Original Article

Efficiency of Coagulation and Flocculation Process Combined with Chemical Sequestration in Removal of Organic and Inorganic Contaminants from Aautomotive Industry Sewage

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Abstract

Introduction: The most important environmental problem of automotive industries is the produced wastewater due to its various processes. The flocculation and coagulation along with chemical sequestration are among important processes for removing contaminants from wastewaters. The aim of this study is to investigate the efficiency of coagulation and flocculation process along with chemical sequestration in the removal of organic and inorganic pollutants from automotive industry sewage.

Materials & Methods: This study is an applied-experimental study. The removal of organic and inorganic substances by coagulation, flocculation process combined with chemical sequestration was carried out in batch reactors. The parameters turbidity, heavy metals' concentration, color, phosphate, coagulants concentration, exposure time, TSS, pH and COD were studied. The concentration of color and residue of heavy metals were determined using spectrophotometer -UV and atomic absorption.

Results: The research results showed that the removal percentage of Cr, Ni, Pb and Zn by ferric sulfate combined with lime at a pH equal to 10 and the exposure time of 100 minutes were 52.65, 96.3, 3.27 and 100 respectively, and percentage of removing them by aluminum sulfate combined with lime was 52.65, 97.8, 3.37 and 99.81 respectively. the removal percentage of TSS, COD, color, turbidity, phosphates ferric sulfate was also 68.9, 83, 94, 84 and 47.2 respectively, and this amount of removal by aluminum sulfate was 62, 80, 94, 73.5 and 48 respectively at neutral pH and concentration of coagulant was obtained equal to 150 mg/ L.

Conclusion: According to the results, the use of coagulation and flocculation process combined with chemical sequestration in the removal of organic and inorganic pollutants in wastewaters of automotive industry achieved under optimal conditions is very effective and can be used in water treatment of automotive industry.

Key words: coagulation, flocculation, chemical sequestration, heavy metals, automotive industry sewage

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Introduction

In recent years, with the increased demand for automobiles, the auto industry has evolved rapidly in the world. This growth not only has increases the number of vehicles but also it has emitted toxic and hazardous substances to the environment [1-3]. The automotive industry has different units such as cooling, welding, paint hall, washing, and so on. Some part of the water used in these units becomes sewage. The major wastewater produced in automotive industry contains contaminants such as paint, heavy metals, phosphate, suspended solids, COD, BOD, detergent, oil, and lubricant [1, 4, 5]. The dyestuffs in wastewater have been taken into consideration due to their toxicity on aquatic organisms, disorder in function of conventional wastewater treatment systems, and aesthetic environment [6, 7]. While paints have carcinogenic and mutagenic properties, they can cause allergies and skin problems [8, 9]. Dyestuffs due to being artificial and having complex aromatic molecular structure are stable in the environment and have little degradation ability [10]. Today, pollution of water sources by colored pollutants is considered as a major problem for the environment. The existence of paint blocks out the light and disrupts photosynthetic activity. On the other hand, paint forms a bond with metal ions and produces some compounds that are toxic for fish and other organisms in the water [11, 12]. Additionally, environmental pollutions made by heavy metals have caused serious problems in the world. Most of the heavy metals are toxic and carcinogenic. These metals can easily accumulate in the food chain and are considered harmful to human health. Currently, heavy metals are one of the earliest contaminants which create the most serious and dangerous environmental problems [2, 13, 14]. For example, the entry of nickel compounds into the body causes nausea, vomiting, diarrhea, headache, cough, and shortness of breath. Chronic inhalation of nickel compounds can cause diseases such as rhinitis and sinusitis. The International Agency for Research on Cancer (IARC) has classified nickel as a carcinogen for humans [15, 16]. The selection of appropriate methods for removing heavy metals from industrial wastewater is significant and can be studied from an economic and ecological perspective. The most common methods of their removal include electrochemical, chemical sequestration, adsorption coagulation and flocculation, and ion exchange. In the meantime, the use of fusion processes such as coagulation and flocculation along with chemical sequestration due to their simplicity, low cost, high efficiency, non- manufacture of hazardous secondary products, non-sensitivity to pollutants, reusing wastewater, and recyclability of removed contaminants are preferred [17-20]. In this regard, Hamawand (2015), reported that the use of coagulants is able to remove the relatively high levels of BOD, TSS, and COD found in wastewater [21]. The chemical sequestration using lime is able to remove heavy metals at concentrations greater than 1000 mg per liter [22]. In a study

conducted by Ohialy in Egypt, it was found that the removal of TSS, COD, heavy metals, and phosphate from wastewater of automotive industry by coagulants and chemical sequestration was 84%, 64%, 75%, and 77%, respectively [4]. Ismail and colleagues also considered the use of effective combinational processes of coagulants and lime in removing organic and inorganic substances in wastewater [23]. Therefore, in order to determine the best possible conditions in removal of intended pollutants, this study was carried out with the aim of investigating the efficiency of coagulation, flocculation, and chemical sequestration process on organic and inorganic contaminants' removal from automobile manufacturing wastewater.

