

Chemical Treatment of Petroleum Wastewater and its Effect on the Corrosion Behavior of Steel Pipelines in Sewage Networks

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Abstract

The sources of wastewater from municipal and different industries act as a substantial pressure on the surrounding environment, so the waste management is ordinarily required before drainage. The environmental protection agency added specific and limited levels for discharging the pollutants into the municipal networks or into the sea. The treatment process of industrial wastewater became must to remove the contaminants or pollutants, which produced from the production procedure to a maximum, which does not negatively affect the environment. Chemical coagulation process is the highest important technique for industrial wastewater treatment because of its efficiency to minimize the contaminants in wastewater. The coagulants for higher removal of the contaminants and have a low cost is the most important choice of wastewater treatment. In this paper, chemical coagulation process for a petroleum wastewater sample by using ferric chloride, aluminum sulfate and polyacrylamide separately or as a mixture as well as the corrosion behavior of untreated and treated wastewater samples have been investigated. According to the obtained results the best formula, which gives the best result in removal of the organic and inorganic wastes as well as the best corrosion results is the mixture of aluminum sulfate and polyacrylamide. This formula have double functions, decreasing the total dissolved salts of about 21.11% and decreasing the COD and BOD content with about 47.95% and 53.57% respectively. These results proved that this formula is the best in corrosion behavior on mild steel pipelines.

Keywords: Wastewater treatment; Chemical treatment; Corrosion control; Steel pipelines

Introduction

Petroleum industry is important due to its impact on the environment because of the generated huge amount of water during its process. The wastewater from this industry is generally strong and may contain toxic pollutants. Petroleum industrial wastewater usually contains organic and inorganic matters in different concentrations and contains heavy metals, surfactants, grease, oils and different salts. It is well known that the wastewater causes severe problems for the environmental due to their toxicity of coloring materials, huge amount of suspended organic compounds and high chemical oxygen demand (COD). Therefore, they have to treat these pollutants before discharging into the environment [1]. There are many different common and conventional techniques for wastewater treatment; chemical physicochemical and biological methods are used in the treatment of the petroleum wastewater. The most abundant and effective is the chemical treatment [2-8]. Chemical treatment permits reduction of dissolved and suspended pollutants as well as the high concentration of fat, oil and grease from petroleum industrial wastewater. Precipitation process by using coagulants in wastewater treatment includes the addition of organic or inorganic chemicals to alter dissolved and suspended solids and enable their removal by sedimentation. Generally, coagulation is the method in which colloidal particles in water is accumulated together into larger particles, called flocs. Coagulants have been known since early in the twentieth century and they play an essential role in the removal of many impurities from polluted waters [9]. Coagulation is used to achieve maximum removal of COD and TSS [10]. Chemical coagulation [11] is not only the applied technique but also there are many other techniques; adsorption [12], photocatalytic processes [13] and microfiltration [14]. Electrocoagulation is one of the best techniques in petroleum wastewater especially in oil and greasy wastewaters [15,16]. The evaluation of successive technique depends on the removal capacity and reduction of organics, inorganics and toxic materials in oily wastewater. The

chemical treatment process depends on the type of coagulants. The most famous and available in the field is inorganic metal based-coagulants. Other examples of inorganic metal coagulants are aluminum sulfate, ferric chloride and ferric sulfate and it is well notorious that the alum is very imperative in water purification for a long time. In the recent years, the pre-polymerized inorganic coagulants have become massive applications due to their availability such as poly aluminum chloride and aluminum chlorohydrate [17]. The poly aluminum chloride has several uses, including the removal of suspended materials and organic matters, metal and heavy metal ions as well as coloring agent [18]. During the last twenty years, the researchers are in a challenge for improving the exclusion of pollutants from the wastewater. The exclusion of organic materials by coagulation process is subjective by many factors such as the conditions and the characteristics of these materials. Consequently, the removal of organic matters by coagulation varies widely between 10% and 90%. The effectiveness of these coagulants were found to be dependent on the constituents of the wastewater, temperature, dose, mixing rate [19]. The present work aims to evaluate and compare the capability of polyacrylamide or ferric chloride or aluminum sulfate individually and mixed in treatment of the petroleum wastewater. The second task is concerned with the investigation of the corrosion behavior for untreated and treated wastewater.

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Materials and Methods

Materials

The collection of wastewater under study is coming from petroleum company, situated in industrial area, El-Ain El-Sukhna, Suez, Egypt. The coagulant Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) were purchased from El-Nasr Company, Cairo, Egypt. Polyacrylamide, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were come from Ultra Extract Company for water and wastewater treatment.

Methods

Take known weight of the coagulants of ferric chloride, aluminum sulfate and/or polyacrylamide before starting the experiment. We need to filter the petroleum wastewater sample before the treatment as a control. Adjust the pH of the filtered sample by sodium hydroxide to be more than 10. Divide the adjusted sample into seven filtered samples. Chemical treatments were occurred for six of them and the seventh one was remained without any chemical treatment as a blank. On the other hand, one sample was taken before any filtration or pH adjustment or chemical treatment was subjected to full analysis for comparison of the treated samples. A conventional jar test apparatus was used in the experiments to coagulate the six pH adjusted filtered samples of petroleum wastewater by using ferric chloride, aluminum sulfate and polyacrylamide. A batch test was carried out by it, accommodating a series of six beakers together with six-spindle steel paddles; then the samples were mixed homogeneously. After the desired amount of polyacrylamide, aluminum sulfate and ferric chloride was added to the samples, the beakers were agitated at mixing 150 rpm for 10 minutes to coagulation. After stopping the agitation, the suspension was allowed settling for 30 minutes. Then it was filtered to collect 1500 ml where pH is readjusting for them adding HCl or NaOH to be at range 7 to 8 and the gained volume is divided into two portions; one portion is 1400 ml for chemical analytical analysis and another portion is 100 ml for making corrosion experiments.

pH measurements: The efficiency of the wastewater treatment is very much pH sensitive. Monitoring of pH can indicate changes in raw and finished water quality. The efficiency of chlorination and coagulation, and the corrosively of treated water, depends on the pH values. The pH meter is consisted of potentiometer, glass electrode, reference electrode and a temperature in compensating device. Most modern pH meters use a single combined electrode. Set the set points of buffers b1, b2 or b3. Normally the used set points are; 4.0, 7.0 and 10.0, the pH meter will recognize these set points automatically when in calibration mode. The measuring of the pH values are highly required as soon as possible after sample collection, preferably within 15 minutes. If sample must be stored, it should be refrigerated at 4°C with no preservatives added and the test must be performed not later than six hours after collection. If pH values vary widely, standardize for each sample with a buffer solution having a pH within 1 to 2 pH units of the sample.

