



Sulfate Reduction and Heavy Metals Removal from Industrial Wastewater via Advanced Calcium-Aluminum Precipitation Method



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THE reduction of sulfate ions from the industrial wastewater using advanced calcium-aluminum precipitation method (ACAPM) has been evaluated. The ACAPM involved the precipitation of sulfate ions as minerals like gypsum and ettringite via calcium/ aluminum compounds. Factors affecting the reduction of sulfate ions such as: pH, Ca(OH)₂ and NaAlO₂ dosages have been investigated, while the optimal experimental conditions for sulfate ions reduction were determined. The precipitated solids have been characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and energy dispersive spectroscopy (EDS), respectively. Experimental results indicate that the ACAPM was effectively reduced sulfate with removal efficiency exceed 98%. It also effectively removed heavy metals including: Cr, Ni, Cd, Pb, Fe, Mn & Zn, with removal efficiencies up to 99%. Results showed that the ACAPM has remarkable sulfate ions removal efficiency with high concentrations.

Keywords: Sulfate Reduction, Industrial Wastewater, Chemical Precipitation, Heavy Metals Removal

Introduction

High concentrations of sulfate ions in industrial wastewater cause environmental problems, leading to corrosion for metal containers and pipes. It also released toxic hydrogen sulfide H₂S(g) as a result of biological reactions. Hence, in order to protect the environment, it is necessary to reduce the sulfate ions in the industrial wastewater to meet the discharge standard limits. Several technologies such as adsorption [1-3], bio-electro chemical cell [4-6], electro-dialysis [7-9], electro-coagulation [10-11], crystallization [12-13], biological treatment [14-16], micro-algal [17-18], membrane filtration [19-20], chemical precipitation [21], separately and/or in combination of these processes were developed to reduce sulfate ions in wastewater in order to be complied with the regulatory standards for safe disposal. At 2015, M.H. El-Awady et.al detected the optimal coagulation/flocculation process for raw water treatment in the River stream [22].

According to H.El-Ghetany and M.H. El-Awady, 2015, the treated industrial wastewater can be reused as safe usable water and to pay-pack via a novel solar industrial wastewater treatment system [23]. Moreover, M.H El-Awady et al 2014; designed and run an integrated solar green house for water desalination and wastewater treatment in remote arid Egyptian communities [24]. M.H. El-Awady, et al., 2019 used Alum, FeCl₃, Lime, and Solar energy in industrial wastewater treatment to obtain zero-liquid discharge [25].

However, those methods were partly suitable for the treatment of highly concentrated sulfate in wastewater. In addition, ion exchange and membrane separation involved the generation of liquid waste stream that required proper management, except the chemical precipitation method. The chemical precipitation method was mainly included barium chloride precipitation [26-27] through precipitation of sulfate as barium

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sulfate. Although this method has high sulfate removal efficiency, but the salt was very costly besides the residual chloride and barium ions have corrosive and toxic effects. Consequently, this method was rarely used for wastewater treatment, if compared with lime and limestone precipitation methods to produce sulfate as gypsum [28, 29].

However, lime and limestone precipitation methods were widely used in the field of sulfate reduction from wastewater; but the Sulfate reduction efficiency is limited, due to the relatively high solubility of gypsum, 2000 mg/L, and the Advanced Calcium/Aluminium precipitation method [30] is considered as an effective method for treating wastewater effluents containing sulfate ions to minimum concentration of sulfate ions.

This study aims to: (i) study sulfate reduction/removal from the synthetic aqueous as well as real wastewater through using the ACAPM, (ii) investigate particularly the effect of different treatment parameters on sulfate's ions and heavy metals reduction from aqueous solutions, (iii) identify the removal of combined heavy metals with sulfate ions in real industrial wastewater via ACAPM at their optimal experimental operating conditions.