Materials and Methods

As an applied-experimental study, this research was carried out with the aim of investigating the efficiency of coagulation and flocculation process combined with chemical sequestration in organic and inorganic contaminants' removal from automotive industry sewage. Sampling from raw sewage of an automotive industry was carried out for 3 months. The desired physical and chemical parameters were determined after transferring the samples to research laboratories (Table 1). According to previous studies and experiments performed as pre-test in the present study concerning the effect of variables (pH, exposure time, concentration of coagulants, and pollutant concentrations) in removing contaminants the best condition was chosen. The software applied for data analysis were, Excel and Spss version 17.

Table 1: Specifications of automotive industry raw sewage average

Row	Parameters	Values
1	pH	6.4
2	Temperature mean (c)	16.8
3	Turbidity (FTU)	45
4	Color (mg/L)	86
5	EC (us/cm)	1081
6	COD (mg/L)	875
7	TSS (mg/L)	630
8	Phosphate (mg/L)	42.75
9	Nickel (mg/L)	5.1
10	Chromium (mg/L)	2.66
11	Zinc (mg/L)	8/8
12	Lead (mg/L)	0.1

Table 2. The MCL standards for the most hazardous heavy metals[22].

Heavy metal	Toxicities	MCL (mg/L)
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	0.006

In order to do coagulation and chemical sequestration, aluminum sulfate [Al2 (SO4) 3.18H2O] with 99% of purity, ferric sulfate [Fe2 (SO4) 3] with a purity of 97%, and lime [Ca (OH) 2] with a purity of 99% were used. The devices Jar, centrifuges, turbid meter, electrical conductivity, multi-parameter with Do meter probe, digital COD meter, DR-890, UV-vis spectrophotometer, and atomic absorption model AA- 6300 were applied to carry out the experiments. Initially, a liter of wastewater samples was added in each container. Then, coagulation was carried out for a minute separately in neutral PH in 120 rpm using aluminum sulfate and ferric sulfate coagulants with a dosage of 150 mg / L. The flocculation in times of (120,100,80,60, 40, and 20 minutes), under study parameters was analyzed (Table 1) and the optimal exposure time to remove any of them was determined. Then, PHs (3,4, 5,6,7,8,9,10,11,12) were used under optimal time to determine the optimal PH. In the next step, different concentrations (30, 50, 70, 90,120,150,200,250,300 mg) were used under optimal conditions to determine optimum doses of coagulants.

The analysis of all parameters was carried out based on the standard test method of Water and Wastewater. After coagulation and flocculation of alum and ferric sulfate coagulants, lime was used for chemical sequestration. The chemical sequestration was only applied for removal of heavy metals. This was conducted in two modes.

First: Lime impact on the real raw sewage samples: In this case, the sequestration of metals nickel, chromium, lead, and zinc from lime was performed in different concentrations (30,50,100,120,160,200,250,300 mg 1) under the impact of various pHs (12-7) (table 3).

Second: Lime effect on sewage samples of different concentrations (30, 50, 100, 120, 160 ,200, 250 ,300 milligrams per liter) which were previously under the influence of coagulants were investigated. All tests were repeated three times and mean of the results was reported. In each of the above steps, remaining concentration of pollutant was measured after the experiment. The following equation (1) was used to calculate the removal efficiency.

$$(1) \qquad RE = \frac{(C_0 - C_t)}{C_0} \times 100$$

At the end of experiments, paired t-test analysis was used to determine the mean difference between the efficiency of removing contaminants under study by coagulation, flocculation process, and chemical sequestration. The repeated measure was applied for the comparison of means before and after using the mentioned process.

Results

Under the influence of coagulation and flocculation by aluminum sulfate and ferric sulfate, removal of contaminants was carried out saliently. The rate of turbidity, color, phosphate, TSS, and COD removal in