Alkalinity: The alkalinity of any water represents a measure of its capacity to neutralize an acid. The alkalinity of natural water may exist as carbonates, bicarbonates, hydroxides, silicates, and phosphates. The presence of one or more of these ions depends on the pH of the water. Two titration procedures exist for determination of the alkalinity, the first one is concerned with measuring the pH by using a pH meter and the

second one is arisen by using traditional pH indicators. The procedure involves titrating first to a pH of 8.3 using phenolphthalein indicator, the color change of pink to colorless and then continuing the titration to a pH of about 4.5 using methyl orange indicator with a color change from yellow to pink. Calculations are processed form determining carbonate, bicarbonate, and total alkalinity. All values are expressed in terms of equivalent calcium carbonate (CaCO_3).

Total residual chlorine: The chlorination of the treated effluent serves primarily to destroy or deactivate disease-causing microorganisms. Chlorination may produce adverse effects due to formation of potentially carcinogenic compounds such as chloroform. Combined chlorine formed on chlorination of ammonia or amine-bearing water adversely affects some aquatic life. To minimize any adverse effects, it is essential that proper testing procedures by using the optimum dose of chlorine. In wastewater, total residual chlorine usually measured while chlorination seldom is carrying far enough to produce free chlorine. Select a sample volume that will require not more than 20 ml 0.01 N $\text{Na}_2\text{S}_2\text{O}_3$ and not less than 0.2 ml for the starch iodide until the end of reaction. For a chlorine range of 1 to 10 mg/l, use a 500 ml sample; above 10 mg/l, use proportionately less sample. Place 5 ml acetic acid, or enough to reduce the pH to between 3.0 and 4.0, in a flask or white porcelain casserole. Add about 1 g KI estimated on a spatula. Pour sample in and mix with a stirring rod. Titrate away from direct sunlight. Add 0.025 N or 0.01 N $\text{Na}_2\text{S}_2\text{O}_3$ from a burette until the yellow color of the liberated iodine is almost discharged. Add 1 ml starch solution and titrate until the disappearance of the blue color.

Total Suspended Solids (TSS): Filter a well-mixed sample through a pre-washed, pre-weighed, glass fiber filter. The suspended solids are retained on the filter then rinsed, dried, and weighed. The increasing in weight represents the suspended solids. TSS samples can be either composite or grab samples and can be collected in either glass or plastic. Analyze the samples as soon as possible or preserve it by ice or refrigeration to reduce microorganism activity. Holding time is no longer than 7 days. Obtain a clean, dry gooch crucible, filtering flask, and vacuum hose then warm the sample to room temperature. Tare weight determination and remove a gooch crucible containing a prewashed filter from the desiccators. Zero the analytical balance, place the gooch crucible containing the filter on the balance using crucible tong. Remove the gooch crucible from the desiccators using the tong and place on the filtering flask. Wet the filter with a small volume of reagent water to seat the filter. Stir the sample on magnetic stirrer with sufficient speed to provide a homogenous solution. Stirring too fast may cause particles to separate by size and weight. Pipet the desired volume from a point mid-depth and mid-way between the wall and the vortex. Exclude large floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not representative. Because excessive residue on the filter may form a water-trapping crust, limit the sample size to that yielding not more than 200 mg residue. For samples of high dissolved solids, thoroughly wash the filter to ensure removal of the dissolved material. Prolonged filtration times resulting from filter clogging may produce high results owing to the increased colloidal materials captured on the clogged filter. Some chloride and nitrate salts may be lost. Choose sample volume to yield between 2.5 and 200 mg dried residue. If volume filtered fails to meet minimum yield, increase sample volume up to one liter. If complete filtration takes more than 10 min, increase filter diameter or decrease sample volume.

Oil and grease: The experiment oil and grease could be defined as any recovered material as a substance soluble in the solvent. It includes other material extracted by the solvent from an acidified sample (such as sulfur compounds, certain organic dyes, and chlorophyll) and not volatilized during the test. Collect a representative grab sample in a wide-mouth glass bottle. Then wash it with soap and rinse it with water. Finally it is rinsed with solvent to remove any residues that may be interfered with the analysis. Do not overfill the sample container and do not subdivide the sample in the laboratory. In case of delaying the analysis for more than 2 h, acidify to pH 2 or lower with either 1:1 HCl or 1:1 H₂SO₄ and refrigerate. Mark the sample bottle at the water meniscus just it is coming into the laboratory. If the sample is not previously acidified, acidify it with either 1:1 HCl or 1:1 H₂SO₄ to pH 2 or lower (generally, 5 ml is sufficient for one liter sample). Using liquid funnel, transfer sample to a separating funnel. Carefully rinse sample bottle with 30 ml extracting solvent (either 100% n-hexane, or solvent mixture) and add the solvent washings to a separating funnel. Shake it vigorously for 2 min. Let layers separate and drain the aqueous layer and small amount of organic layer into original sample container. Drain solvent layer through a funnel containing a filter paper solvent rinsed, into a clean, tared evaporating dish. If a clear solvent layer is not obtained and an emulsion of more than about 5 ml exists, drain emulsion and solvent layers into a glass centrifuge tube and centrifuge for 5 min at approximately 2400 rpm. Transfer centrifuged material to an appropriate separating funnel and drain solvent layer through a funnel with a filter paper into a clean, tared evaporating dish. Recombine aqueous layers and any remaining emulsion or solids in separating funnel. For samples with <5 ml of emulsion, drain only the clear solvent through a funnel with pre-moistened filter paper. Recombine aqueous layers and any remaining emulsion or solids in a separating funnel. Extract twice more with 30 ml solvent each time, but first rinse sample container with each solvent portion. Repeat centrifugation step if emulsion persists in subsequent extraction steps. Combine extracts in tared evaporating dish. Evaporate in a water bath at 85°C. Dry the dish with the oil layer in an oven for at least two hrs. Cool in desiccator for at least 30 min and weigh. To determine initial sample volume, fill sample bottle to mark with water and then pour water into a one liter graduated cylinder.