Materials and Methods

Materials:

Chemicals:

Sodium sulfate anhydrous, Na_2SO_4 and Sodium aluminates' NaAlO_2 have been used as sulfate and aluminum ions source, while analytical grade of lime, CaO was used as calcium source, while FeCl_3 , $\text{Pb}(\text{NO}_3)_2$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, AgNO_3 , $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, CrCl_3 and $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, were used as metals salts for Iron, Lead, Nickel, Silver, Zinc, Manganese, Chromium & Cadmium ions, respectively. Consequently, Na_2SiO_3 and KH_2PO_4 were used as silicates and phosphates sources. The sulfate-rich synthetic aqueous sample was prepared by dissolving 9.0 gram from Na_2SO_4 in 1.0-liter distilled water to get initial sulfate ions concentration equivalent to 6000 mgSO_4/L . On the other hand, the real industrial wastewater was frequently collected along three months from sugarcane manufacturing company located at south-west Cairo Giza, Egypt. Selected parameters followed by identified physico-chemical analyses for samples were

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carried out and tabulated in Table 1.

Semi-pilot Chemical Treatment Plant:

In this study, a-semi pilot chemical treatment plant has been manufactured from Poly Vinyl Chloride, PVC sheets, due to its resistant to corrosion, acids, alkalis and fouling. Its total volume is about 20.0 liters. The unit is divided into three separate compartments connected to each other in series through hole. Each basin is fulfilling its function along the treatment pathway. The first is used for coagulant chemical addition followed by coagulant aid. The second compartment has lamella sheets to encourage the flock's formation. The third stage represents the final settling tank where the treated effluent is separated from settled sludge through a PVC baffle.

Figure (1) shows the constructed Lab scale plant which involves three basins:

Flash-mixing:

In this basin, the calculated doses of lime and sodium aluminates have been added at the optimum retention time. High-speed flash mixing of chemicals with wastewater in the first basin with about 3.0 liters volume is carried out. This process helps the dissolution of the reagents and encourages the sulfate ions reduction.

Coagulation basin:

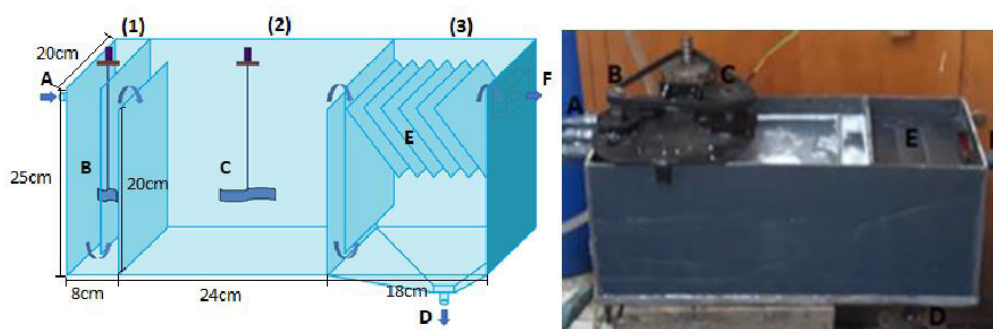
In this basin with 10.0 liters volume, chemical reaction between wastewater with coagulants is performed and agglomerates the fine precipitates (gypsum and ettringite) during flocculation process at low-speed mixer.

Sedimentation basin:

This basin represents the final settled sludge collected and passed from coagulation basin. It consists from some sliding partitions (Lamella) that enhance sedimentation process. The treated water is collected in this basin with 7.0 liters, as final discharging point.

Analytical Methods:

The concentrations of sulfate, phosphate, and silica were analyzed using a spectrophotometer Model Carry-100 UV-Vis Spectrophotometer, Agilent Technologies; while pH, TDS & EC



Influent	.A	Flash-mixing Basin	.B	Coagulation Basin	.C
Sludge Drainage	.D	Sedimentation Basin	.E	Effluent	.F

Figure (1): a semi-pilot chemical treatment plant



Figure (2): 200-ml of solution sample was taken in a six-league electric blender

parameters were measured via multi-Detector model ADWA-8000. Moreover, heavy metal ions, such as: Cr, Fe, Mn, Ni, Cd, Pb and Zn have been measured using inductively coupled plasma emission spectrometer: ICP-AES 5000, Agilent Technologies. Turbidity was determined as NTU meter. Chemical oxygen demand, COD was tested with 5220-D Closed Reflux Colorimetric Method and TSS was analyzed with 2540-D Dried at (103–105) °C using gravimetric method. Most experimental analyses have been carried out according to APHA, 2017 [31]. On the other hand, X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) /energy dispersive spectroscopy (EDS) were utilized to characterize the precipitated sludge.