equilibrium time of 100 minutes by aluminum sulfate was 72, 94, 48, 62, and 80 percent, respectively. The rate of removal by ferric sulfate in equilibrium time of 80 minutes was 82, 94, 47, 73, and 78 percent, respectively (Figures 1 and 2). Additionally, by the increase in exposure time from 20 to 80 minutes, removal percentage of the metals, i.e., chromium, nickel, lead, and zinc increases too, however, their removal rate by aluminum sulfate at the exposure time of 80 minutes was 30.3, 70.3, 3.3, and 41. This rate by ferric sulfate was obtained as 29, 70.15, 3, and 44 percent, respectively ($p < 0.05$).
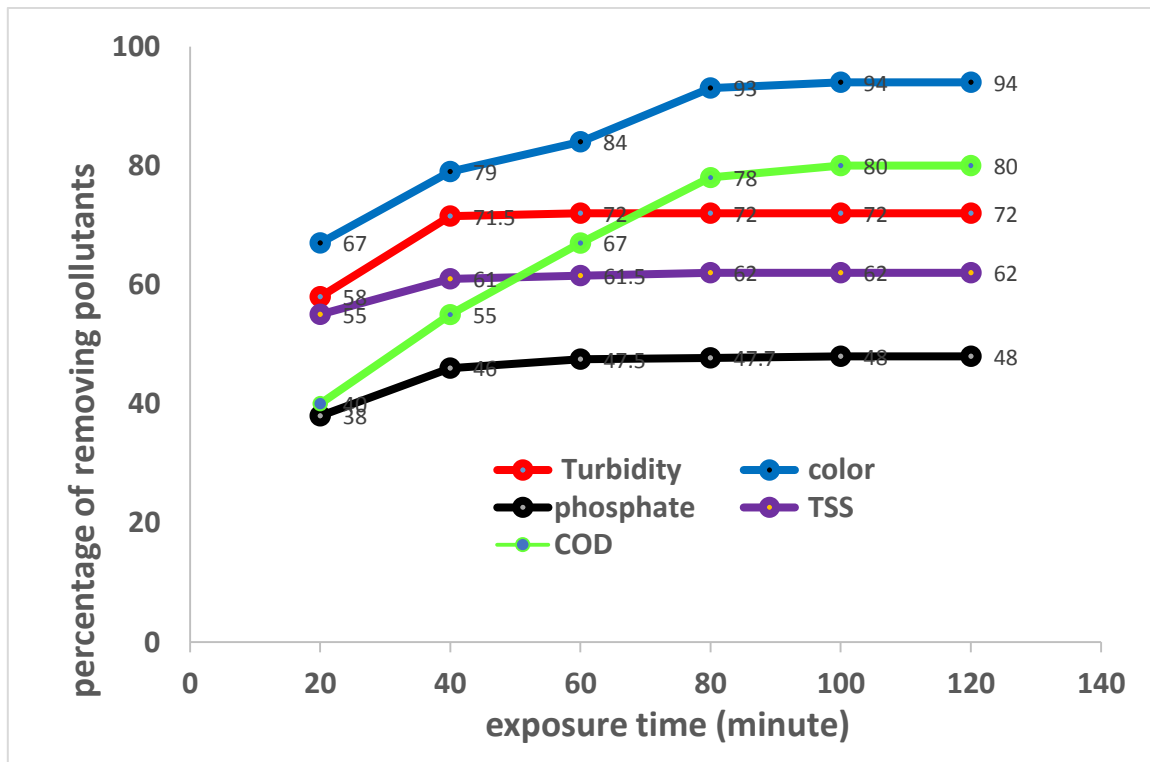
Fig 1. Percentage of removing pollutants at different times using aluminum sulfate (neutral pH, 150 mg / L of coagulant concentration)
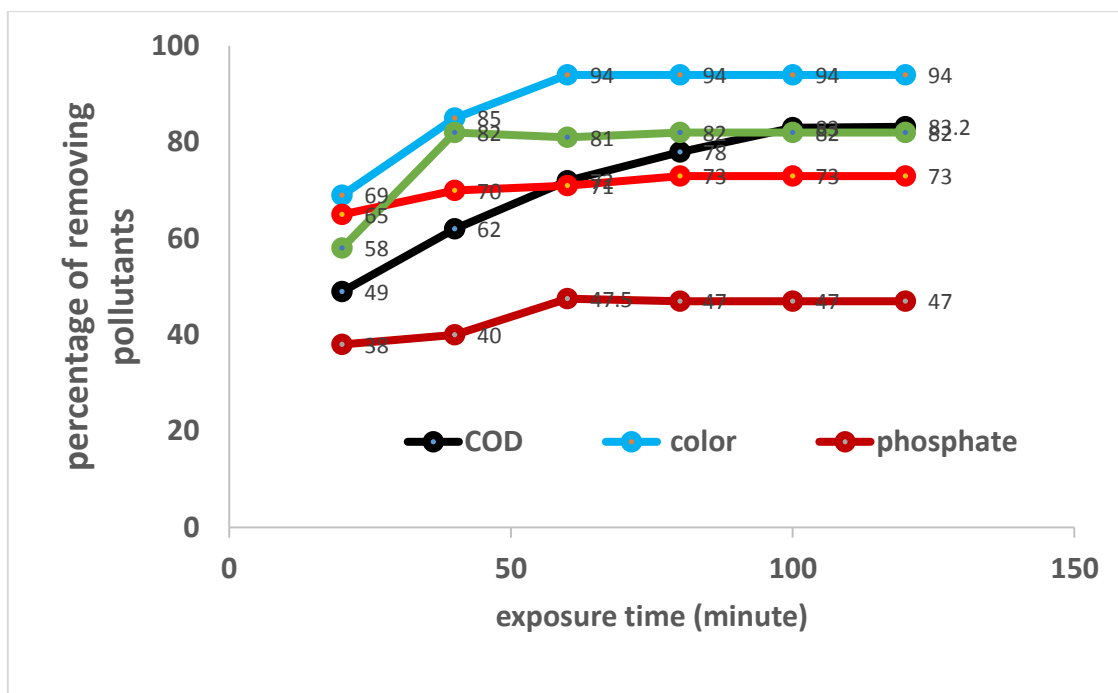
Fig 2. Percentage of removing pollutants using ferric sulfate at different times (neutral pH, 150 mg / L of coagulant concentration)

The effect of pH performance on coagulation, flocculation, and chemical sequestration of metals are represented in Table 3.