Nitrates: Nitrate is the highest oxidation state of nitrogen. It may occur in a water supply due to the oxidation of organic nitrogen to ammonia and then to nitrite and then to nitrate. The pollution by organic wastes is identifying by the presence of nitrate in water, since nitrate is presented in trace amounts in surface water, but may reach high levels in ground water. Nitrate at levels above 105 mg/l as N can cause an illness known as Methemoglobinemia in infants. Nitrogen is also one of the fertilizing essential elements of the growth of algae. Samples are collected in glass or plastic bottles with a volume of at least 100 ml. Samples should be analyzed as soon as possible after collection (within 1 hour), but may be stored at 4°C for up to 24 hours. For longer storage, up to 7 days, preserve the sample with 2 ml concentrated sulfuric acid per liter and store at 4°C. Note, when samples are preserved with acid, the result measurement will include nitrite and nitrate.

Biochemical Oxygen Demand (BOD₅): The BOD test is one of the most difficult tests to run because there are so many variables that

affect the outcome. The BOD dilution water must be aerated and non-contaminated and the pH environment must be acceptable (6.5-7.5). The incubation temperature must be controlled and consistent (20 ± 1°C) and the microorganisms must be viable, must be acclimated to the waste material must be active and must be at acceptable concentration. The sample strength must be sufficient to cause a DO depletion of at least 2 mg/l but leave at least 1 mg/l residual and toxic materials must be absent. In summary, the BOD test must create ideal growing conditions, which will encourage microorganisms to affect and efficient utilize the digestible organic materials. In the BOD test, microorganisms are characterized with eating all the organics. In a BOD bottle, organics from a sample are added to dilution water containing nutrients, oxygen, and microorganisms, then capped and incubated at 20°C for 5 days. Initially the microorganism level is low, but the environmental growing conditions are excellent, so the microorganisms quickly enter the logarithmic growth reproduction phase and begin to consume the organics. The large number of microorganisms consumes the organics and because of consumes the oxygen. If the BOD bottle is capped tightly, no external oxygen can enter. The microorganisms can only utilize the oxygen initially available. Over the next couple of days, the microorganisms continue to digest the organics, reproduce logarithmically, and utilize oxygen rapidly. By the 4th day of the BOD test, the organics have begun to become limited, just barely able to maintain the current microorganism population, which is called stationary growth phase. The lack of food causes a slowing in the reproduction rate as well as a decrease for oxygen used. With the high microorganism population, the remaining organics are quickly consuming and the microorganism enters the endogenous phase. During the endogenous phase, the microorganisms utilize internal food reserves, and many die (endogenous phase). The amount of oxygen that has been consumed over the 5 days is proportional to the amount of organics BOD consumed. The BOD represents the total amount of food used up over the 5 days. Complete stabilization of a sample may require a period of incubation too long for practical purposes; therefore, five days have been determined as the standard incubation period.

Chemical Oxygen Demand (COD): The chemical oxygen demand (COD) test represents the amount of chemically digestible organics. COD measures all organics that were biochemically digestible as well as all the organics that can be digested by heat and sulfuric acid. Most permits specify BOD₅ because it gives a better representation of the organics that are affecting the receiving stream. COD has the advantage over BOD₅ in that the analysis is completed within a few hours whereas BOD₅ requires 5 days. The major drawback of the COD test is the presence of hazardous chemicals and toxic waste disposal. COD often is used as a measurement of pollutants in wastewater and natural waters. In domestic wastewater, BOD₅ represents about 50-60% of the COD. Presence of toxic materials or industrial wastewater can alter this ration. Like the BOD test, where, oxygen is used to oxidize the organics to carbon dioxide and water. However, instead of free dissolved oxygen, chemically bound oxygen in potassium dichromate K₂Cr₂O₇ is used to oxidize the organics. As the potassium dichromate is used up the Cr⁺³ ion is produced. The amount of dichromate used is proportional to the amount of organics present. Likewise, the amount of Cr⁺³ ion presence is proportional to the amount of organics digested.

Organics+K₂Cr₂O₇, Cr⁺³

(Hexavalent Orange) (Trivalent Green)

Most labs use the Hach method to measure COD. This method uses test tubes with pre-measured amounts of potassium dichromate, sulfuric acid, and catalyst. Be sure the cap is on tight before mixing and mix just prior to place in the digestion reactor. The catalyst is silver. However, silver must be soluble and will precipitate if chlorides are present in the sample. To prevent silver precipitation, mercury is added to the reagents in the tube. The mercury will remove the chloride interference. Once the two hours refluxing period is finished, the remaining potassium dichromate is measured using the spectrophotometer. A reagent blank and standard must be prepared to zero the spectrophotometer. The sample is usually collected the same as BOD₅. The COD sample may be a composite or a grab sample. Because there are no microorganisms involved in this procedure, preservation is usually acidification using sulfuric acid to a pH below two. Refrigeration is acceptable if BOD₅ are also to be running on the sample. The sample holding time is seven days, much longer than the 24 hours allowed for the BOD₅ test. The sample volume is used for the COD test is 2.0 ml so measuring the sample volume is critical. Be sure to mix the sample well and homogenize if necessary. Pipet quickly to avoid settling errors. COD is running on industrial samples that may have high BOD₅. If the COD strength is greater than 1650 mg/l, the sample must be dilute. Make a 1:2 dilution by measuring 50 ml of sample and adding to 50 ml of deionized water, and then add 2.0 ml of the well-mixed dilution to the test tubes.

