# Petroleum and Coal

## EXPERIMENTAL STUDY OF TREATMENT PROCESS OF EXIT WASTE WATER FROM PETROLEUM COMPANIES

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**Abstract**

Nowadays, lake of potable water, development of industries and population growth, extend desalination units. About 72% of the feed is drained into the sea as concentrated brine wastewater. This large amount of concentrated brine wastewater threatens sea ecosystem as thermal shocking and high salinity. The pretreatment of effluent stream from petroleum refinery is a logical solution to decrease damages which threaten the sea ecosystems. To reach the goal of Zero Discharge Process (ZDP) some experiments were conducted to decrease the total hardness of effluent stream from this desalination unit. The determination of the effects of some parameters is considered for decreasing of total hardness in this research. The experiments were conducted for three mineral coagulants by using each coagulant, separately also by coupled coagulants.

*Keywords:* Treatment process, flocculation; sedimentation; water; calcium hardness; magnesium hardness.

## 1. Introduction

Published researches about the pretreatment of exit wastewater from desalination units are rare. Nowadays, lake of potable water, development of industries and population growth, extend desalination units. Although desalination units have been grown up, but exit brine stream is usually drained into the sea ecosystem [1-4]. Moreover, annually a large quantity of concentrated brine is discharged into the sea [5-6]. By treatment of this saline wastewater, it is possible to eliminate the hazardous effects of salinity on sea ecosystem. Additionally, two valuable matters, salt and sweet water can be produced.

Total hardness and turbidity of wastewater must be reduced during pretreatment process of wastewater to produce sodium chloride salt [4,7]. Coagulants are the matters used to decrease total hardness of wastewater. The pretreatment process includes 3 steps: coagulation, flocculation and sedimentation. Improving the efficiency of pretreatment process depends on water specifications and also the operating parameters [7-10]. The optimum mixing rate of first pretreatment reactor, type of coagulant, ratio of sodium carbonate to coagulant and sodium hydroxide to coagulant are some of the important factors in operating conditions. Polyelectrolytes or mixture of coagulants can be used to improve the efficiency of total hardness removal [8,11-12].

In this research, various binary mixtures of three mineral coagulants were investigated quantitatively and qualitatively. The optimum amounts of sodium carbonate to coagulant and sodium hydroxide to coagulant were studied for each coagulant individually. This shows that the best ratio for sodium carbonate to coagulant is three and for sodium hydroxide to coagulant is four.

## 2. Materials and methods

### 2.1. Materials

The experiments are managed for the wastewater of petroleum refinery. Three commercial mineral nano coagulants, zinc oxide, ZnO, lead II oxide, PbO and titanium dioxide, $TiO_2$, are used

in the pretreatment process. Moreover, in softening process sodium carbonate and sodium hydroxide must be added to the wastewater. The previous researches in this field are focused on finding the optimum ratio of sodium carbonate to coagulant and also, sodium hydroxide to coagulant and these ratios are used in this work too. These proper values are 3 and 4 respectively.
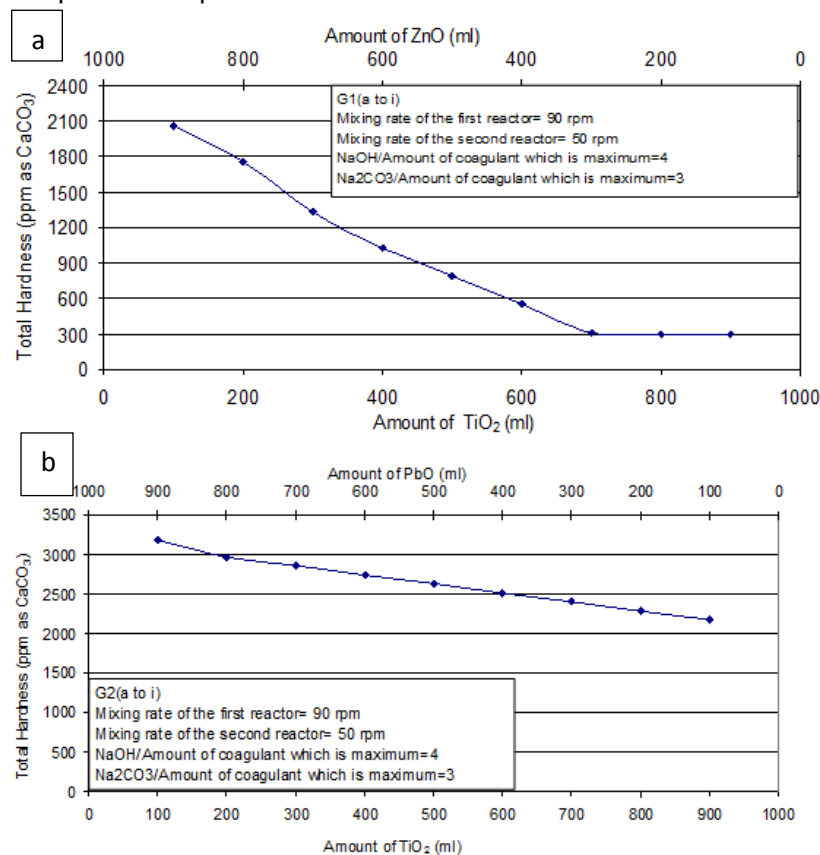
## 2.2. Experimental apparatus