Methodology:

In this method, calcium and aluminum compounds were added to the raw wastewater to enhance the sulfate ions to form partially soluble gypsum CaSO_4 with precipitated ettringite $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ($\text{pK}_{\text{sp}} = 111.6$) [32]. In this experiment, the optimal experimental conditions of the reaction have been detected. The pH range was from 3.5 to 13.5, lime $\text{Ca}(\text{OH})_2$ dosage was calculated according to molar ratios of $\text{Ca} : \text{SO}_4^{2-}$ with 1:1~5:1, the sodium aluminates' NaAlO_2 dosage with molar ratios of $\text{Al} : \text{SO}_4^{2-}$ of 1:3~3:1, and all at retention time 15~120 min. The mixture was filtered under vacuum using a $0.45\mu\text{m}$ micro-porous membrane and analyzed. The treatment removal efficiencies were calculated according equation (1).

$$\eta = \frac{C_o - C_t}{C_o} \times 100\% \quad \eta = \frac{C_o - C_t}{C_o} \times 100\% \quad \dots\dots\dots (1)$$

Where, η represents the removal efficiency for sulfate or other ions, C_o and C_t are the initial and final concentrations of sulfate or other ions in mg/L, respectively. Finally, to adjust pH and reduce TDS, it was necessary to carry out carbonation for the treated wastewater by bugging Carbon dioxide, CO_2 in the solution.

Results and Discussion

Optimization of reaction pH:

Figure (4) shows that the reduction of sulfate was affected by the pH-value ranging from 3.5 to 13.5. The sulfate reduction efficiencies increased with increases the pH-values from 3.5

to 10.5. Then, optimum pH range for stability of ettringite was detected from 11.0 to 12.5 [33-34]. On increasing the pH than 12.5, sulfate reduction efficiencies will decrease with increasing the hydroxide ion concentration in the solution that promoted the decomposition of ettringite [35]. Therefore, to achieve higher sulfate reduction efficiency, it is necessary to adjust the pH value between 11 and 12.5.

On increasing the solution temperature, the solubility of $\text{Ca}(\text{OH})_2$ inhibited. Also, with increasing the pH- values the sulfate reduction will decrease the removal efficiency. Consequently, the ettringite stability decreased with increasing the reaction temperature. Therefore, to achieve a higher Sulfate reduction efficiency, it is necessary to reduce the temperature in the chemical treatment plant to less than 50°C [36].

Optimization of calcium, $\text{Ca}(\text{OH})_2$ dosage

The effect of lime dosage on sulfate reduction efficiency was investigated and the results are shown in Figure (5). Results showed that, on using aluminum/sulfate in molar ratio with 1:3; an increase of lime dosage, the sulfate reduction increased on starting the reaction, then slowly decreased. This is because calcium ions concentration in the solution increased with increasing the lime dosage that facilitated the sulfate reduction efficiency due to the increase of the solution pH than 12.5. When the Al/SO_4 molar ratio was higher than 1:3, sulfate reduction increased with the increase of Lime dosage. The main reason is sulfate ions removal in the mono-sulfate form, $\text{Ca}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12}$ at the high aluminum dosage [35]. On increasing the concentration of calcium ions in the solution, this led to generate ettringite $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ with further increasing sulfate reduction.

However, results deduced that sulfate reduction decreased with further increase in the lime dosage, because the hydroxide ions were not desirable in the formation of ettringite. Lime overdosing is neither desirable nor cost-effective; consequently, the optimum Ca/SO_4 ratio is 2:1.