Electrochemical measurements: Mild steel is used as a working electrode with rod shape was subjected for XRF elemental analysis. The electrode is stacked in a Teflon holder with exposed area of 0.785 cm². Platinum wire and SCE electrodes were used as a counter and reference electrodes, respectively. The electrode surface was abraded successively by emery papers of different grades i.e., 150, 320, 400 and 600 then finely polished with a 2400 polishing paper to obtain uniform mirror like finish, degreased with acetone and washed with distilled water before the experiment. The open circuit potential of mild steel electrode was subjected for 30 min in the electrolyte (sediments) in free corrosion conditions before recording the polarization curves. Polarization curves were recorded at scan rates of 1 mV s⁻¹ to study the effect of chemical treatment on the corrosion behavior of mild steel. The corrosion behavior is subjected to the untreated and treated wastewater to select the best mixture of chemical treatment on the corrosion results. All the polarization measurements were performed in the potential range from the cathodic to the anodic side (-0.8 to 0.1 V) and at room

pH Experiment	pH before adjustment	pH after adjustment	pH after chemical treatment	pH after Readjustment
Blank	5.57	-----	-----	-----
Filtered blank	6.01	-----	-----	-----
1	5.72	10.6	4.46	7.62
2	5.72	10.60	7.97	7.43
3	5.72	10.60	9.66	7.58
4	5.72	10.60	7.62	7.63
5	5.72	10.60	7.29	7.81
6	5.72	10.60	8.60	7.96

Table 1: pH measurements of wastewater samples before and after treatment.

Experimental Items	Blank	Filtered blank	Standard limit
Temperature	48	46	43
pH	5.57	6.01	Not less 6 and not more 9.5
Biological Oxygen Demand (BOD)	883	790	600 ppm
Chemical Oxygen Demand COD	1633	1560	1100 ppm
Total Suspended Solids (TSS)	926	580	800 ppm
Grease and Oils	170	120	100 ppm
Precipitated materials after 10 min	4.19	2.19	8 cm ³
Precipitated materials after 30 min	6.54	4.54	15 cm ³
Electric Conductivity	100000	100000	Unlimited
Total Dissolved Salts (TDS)	60000	60000	Unlimited
Alkalinity	762	762	Unlimited
Total Organic Carbon (TOC)	1321	1321	Unlimited
Chlorides (Cl ⁻)	3798.5	3798.5	Unlimited
-2 Nitrates NO ₃	7.5	7.5	Unlimited
-- Sulfates SO ₄	131264	131264	Unlimited
-2 Carbonates CO ₃	77	77	Unlimited
-Bicarbonates HCO ₃	317.2	317.2	Unlimited
Na ⁺	54788	54788	Unlimited
K ⁺	933.48	933.48	Unlimited
Mg ⁺²	960.1	960.1	Unlimited
Ca ⁺²	48033.89	48033.89	Unlimited

Table 2: Analysis of wastewater sample before treatment without and with filtration compared with the permissible limits.

temperature. The corrosion tendency could be observed by measuring the open circuit potential and by using the Tafel extrapolation method for calculating the corrosion current density (i_{corr}).

Results and Discussion

Adjustment of pH for wastewater samples

Table 1 represents the pH values before the treatment and at the same time, the pH is measured for filtered sample to compare the wastewater constituents before and after filtration to overcome the effect of the filter paper. It is acknowledging that the chemical treatment is pH dependent reactions; the highest effect for coagulation is obtained at higher pH values. For the Egyptian standard for disposal to the municipal wastewater it is recommended to make the treated wastewater at pH from 6-8, so it is necessary to readjust the pH after treatment.

Chemical analysis of wastewater before treatment

Table 2 presents the chemical analysis of petroleum wastewater before treatment compared with the permissible limits for Egyptian standard.

Treatment of wastewater samples

Treatment of wastewater samples by separate coagulant: Three filtered wastewater samples were used in this experiment, firstly the pH was adjusted, then these samples became ready for the treatment with

Materials Experiment	FeCl ₃ g/100 ml	Al ₂ (SO ₄) ₃ g/100 ml	Polyacrylamide g/100 ml
1	3 gm	----	----
2	----	3 gm	----
3	----	----	1.5 gm

Table 3: Treatment of wastewater samples by separate coagulant.

Experimental Items	Treated sample with FeCl ₃	Treated sample with Al ₂ (SO ₄) ₃	Treated sample with polymer	Standard limit
Temperature	33	33	33	43
pH	7.62	7.58	7.97	6-9.5
Biological Oxygen Demand (BOD)	520	430	470	600 ppm
Chemical Oxygen Demand COD	1070	890	980	1100 ppm
Total Suspended Solids (TSS)	352	190	220	800 ppm
Grease and Oils	47	38	45	100 ppm
Precipitated materials after 10 min	1.1	0.85	0.9	8 cm ³
Precipitated materials after 30 min	1.4	1.0	1.2	15 cm ³
Electric Conductivity	286.8	260.2	272	Unlimited
Total Dissolved Salts (TDS)	57000	47644	56887	Unlimited
Alkalinity	703	598	680	Unlimited
Total Organic Carbon (TOC)	877	844	874	Unlimited
Chlorides (Cl ⁻)	3672.5	2917	3392	Unlimited
-2 Nitrates NO ₃	6.8	6.3	6.7	Unlimited
-2 Sulfates SO ₄	122352	86160	89976	Unlimited
-2 Carbonates CO ₃	60	44	54	Unlimited
- Bicarbonates HCO ₃	148.8	142.8	144.4	Unlimited
Na ⁺	48033.89	37659.92	47012	Unlimited
K ⁺	787.9	735.93	783.96	Unlimited
Mg ⁺²	761.16	361.48	580	Unlimited
Ca ⁺²	46011.2	41241	42723	Unlimited

Table 4: Analysis of wastewater samples after treatment with 3 gm/100 ml of ferric chloride (FeCl₃), 3 gm/100 ml aluminum sulfate Al₂(SO₄)₃ and 1.5 gm/100 ml polyacrylamide compared with the standard limit.

Materials xperiment	FeCl ₃ g/100 ml	Al ₂ (SO ₄) ₃ g/100 ml	Polyacrylamide g/100 ml
4	1.5 gm	1.5 gm	----
5	1.5 gm	----	0.75 gm
6	----	1.5 gm	0.75 gm

Table 5: Treatment of wastewater samples by mixing the coagulant.

3 g/100 ml ferric chloride, 3 g/100 ml aluminum sulfate and 1.5 g/100 ml polyacrylamide. To 1500 ml of untreated wastewater the coagulant was added and stirred for about 30 min by using magnetic stirrer, then the samples were filtered and the filtrates were collected for the chemical analysis. Table 3 represents the treatment for the selected wastewater by separate coagulant to identify the best one. The chemical analysis after treatment were listed in Table 4a, 4b and 4c respectively. From the gained results, it is found that the chemical analysis depends on the coagulant and the chloride ion is decreased in case of aluminum sulfate treatment if it is compared with ferric chloride or polyacrylamide.