According to the results, the highest percentage of removal of turbidity, phosphate, color, COD, and TSS by aluminum sulfate was obtained respectively at pHs 72 = 5, 48 = 8, 94 = 6, 80 = 6, and 62 = 6. Moreover, the highest percentage of their removal for ferric sulfate was observed at, pHs 84= 7, 6, 47 = 9, 95 = 6, 82 = 6, and 71 = 6, respectively.

The highest percentage of removing heavy metals by lime was carried out at pHs equal from10 to 11 and this rate of removal percentage for chrome, nickel, lead, and zinc was 50, 68, 3, and 88, respectively.

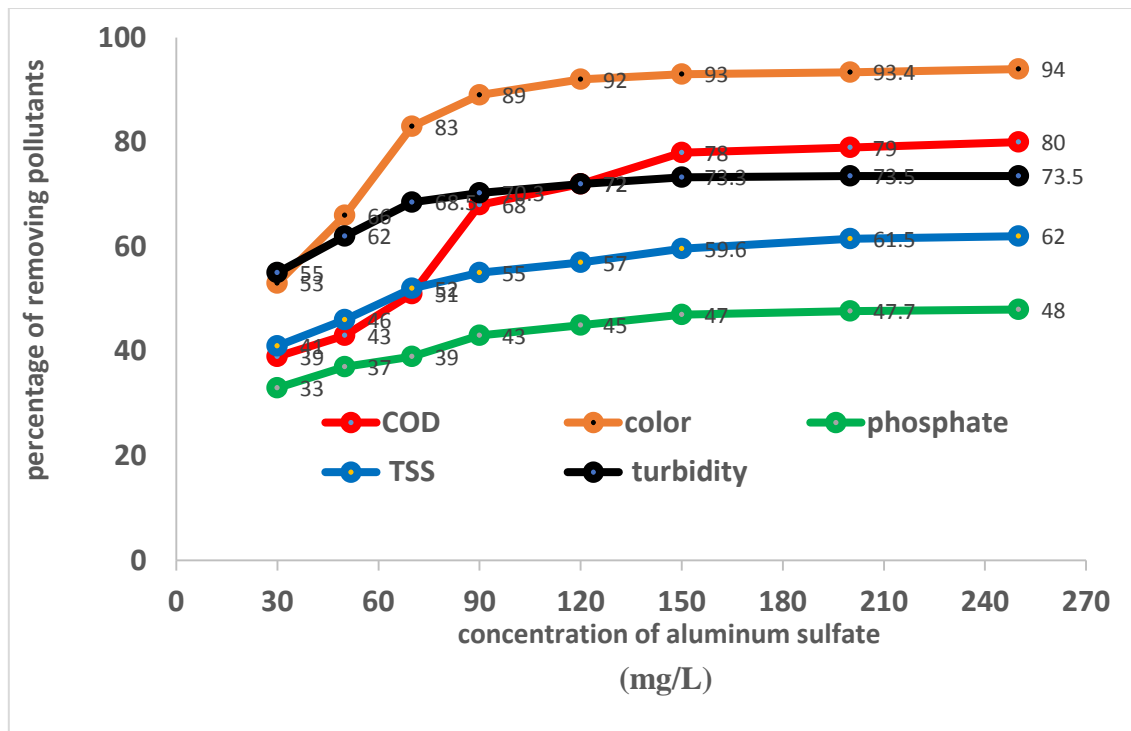Table 3: Percentages of removing contaminants at different pHs (exposure time of 100 minutes).

With increasing concentration of pollutants, coagulant removal rate increases. At the neutral pH and exposure time of 100 minutes, percentage of turbidity, phosphate, color, COD, and TSS removal by aluminum sulfate with concentration of 200 milligrams per liter was 73.5, 47.7, 93.4, 79, and 61.5, respectively. Further, for ferric sulfate at the same concentration it was 79.3, 46.6, 93.4, 82, and 67.5 percent, respectively (Figures 3 and 4)

Additionally, with increase in concentration of coagulants, heavy metals removal rate increased; as this amount of removal by aluminum sulfate, chromium, nickel, lead, and zinc was 30.3, 70.35, 3.3, and 41 percent, respectively. For ferric sulfate, it was obtained as 29, 70.15, 3 an d 44 percent.