Optimization of Aluminum, NaAlO_2 Dosage:

The effect of Aluminum, NaAlO_2 dosage on sulfate reduction efficiency was investigated and the results are shown in Figure (6). The effect of aluminum dosage on the reduction of sulfate was varied under different molar ratios of $\text{Ca} : \text{SO}_4$

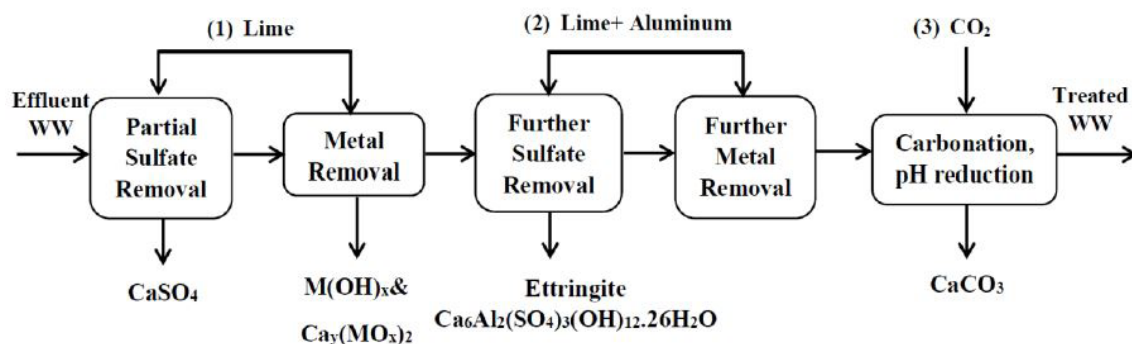


Figure (3): Schematic diagram for methodology of the advanced calcium- aluminum precipitation method (ACAP)