Experiments are held in two pretreatment reactors. The capacity of each reactor is 8 liters and each of them equipped by a mixer. The speed of the mixers can be changed by a "control box". Figure 1 shows the pre-treatment set up. 27 types of binary mixtures of coagulants are examined by three mentioned speeds. Total hardness removal reveals the efficiency of softening pretreatment process. The initial total hardness of wastewater is about 50696.3 ppm as $CaCO_3$. The electric conductivity of the waste water is about 29543 micro mho per centimeter and with different pH values.
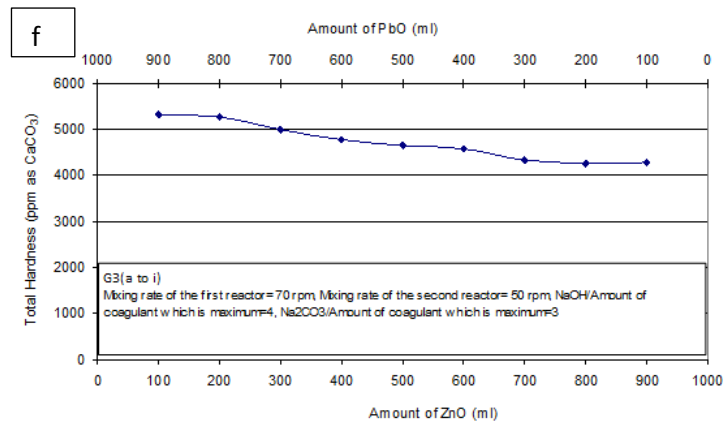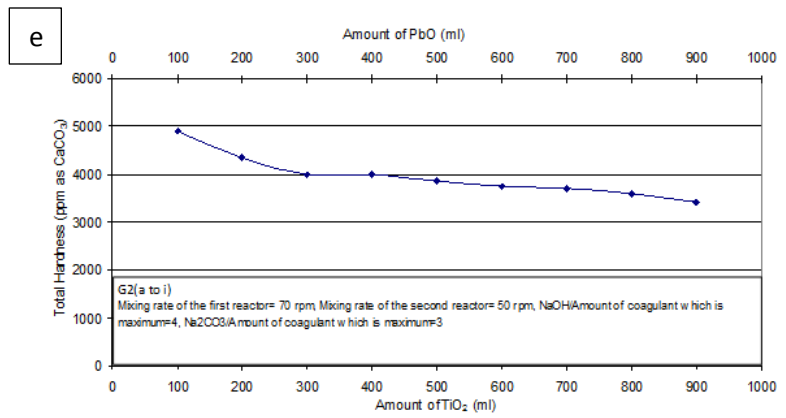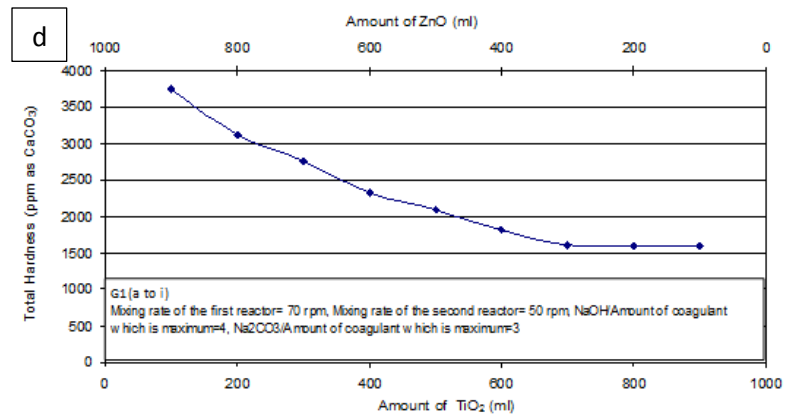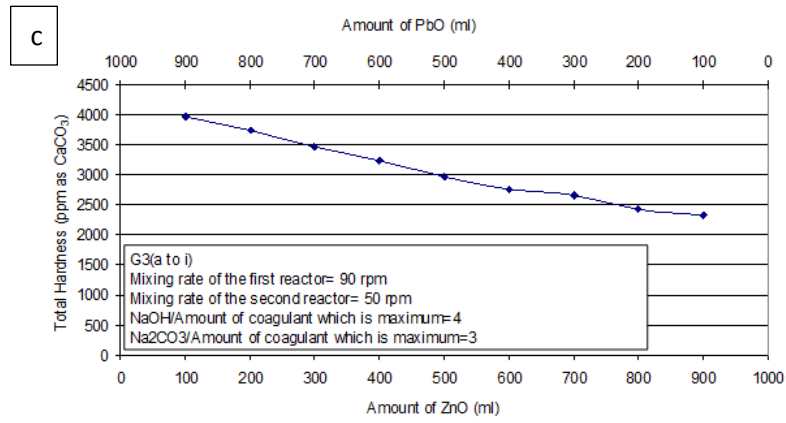
## 3. Results and discussion