Treatment of wastewater samples by mixing the coagulant: In this experiment, the wastewater samples were treated by mixing the coagulants as mentioned in Table 5. After treatment the water samples

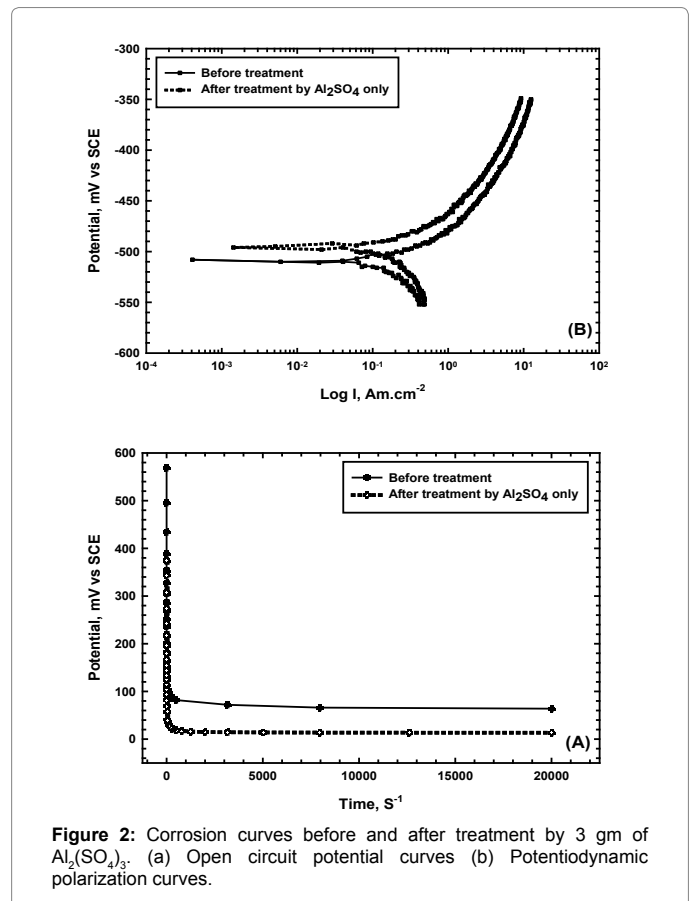
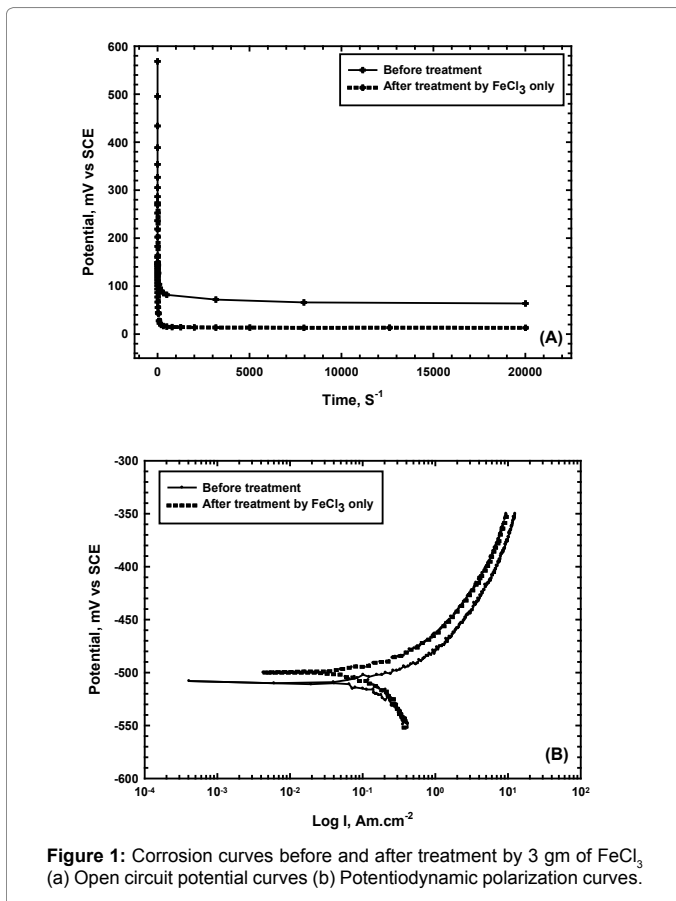
were collected and subjected to the chemical analysis and the obtained results were listed in Table 6a, 6b and 6c respectively. The results show that varieties cations and anions values, these values proved that the polyacrylamide when mixed with aluminum sulfate gives lowest concentration of chloride ions. The mixture between the polymer and Al₂(SO₄)₃ decreases the salt content, which is preferable in decreasing the corrosion process.

Corrosion experiments

Corrosion behavior of single coagulant: Secondly, 100 ml from each one of six chemically treated samples after adjusting the pH is used to evaluate the corrosion behavior. The 100 ml filtered sample without treatment is used as a blank experiment. All experiments are adjusted as the permissible limit and the recommendation of Egyptian

	Treated sample with mix. FeCl ₃ and Al ₂ (SO ₄) ₃	Treated sample with mix. FeCl ₃ and polymer	Treated sample with mix. Al ₂ (SO ₄) ₃ and polymer	Standard limit
Temperature	33	33	33	43
pH	7.62	7.29	7.96	6 - 9.5
Biological Oxygen Demand (BOD)	460	465	410	600 ppm
Chemical Oxygen Demand (COD)	910	980	850	1100 ppm
Total Suspended Solids (TSS)	230	260	180	800 ppm
Grease and Oils	39	42	31	100 ppm
Precipitated materials after 10 min	0.8	0.88	0.75	8 cm ³
Precipitated materials after 30 min	1.1	1.2	0.9	15 cm ³
Electric Conductivity	263.8	268.2	254.8	Unlimited
Total Dissolved Salts (TDS)	56698	56998	47334	Unlimited
Alkalinity	672	682	586	Unlimited
Total Organic Carbon (TOC)	863	872	825	Unlimited
Chlorides (Cl ⁻)	2946.5	3337	2692	Unlimited
-2 Nitrates NO ₃	6.1	6.2	6.0	Unlimited
-2 Sulfates SO ₄	87816	110768	70160	Unlimited
-2 Carbonates CO ₃	47	53	35	Unlimited
- Bicarbonates HCO ₃	140.6	146.6	126.4	Unlimited
Na ⁺	36791.95	42659.92	30345	Unlimited
K ⁺	703.95	720.92	671.97	Unlimited
Mg ⁺²	732	744	276.52	Unlimited
Ca ⁺²	33636	36636	30468	Unlimited