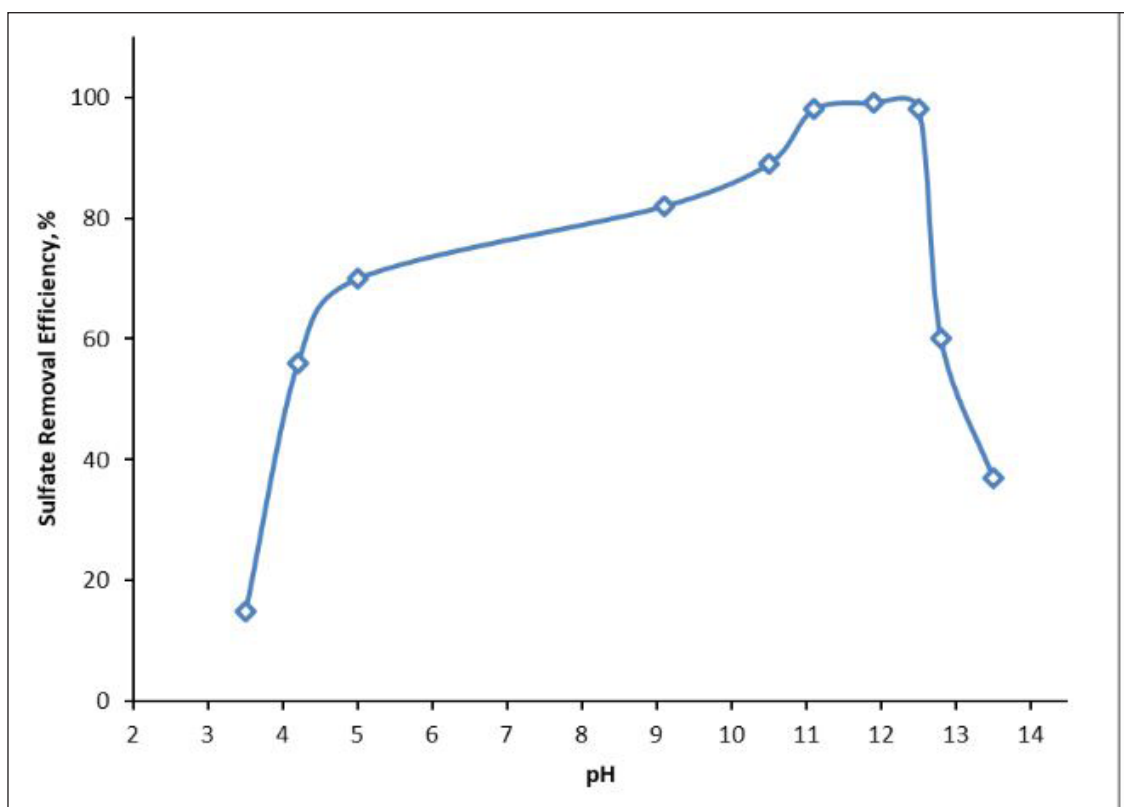


Figure (4): Optimization of pH

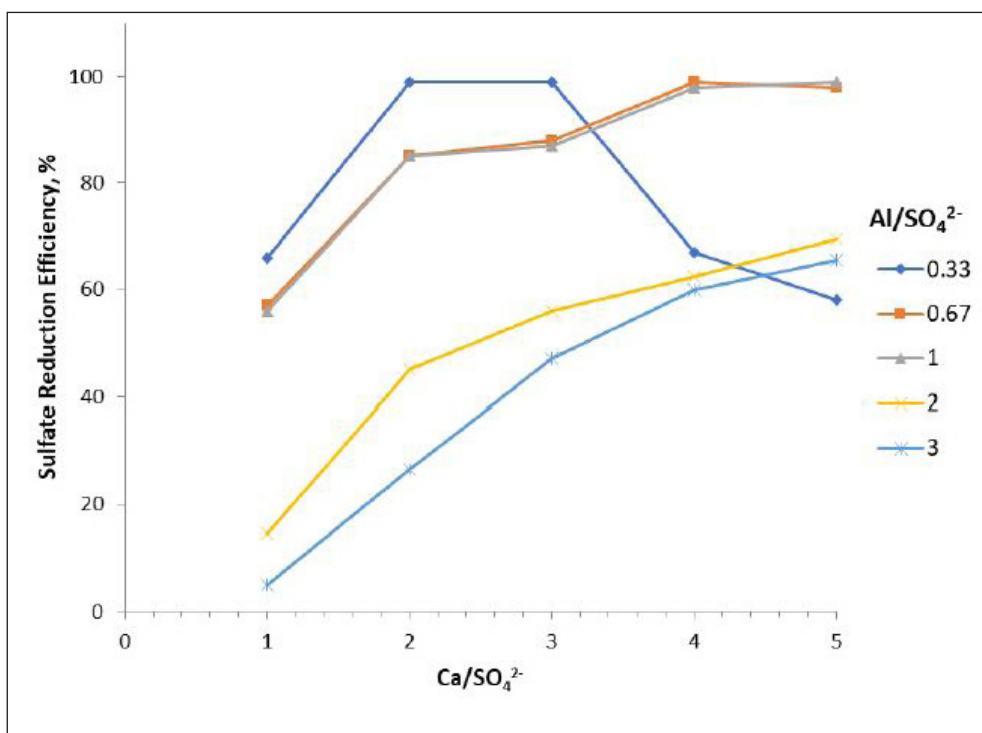


Figure (5): Optimization of Calcium dose

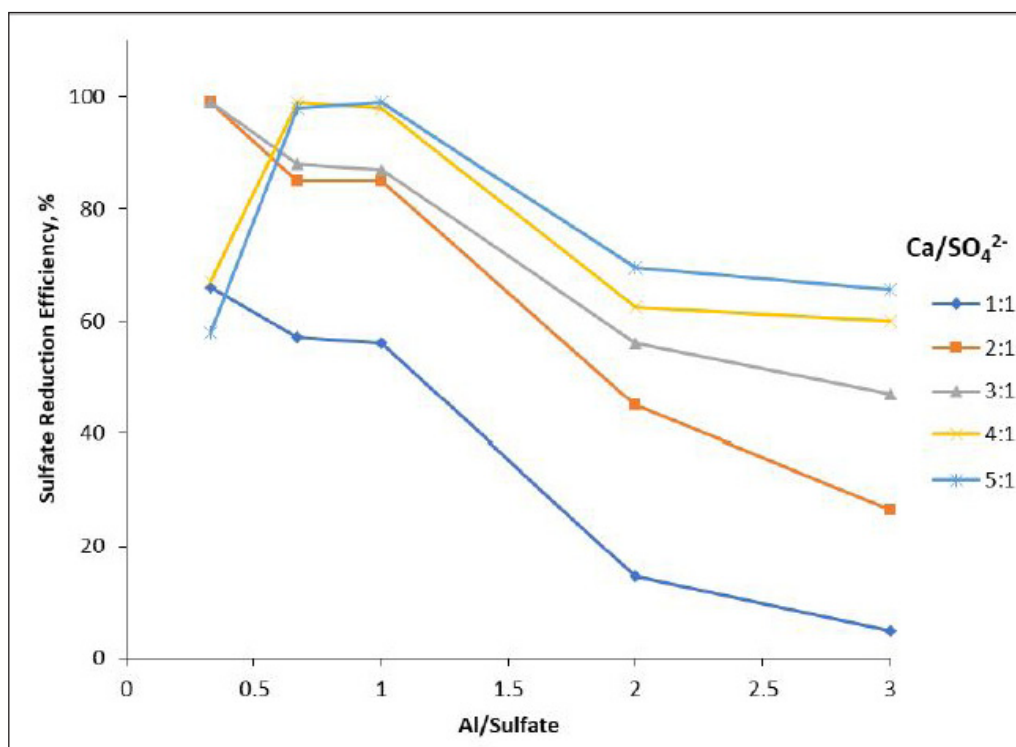
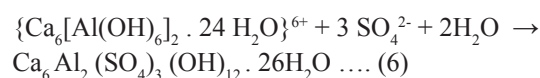
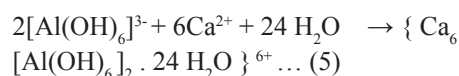
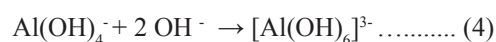
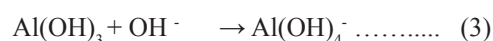
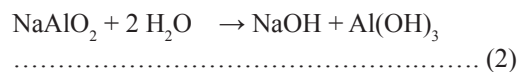


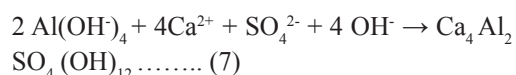
Figure (6): Optimization of Aluminum dose

molar ratio. When this molar ratio was less than 3:1 with NaAlO_2 dosage increased, the sulfate reduction decreased. On the other hand, when the Calcium/Sulfate molar ratio was more than 3:1 with increasing NaAlO_2 dosage, the sulfate reduction increased at first, and decreased rapidly with increasing NaAlO_2 dosage. It was found that the amount of ettringite generated was reduced with an increase of Aluminum dosage; meanwhile, the mono-sulfate $[\text{Ca}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12}]$ generation increased [35]. The Aluminum/Sulfate ratio in the monosulfate with 2:1 is higher than in the ettringite (2:3), while the Calcium/Sulfate ratio (4:1) in the monosulfate is higher than in the ettringite 2:1. Therefore, sulfate ions are mainly reduced in monosulfate form at the high NaAlO_2 dosage condition, resulting in large consumption of calcium and aluminum, and decrease of sulfate ions reduction. The results have shown that overdosing of aluminum, NaAlO_2 is not desirable to sulfate ions reduction; the optimum Al/SO_4 molar ratio is 0.3:1.

Considering the sulfate reduction in the next series of experiments; the molar ratios of $\text{Ca}(\text{OH})_2$: NaAlO_2 : SO_4^{2-} ($\text{Ca}:\text{Al}:\text{SO}_4^{2-}$) were constant at 6:1:3, respectively. In addition, based on the literatures and experimental results [28],[35],[37], the following chemical equilibrium reactions can be used to describe the sulfate reduction reaction process are shown in the following equations:



While at higher lime and Al doses, the formed monosulfate decreases the sulfate reduction:



Effect of Retention Time:

Figure (10) shows the effect of Retention time on sulfate reduction. The results show that the reaction time has an effect on sulfate reduction

at first, while lime has low solubility. Then, Sulfate reduction remained almost constant with the increase of the reaction time, consequently, the reaction of Ca, Al, and SO_4 is being almost completed within 30-min.