The speed of mixer in the first pretreatment reactor is one of the major operating parameters which affects the size of coagulants and then as a result the softening efficiency. The total hardness removal reveals the efficiency of softening pretreatment process. Figure 1 (a, b, c, d, e, f, g, h, i) shows the trend of total hardness removal. This illustrates that the speed of 90 rpm in coagulation step increases the total hardness efficiently and also the mixture contains $TiO_2$ and ZnO has enough capacity to remove total hardness from 50 696.3 to about 299 ppm as $CaCO_3$.

If this ratio increases to 8/2 or 9/1 the total harness decreases just about 1.5%, so this is concluded that mixture contains 700 cc of $TiO_2$ to 300cc of ZnO is beneficial economically.

One of the important aspects on coagulation process is pH of wastewater. The pH value of clarified water is important in potable water.
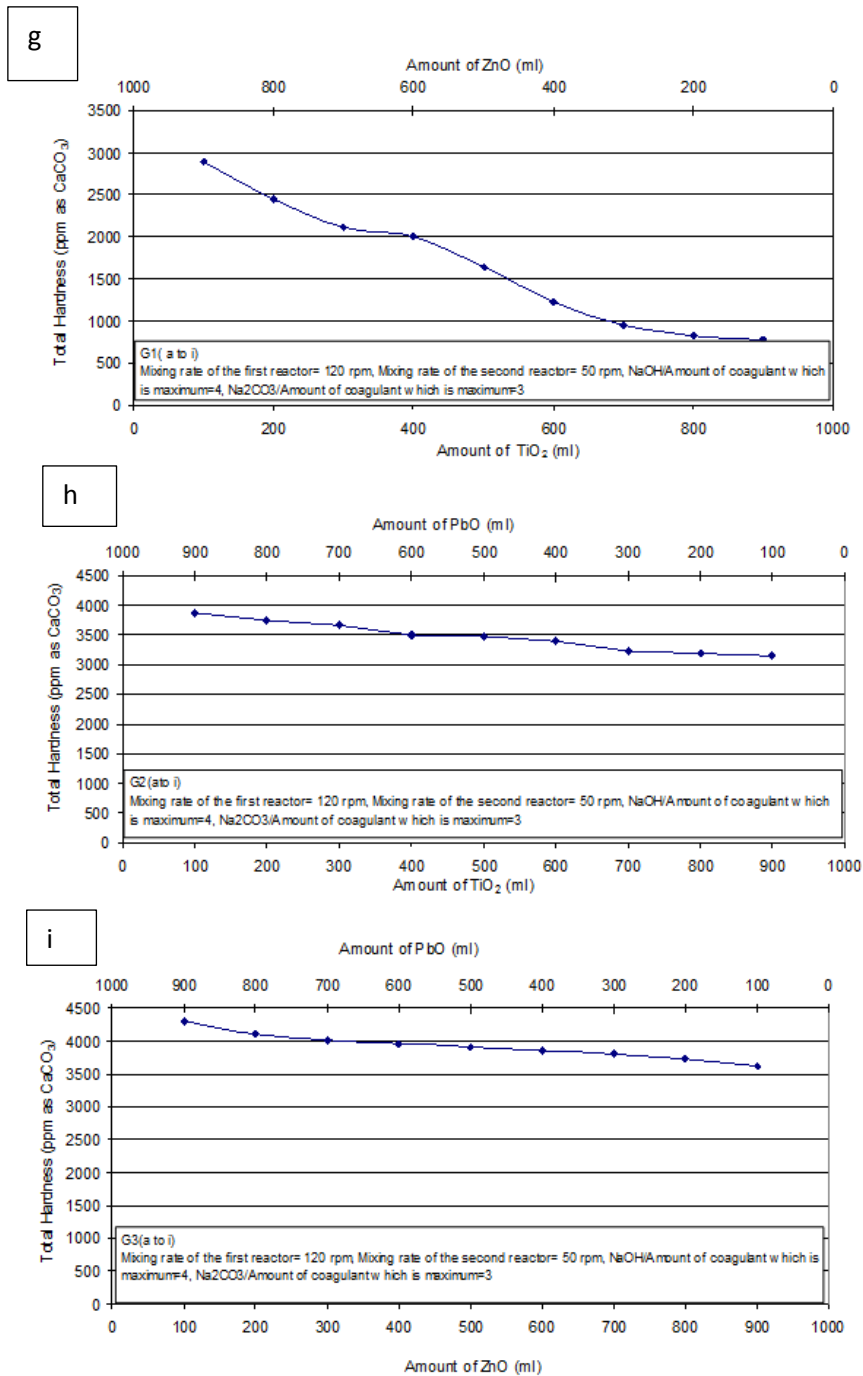
c

Amount of PbO (ml)

G3(a to i)
Mixing rate of the first reactor= 90 rpm
Mixing rate of the second reactor= 50 rpm
NaOH/Amount of coagulant which is maximum=4
Na2CO3/Amount of coagulant which is maximum=3

Amount of ZnO (ml)



d

Amount of ZnO (ml)

G1(a to i)
Mixing rate of the first reactor= 70 rpm, Mixing rate of the second reactor= 50 rpm, NaOH/Amount of coagulant
which is maximum=4, Na2CO3/Amount of coagulant which is maximum=3