Table3. Percentage of removing contaminants at different pH (exposure time of 100 minutes)

pH type of contaminant	3	4	5	6	7	8	9	10	11	12	concentration and type of material
Turbidity	44	58	72	70	68.5	56	53	45	32	32	Aluminum sulfate
Phosphate	19	20	23	30	41	48	47	45	45	31	150mg/L
Color	48	52	88	94	91	73	65	48	33	25	
COD	55	65	75	80	72	55	46	38	30	28	
TSS	45	53	57	62	60	57	46	39	33	30	
Turbidity	52	70	72	84	84	75	61	58	56	53	Ferric sulfate
Phosphate	28	31	31	35.7	39	44	47	46.6	41	38	
Color	69	87	92.6	95	90	72	57	52	43	40	150mg/L
COD	63	74	79	82	79	68	47	33	29	27	
TSS	51	66	70	71	69	59	52	48	45	45	
Nickel	-	-	-	-	38	46	59	68	67	67	
Chromium	-	-	-	-	26	32	46	50	41	32	
Lead	-	-	-	-	1	2	2.7	3	2.2	1.3	Lime
Zinc	-	-	-	-	55	72	81	87	88	70	250mg/L

respectively (Figures 5 and 6)

Fig 3. Percentage of removing contaminants using different concentrations of aluminum sulfate (neutral pH, exposure time of 100 minutes)
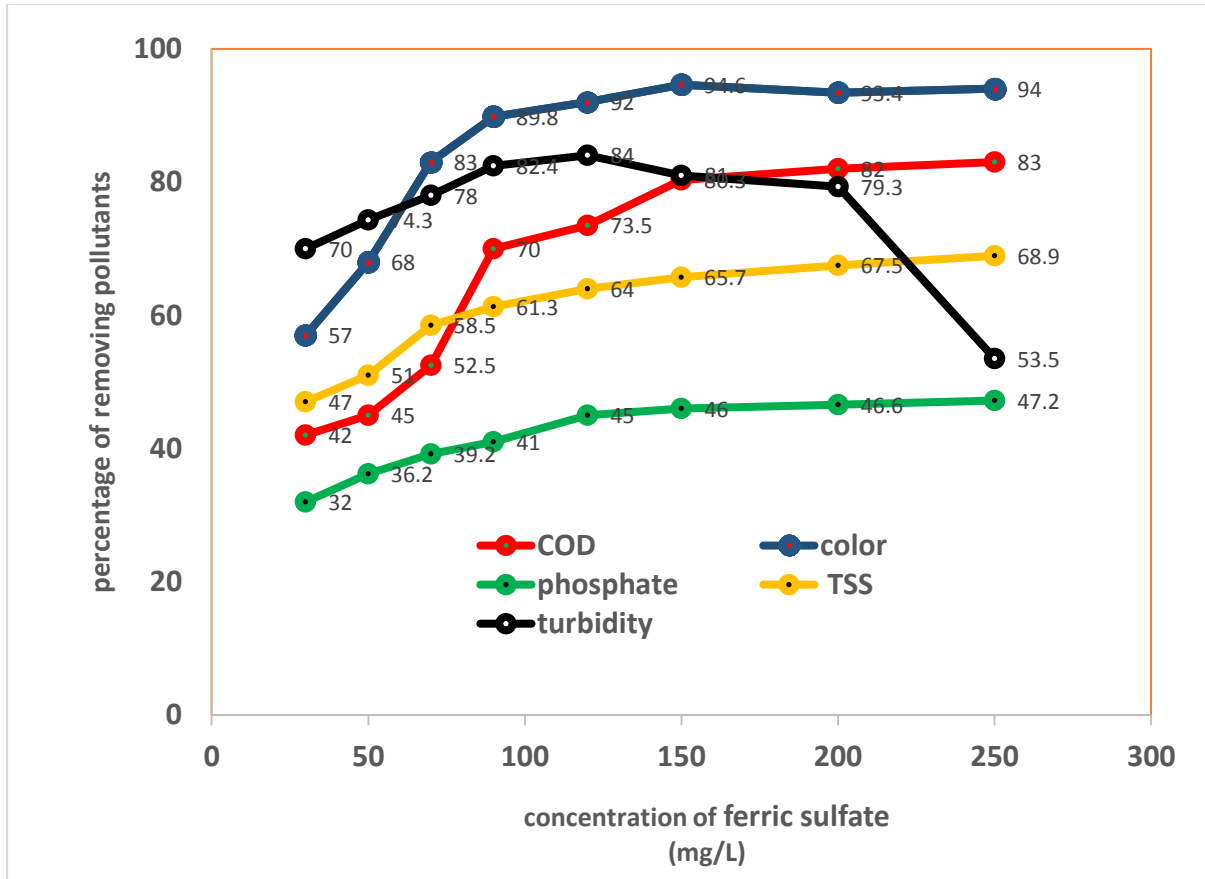
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Fig 4. Percentage of removing contaminants using different concentrations of ferric sulfate (neutral pH, exposure time of 100 minutes)
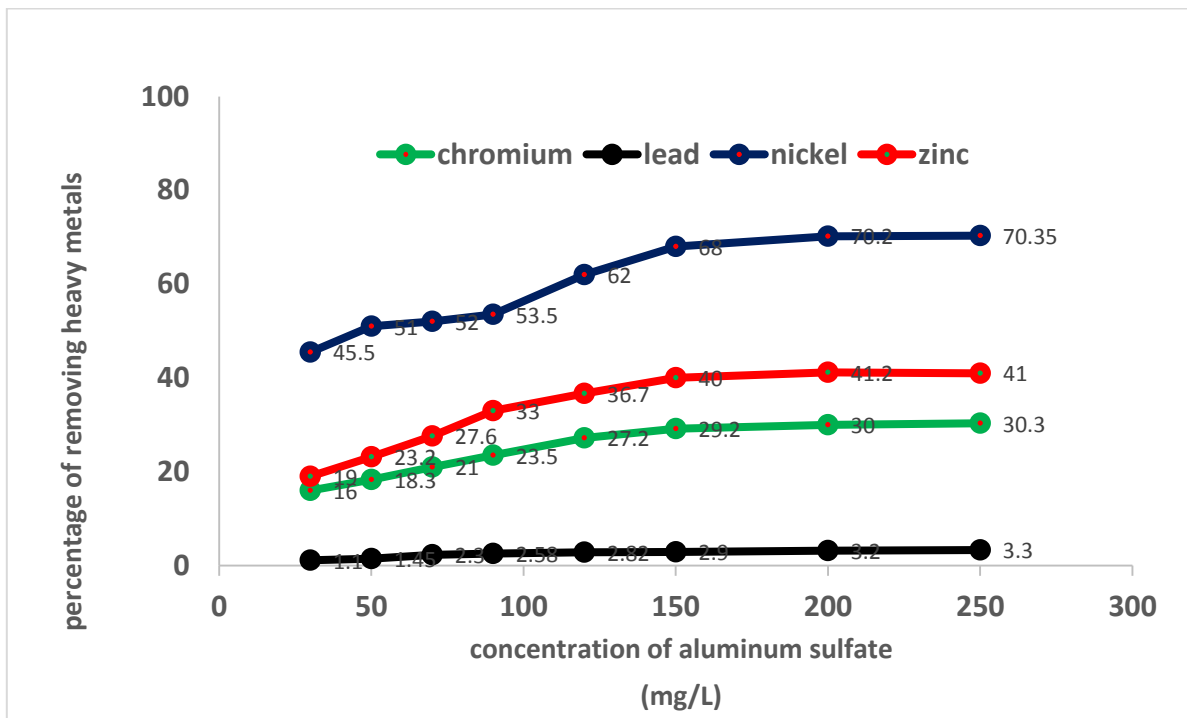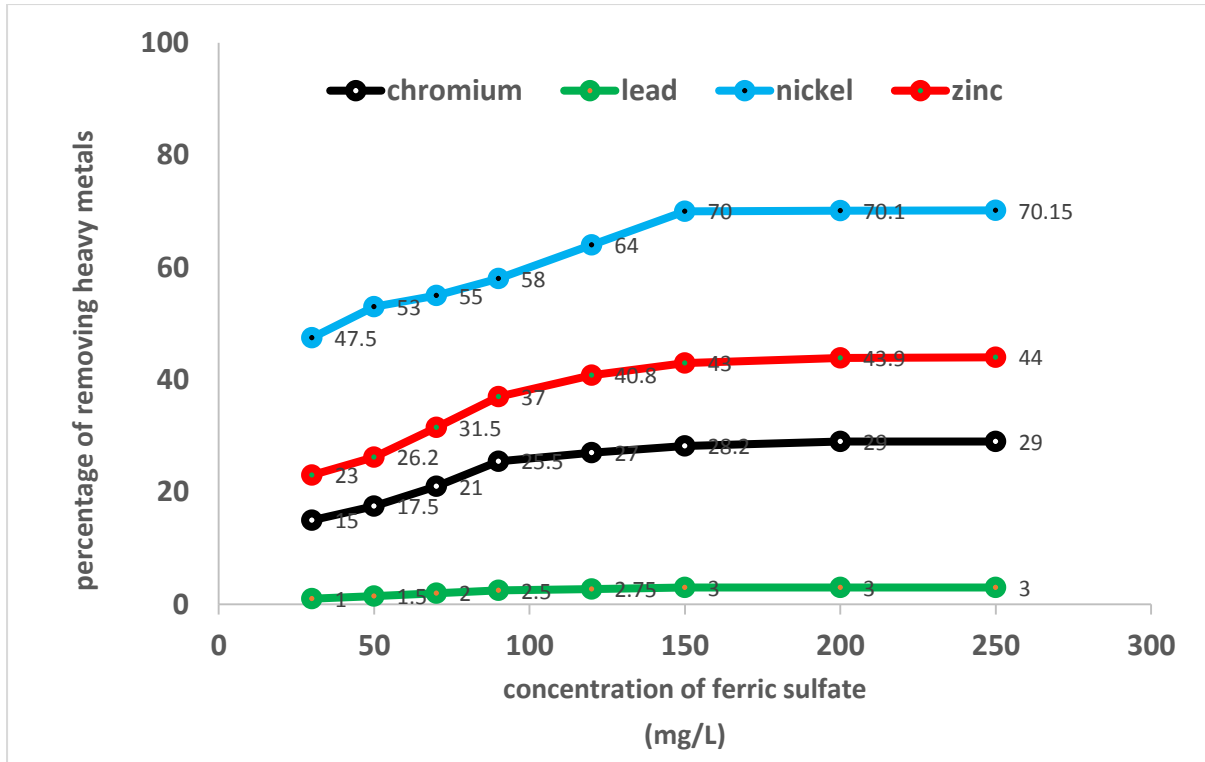
Fig 5. Percentage of removing heavy metals using different concentrations of aluminum sulfate (neutral pH, exposure time of 100 minutes)