Removal of other ions:

Chloride:

The results could be described by the formation of Tetra-calcium Dialuminum Oxide Dichloride Decahydrate, $\text{Ca}_4\text{Al}_2\text{Cl}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$ [98-008-8617] Figure (11). The solubility product of Tetracalcium Di-aluminum Oxide Dichloride Decahydrate was determined with INVRS K using nonlinear regression routine and was found to be, $\text{pKsp} = 25.02$ however the results showed that removal efficiency was minimum removal, approximately 30 %, and sulfate is preferentially removed over chloride as the formation of ettringite and calcium monosulfate is more favorable than formation of Tetracalcium Dialuminium Oxide Dichloride Decahydrate [30]. Therefore, chloride concentration was found to have a negligible effect on sulfate removal with ACAP. On the other hand, increased sulfate concentrations resulted in decreasing the removal efficiency of chloride, even when sufficient calcium and aluminum are present to remove both anions.

Silica and Phosphate, PO_4^{3-} :

Figure (12) shows that Silica can be removed with high efficiency more than 98% with different initial concentrations as Calcium silicate, Hatrurite, Ca_3SiO_5 [98-009-4742] Figure (11). And Phosphate, PO_4^{3-} has 100% removal efficiency.

The concentrations of calcium and aluminum as the same as in reduction of sulfate 1000 ppm and silica concentrations differ from 100, 200, 300, 500, 1000 ppm.

Removal of Heavy Elements:

Table 3. shows that heavy metals removed with high efficiency through the Chemical treatment of sulfate by using advanced calcium- aluminum precipitation method.

Carbonation:

After removal of sulfate to minimum concentration, carbonation process required to

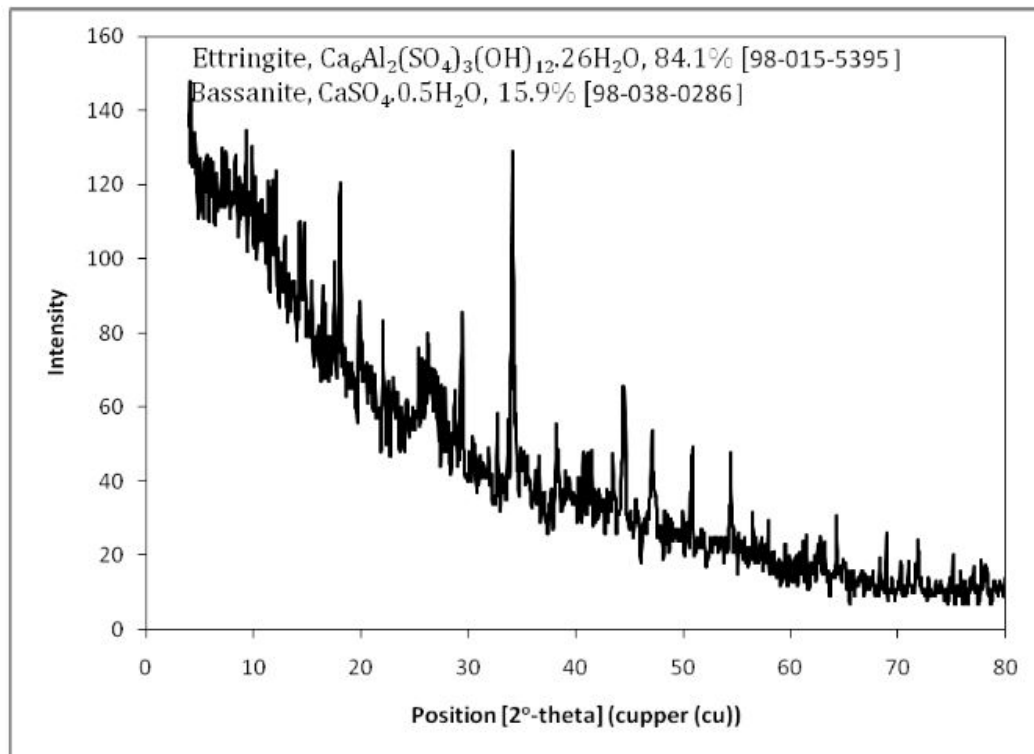


Figure (7): XRD- Sulfate reduction via Ettringite formation,
 $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$