Amount of TiO$_2$ (ml)



e

Amount of PbO (ml)

G2(a to i)
Mixing rate of the first reactor= 70 rpm, Mixing rate of the second reactor= 50 rpm, NaOH/Amount of coagulant which is
maximum=4, Na2CO3/Amount of coagulant which is maximum=3

Amount of TiO$_2$ (ml)



f

Amount of PbO (ml)

G3(a to i)
Mixing rate of the first reactor= 70 rpm, Mixing rate of the second reactor= 50 rpm, NaOH/Amount of
coagulant which is maximum=4, Na2CO3/Amount of coagulant which is maximum=3

Amount of ZnO (ml)

g



h



i



Figure 1. a-i. The efficiency of softening pretreatment process

## 5. Conclusion

This work focuses on the finding the major aspects for removing the total hardness of wastewater by different binary mixtures of mineral nano coagulants. The used wastewater is the effluent stream of petroleum refinery. The results reveal that the speed of 90 rpm in coagulation step decreases the total hardness efficiently and a mixture containing $TiO_2$ and ZnO has higher capacity to remove total hardness comparing with the other coupled mixtures. The experiments show that another effective factor on coagulation step is the high ratio of number of anions to the number of cations of coagulant. This ratio for $TiO_2$/PbO and also for $TiO_2$/ZnO is 3/1.5. So, by increasing the amount of $TiO_2$ in the mixture the value of total hardness decreases.

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