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Fig 6. Percentage of removing heavy metals using different concentrations of ferric sulfate (neutral pH, exposure time of 100 minutes)

After the effect of coagulants on removal of heavy metals was investigated, lime was used for sequestration of their residual concentration.

The results obtained from the combined effects of coagulation, flocculation, and sequestration have been brought in Figures 7 and 8.

The combined effect of coagulants with Lime causes a relatively high removal of metals, as in pH =10 and exposure time of 100 minutes, alum and lime eliminated 52 to 99.81 percent of Cr, Ni, and Zn.

In a similar condition, ferric sulfate and lime with different percentages were able to remove metals (Cr = 52.65, Ni = 96.3, Zn = 100, Pb = 3.27).
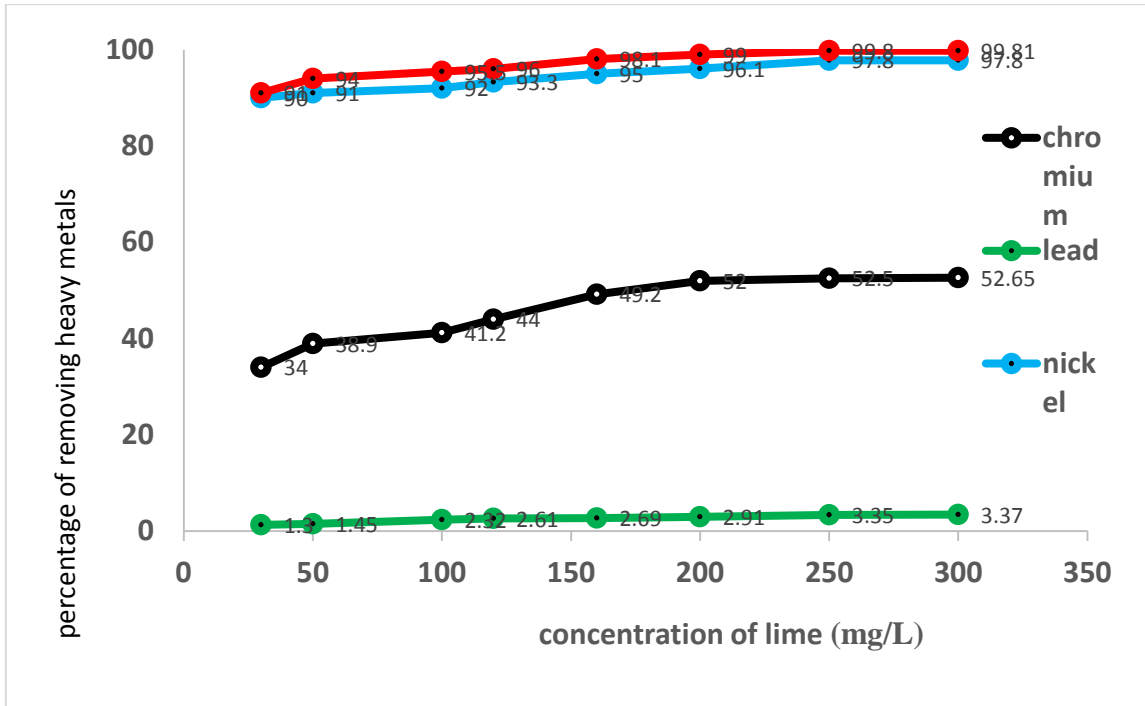
Fig 7. Percentage of removing heavy metals using different concentrations of lime after the impact of alum (pH=10, exposure time of 100 minutes)
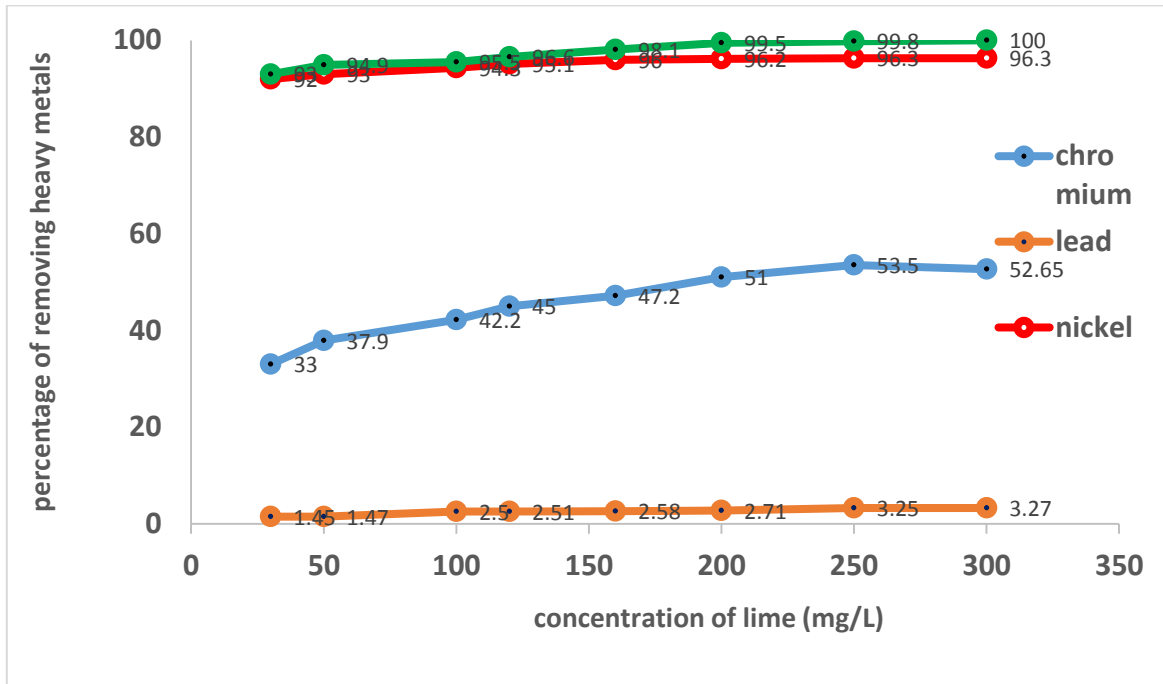