Table 6: Analysis of wastewater samples before and after treatment by 1.5 gm/100 ml of ferric chloride (FeCl₃) and 1.5 gm/100 ml of aluminum sulfate Al₂(SO₄)₃, by 1.5 gm/100 ml of ferric chloride FeCl₃ and 0.75 gm/100 ml of polyacrylamide (P) and by 1.5 gm/100 ml of aluminum sulfate Al₂(SO₄)₃ and 0.75 gm/100 ml of polyacrylamide (P).



Environmental Affairs before carrying out the corrosion experiments. Figure 1 represents the corrosion curves before and after the treatment by 3 gm of FeCl_3 . Figure 1a is attributing with the relation between open circuit potential and the treated sample with ferric chloride alone. It is clearly noticed that the open circuit potential values are shifted to the lower positive values of potential that means that the medium became corrosive in treated sample. The open circuit potential is decreased from 61.54 mV to 15.67 mV this value prove that the corrosion efficiency reached about 74.5%. The Figure 1b prove that the current density increases continuously with increase the potential, which means the corrosion process is in progress. The results are also showed that the untreated sample is more safe for the steel pipeline although the higher salinity, which is proved that this water was injected with corrosion inhibitor during the production process. After treatment the sample became free of corrosion inhibitor so the corrosion rate increases although the decrease of TDS after treatment.

Figure 2 illustrates the corrosion curves before and after treatment by 3 gm of $\text{Al}_2(\text{SO}_4)_3$. The Figure 2a shows that the open circuit potential decreases from 61.54 mV to 11.82 mV with corrosion efficiency of about 80.8% and the current density values are also increased with increasing the potential as mentioned in Figure 2b.

The corrosion curves before and after treatment by 1.5 gm/100 ml of polyacrylamide are mentioned in Figure 3. The open circuit potential is shifted from 61.5 mV to 19.53 mV which indicates the increasing the corrosion process with about 68.3% as seen in Figure 3a and the same behavior is clearly noticed in potentiodynamic polarization curves as mentioned in Figure 3b.

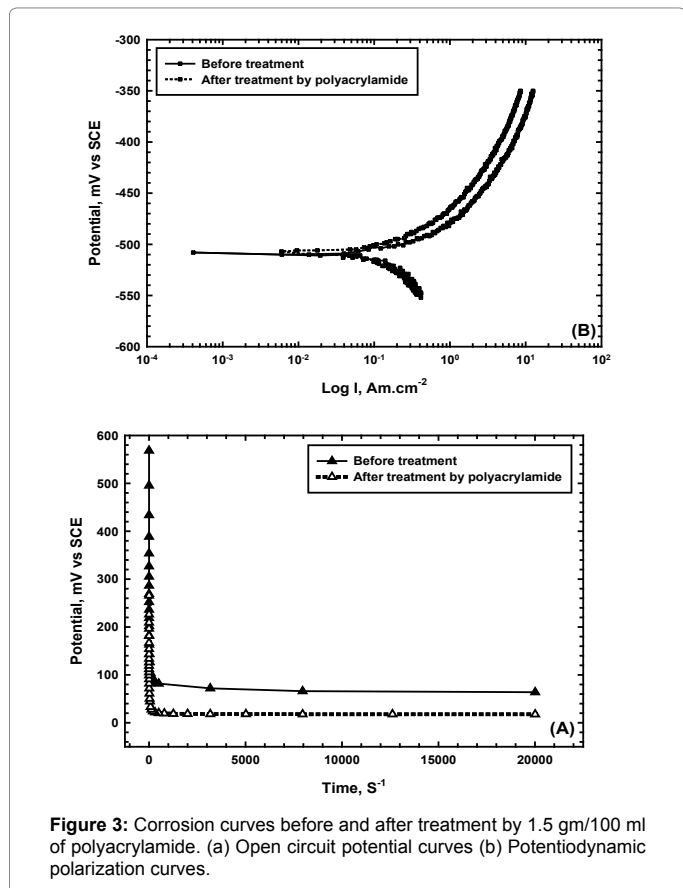


Figure 3: Corrosion curves before and after treatment by 1.5 gm/100 ml of polyacrylamide. (a) Open circuit potential curves (b) Potentiodynamic polarization curves.

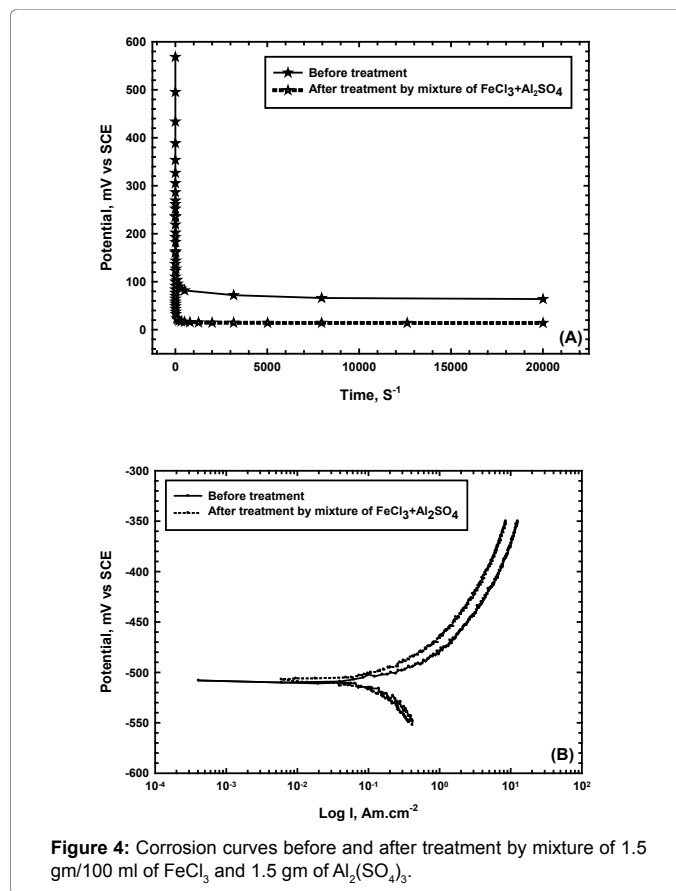


Figure 4: Corrosion curves before and after treatment by mixture of 1.5 gm/100 ml of FeCl_3 and 1.5 gm of $\text{Al}_2(\text{SO}_4)_3$.

