**30**	219^{C}±2.45	**34**	-
Color	Pt/Co	95^{A}±16.7	35^{B}±6.41	**63**	40^{B}±17.55	**58**	-
TDS	mg/L	944.5^{A}±34.65	954^{A}±54.79	**-1**	956^{A}±36.42	**-1**	1000
Turbidity	NTU	71.75^{A}±25.53	16.1^{B}±5.37	**78**	14.5^{B}±4.21	**80**	-
TSS	mg/L	174.5^{A}±19.21	7^{B}±4.57	**96**	6^{B}±3.28	**97**	-
TN	mg/L	15.3^{A}±3.2	7.75^{B}±2.09	**49**	4.75^{B}±1.21	**69**	15
TP	mg/L	4.1^{A}±1.2	<0.2^{B}	**100**	<0.2^{B}	**100**	3
BOD	mg/L	95^{A}±6.4	10^{B}±1.12	**89**	3^{B}±0.52	**97**	30
COD	mg/L	175^{A}±18.52	51^{B}±9.28	**71**	18^{C}±5.21	**90**	50
Calcium	mg/L	62.45^{A}±5.43	50.2^{B}±4.59	**20**	48.92^{B}±4.78	**22**	-
Potassium	mg/L	15^{AB}±0.71	16^{A}±1.12	**-7**	14^{B}±0.75	**7**	-
Magnesium	mg/L	25.75^{A}±1.54	19.92^{B}±2.43	**23**	19.92^{B}±1.62	**23**	-
Sodium	mg/L	259.25^{A}±12.1	140^{B}±19.13	**54**	145^{B}±12.72	**55**	-
Chloride	mg/L	150.4^{A}±37.69	238.8^{A}±59.59	**8**	226^{A}±39.62	**13**	-
Sulfate	mg/L	100.4^{C}±16.16	278.7^{A}±41.36	**-85**	211^{B}±17.50	**-111**	-
Cadmium	mg/L	0.007^{A}±0.0002	<^{C}	**100**	0.001^{B}±0.0002	**72**	0.003
Copper	mg/L	0.0708^{A}±0.006	0.0334^{B}±0.0095	**53**	<^{C}	**100**	1
Iron	mg/L	0.095^{A}±0.11	<^{A}	**100**	<^{A}	**100**	3
Manganese	mg/L	0.2875^{A}±0.06	0.06^{B}±0.009	**79**	0.0022^{C}±0.006	**99**	2
Lead	mg/L	0.016^{A}±0.003	0.006^{B}	**62.5**	<^{C}	**100**	0.01
Zinc	mg/L	0.037^{A}±0.03	0.019^{A}±0.02	**49**	<^{A}	**100**	2
Total coliforms	Count (CFU/mL)	4000000^{A}	0^{B}	**100**	0^{B}	**100**	5000

Negative values represent byproducts of the treatment process or increase the concentration after application of treatment. Data represented as mean±SD of 3 samples. Means with a single letter (A, B, C) in the same row are significant ($p<0.05$).

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