Fig 8. Percentage of removing heavy metals using different concentrations of lime after the impact of ferric sulfate (pH=10, exposure time of 100 minutes)

Discussion

The results of studies conducted by many researchers proved that pH is a very important factor in the coagulation and flocculation process. Every coagulant has an optimum pH in which coagulation and flocculation process is done for certain concentration of coagulant in the shortest possible time and with the highest efficiency. In other words, the efficiency of coagulation and flocculation process is affected by pH action (p<0.02) [24-26]. The results showed that pH changes in removal of contaminants by aluminum sulfate, ferric sulfate, and lime are effective. With regard to the obtained results, optimal pH for the removal of turbidity, color, TSS, and COD by aluminum sulfate was obtained in the range of 5 to 6 while it was equal to 8 for phosphate. The optimal pH in removal of turbidity, color, TSS, COD, and phosphate by ferric sulfate was equal to 9. According to experiment conditions, the best Flukes were formed in these pH values. Except phosphates, the rest of parameters influenced by both coagulants had greater performance in relatively acidic pH. This was due to hydrolysis and easier production of H $^{+}$ in experiment conditions. On the other hand, since colloids have negative charges [27], they are absorbed faster by materials having the opposite charge and their settlement arrangements is provided by becoming more weighty [22, 26, 28]. The obtained results were in accordance with a study conducted by Hamawand and colleagues in 2015 [21]. In chemical sequestration process, in accordance with the following reaction,

hydroxide factor is formed in the removal of heavy metals at high pH and causes clots and sediment containing metals.

$$M^{2+} + 2(OH) \rightarrow M(OH)_2^{\downarrow}$$
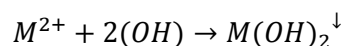
Where M^{2+} and M $(OH)_2$ are respectively soluble metal and insoluble precipitate containing heavy metals [22]. At a concentration of 250 milligrams per liter of lime, under conditions of 10 and 11 percent of PH, removal of nickel, chromium, lead, and zinc was obtained at the percentages equal to 68, 50, 3, and 88, respectively. With increase in concentration of lime and pH, produced OH ions increased in experiment environment and the possibility of chemical sequestration was observed more. Since high consumption of lime for producing hydroxyl increases the produced sludge, it is necessary to obtain optimal pH for sequestration of metals. The obtained results were aligned with a study conducted by López-Maldonado and in 2014 [21]. Coagulant dose is also one of the most important parameters on the performance of coagulation and flocculation process. Accordingly, low and high doses can have a negative impact on coagulation and flocculation performance and this performance is important in terms of process and economy. According to results of a study carried out by Zawami (2015), [30], by increasing the concentration of coagulants, removal rate of contaminants increased so that optimum dose of aluminum sulfate and ferric sulfate for the removal of turbidity, COD, Color, and TSS

was obtained from 120 to 200 milligrams per liter. When the concentration of coagulant is optimal beyond the limit, positive charges are formed around colloids for re-stabilization of colloidal particles and cannot be removed by prekinetic flocculation; thus, the removal efficiency comes down [21, 30].

Conclusion

Results obtained from a series of experiments conducted in this study indicated that due to low cost, simple operation, and relatively high efficiency of coagulation and flocculation process combined with chemical sequestration in the removal of organic and inorganic pollutants found in automotive industry wastewater, they can be used in the environment by considering effluent discharge standards (Table 2).

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