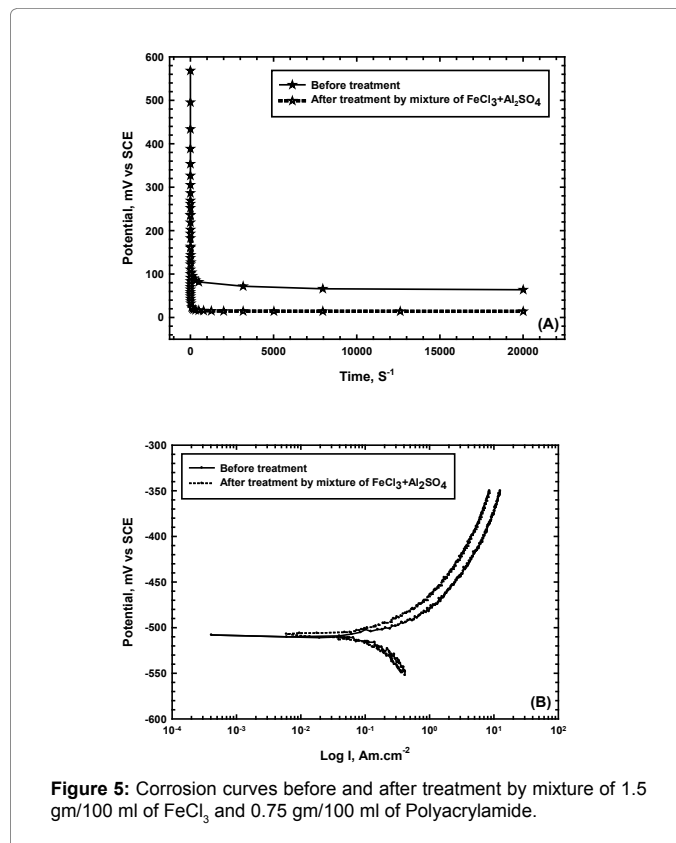


Figure 5: Corrosion curves before and after treatment by mixture of 1.5 gm/100 ml of FeCl_3 and 0.75 gm/100 ml of Polyacrylamide.

Corrosion behavior of mixed coagulant: The treated wastewater samples by mixed coagulant are subjected to corrosion behavior as mentioned in Figures 4-6.

The obtained open circuit potential values are 13.66 mV, 13.66 mV and 15.49 mV in case of the mixtures of $\text{FeCl}_3 + \text{Al}_2\text{SO}_4$, $\text{Al}_2\text{SO}_4 + \text{polyacrylamide}$ and $\text{FeCl}_3 + \text{polyacrylamide}$ respectively. The corrosion process efficiencies are 77.80%, 77.80% and 74.8% respectively. These results proved that the best one against corrosion process is polyacrylamide, which register the minimum corrosion efficiency of about 68.30%. The results of open circuit potentials of treated samples with single coagulant comparing with the untreated sample are mentioned in Figure 7a and 7b and the results of corrosion efficiencies are totally mentioned in the collective (Figure 7c).

Conclusions

The chemically treated wastewater is considered the best method to get rid the most pollutants which exist in the petroleum wastewater. The chemical treatment has the capability to reduce the total suspended materials and so it decreases the total residual carbon and nitrogen by removing the most organic compounds. The chemical treatment did not meet the requirements for the permissible limit of heavy metals especially in the water which contain high concentrations of heavy metals. The chemical oxygen demand and biological oxygen demand are reflected the water quality and the chemical precipitation was succeed to meet the standard level for COD and BOD. The reduction efficiency was calculated for COD and BOD and it is found that the percentages of about 47.95% and 53.57% respectively. By comparing the water quality parameters of the chemically treated wastewater we

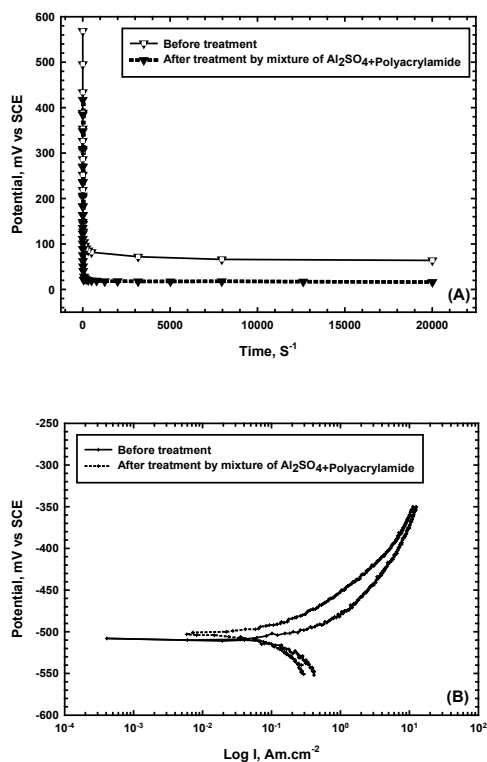


Figure 6: Corrosion curves before and after treatment by mixture of 1.5 gm/100 ml of $\text{Al}_2(\text{SO}_4)_3$ and 0.75 gm/100 ml of Polyacrylamide.

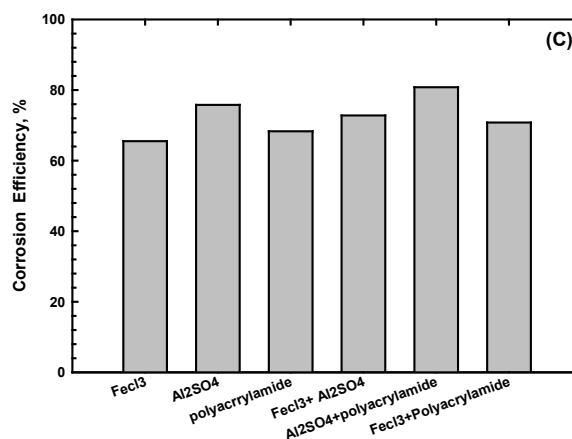
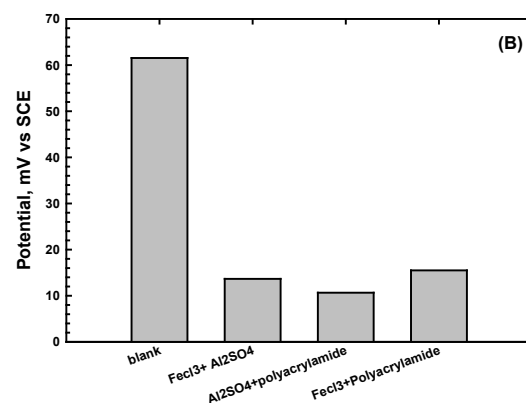
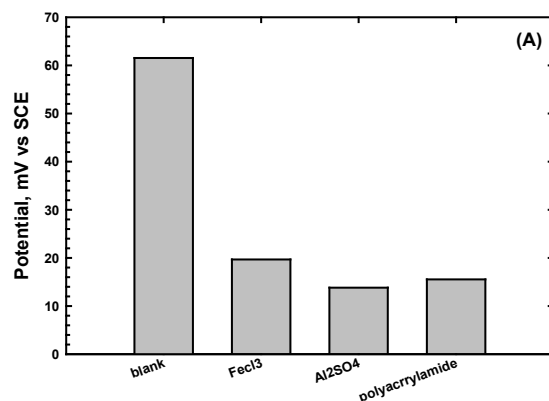


Figure 7: The effect of the treatment method on the calculated corrosion efficiency from the open circuit potential values of mild steel (a) Separate coagulant treatment (b) Mixed coagulant treatment (c) The corrosion efficiency.

can conclude that the treated wastewater with the mixture of aluminum sulfate and polyacrylamide meets the permissible limit of guidelines of water parameters. The corrosion process is depending on the chloride and sulfide ion concentrations so the reduction of these ions concentration will improve the corrosion resistance for the mild steel pipelines. It found that this mixture have the best corrosion results due to its capability to reduce the total dissolved salts which make reduction of chloride and sulfide ions content.

References

1. Farajnezhad H, Parvin G (2012) Coagulation treatment of wastewater in petroleum industry using poly aluminum chloride and ferric chloride. *IJRRAS* 13: 306-310.
2. Pan JR, Huang CP, Chen SC, Chung YC (1999) Evaluation of a Modified Chitosan Biopolymer for Coagulation of Colloidal Particles. *Colloids and Surfaces A* 147: 359-364.
3. Koohestanian A, Hosseini M, Abbasian Z (2008) The Separation Method for Removing of Colloidal Particles from Raw Water. *American-Eurasian J Agric & Environ Sci* 4: 266-273.
4. Abu H, Mohd AT, Pei L, Noor ZZ (2009) Coagulation and flocculation treatment of wastewater in textile industry using chitosan. *J Chem Nat Resour Eng* 4: 43-53.
5. Amokrane A, Comel C, Veron J (1997) Landfill Leachates Pre-Treatment by Coagulation Flocculation. *Water Res* 31: 2775-2782.
6. Amudaa OS, Amoob IA (2007) Coagulation/Flocculation Process and Sludge Conditioning in Beverage Industrial Wastewater Treatment. *J Hazard Mater* 141: 778-783.
7. Guibal E, Roussy J (2007) Coagulation and Flocculation of Dye-Containing Solutions Using a Biopolymer Chitosan. *React Funct Polym* 67: 33-42.
8. Egyptian Environmental Affairs Agency and Egyptian Pollution Abatement Project (2002) Industrial wastewater treatment plants inspection procedures manual, pp: 4-13.
9. Ihsan H (2015) Review of wastewater treatment chemicals and organic chemistry alternatives for abattoir effluent. Australian Meat Processor Corporation.
10. Demirci S, Erdogan B, Ozcimder R (1998) Wastewater Treatment at the Petroleum Refinery, Kirikkale, Turkey Using Some Coagulants and Turkish Clays as Coagulant Aids. *Water Res* 32: 3495-3499.
11. Koh SM, Dixon JB (2001) Preparation and Application of Organo- Minerals as Sorbents of Phenol, Benzene and Toluene. *Appl Clay Sci* 18: 111-122.
12. Masschelein WJ, Rice RG (2002) Ultraviolet Light in Water and Wastewater Sanitation. Rice RG (ed.), Lewis Publishers: Boca Raton, Florida, USA, pp: 9-58.
13. Cheryan M, Rajagopalan N (1998) Membrane Processing of Oily, Streams, Wastewater Treatment and Waste Reduction. *J Membr Sci* 151: 13-28.
14. Chen X, Chen G, Yue PL (2000) Separation of Pollutants from Restaurant Wastewater by Electro coagulation. *Sep Purf Technol* 19: 65-76.
15. Stephenson R, Tennant B (2003) New Electro coagulation Process Treats Emulsified Oily Wastewater at Vancouver Shipyards. *Environ Sci Eng Mag*.
16. Al-Shaikhli S (2013) Optimization of coagulation/flocculation process using natural coagulants in raw water treatment. Master Thesis, The University of Southern Queensland, Toowoomba, QLD, Australia.
17. Bazrafshan E, Biglari H, Mostafapour FK (2012) Determination of Hydrophobic and Hydrophilic Fractions of Natural Organic Matter in Raw Water of Zahedan Water Treatment Plant. *J Health Scope* 1: 25-28.
18. Al-Mutairi NZ (2006) Coagulant toxicity and effectiveness in a slaughterhouse wastewater treatment plant. *Ecotoxicol Environ Saf* 65: 74-83.
19. Demirci S, Erdogan B, Ozcimder R (1998) Wastewater Treatment at the Petroleum Refinery, Kirikkale, Turkey Using Some Coagulants and Turkish Clays as Coagulant Aids. *Water Res* 32: 3495-3499.

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