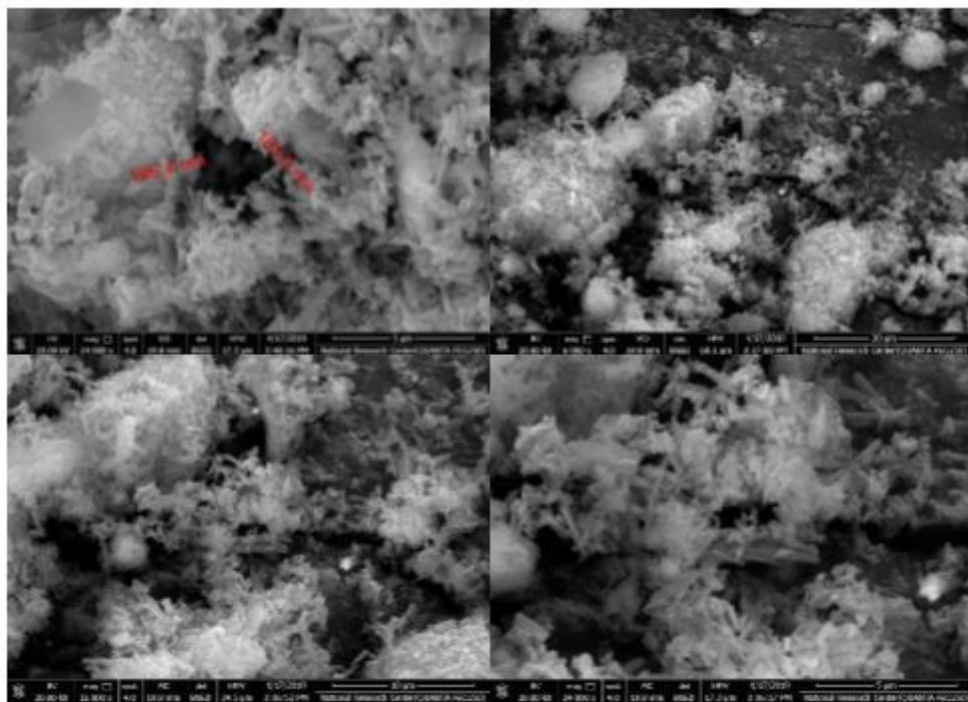


Figure (8): Scanning Electron microscope photos for Ettringite

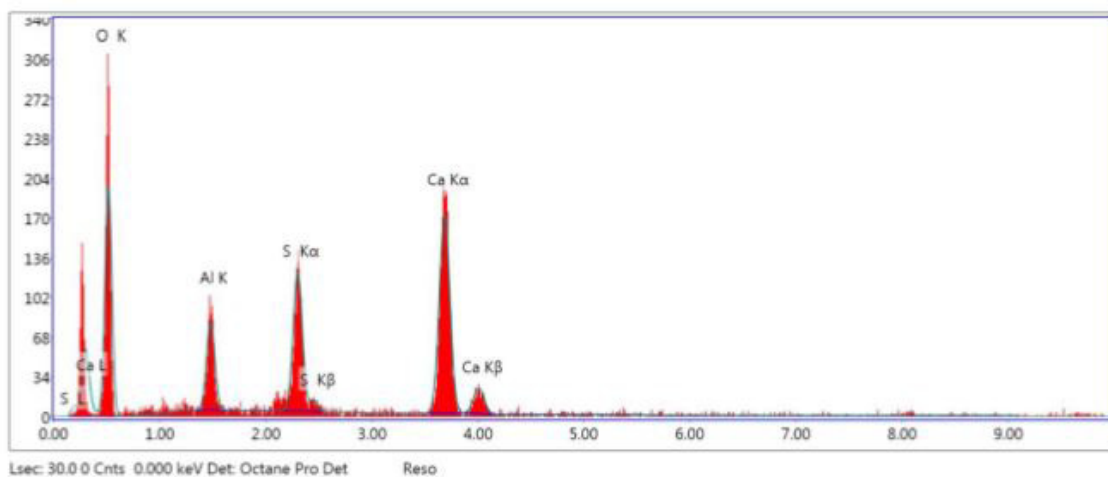


Figure (9): EDS of Ettringite

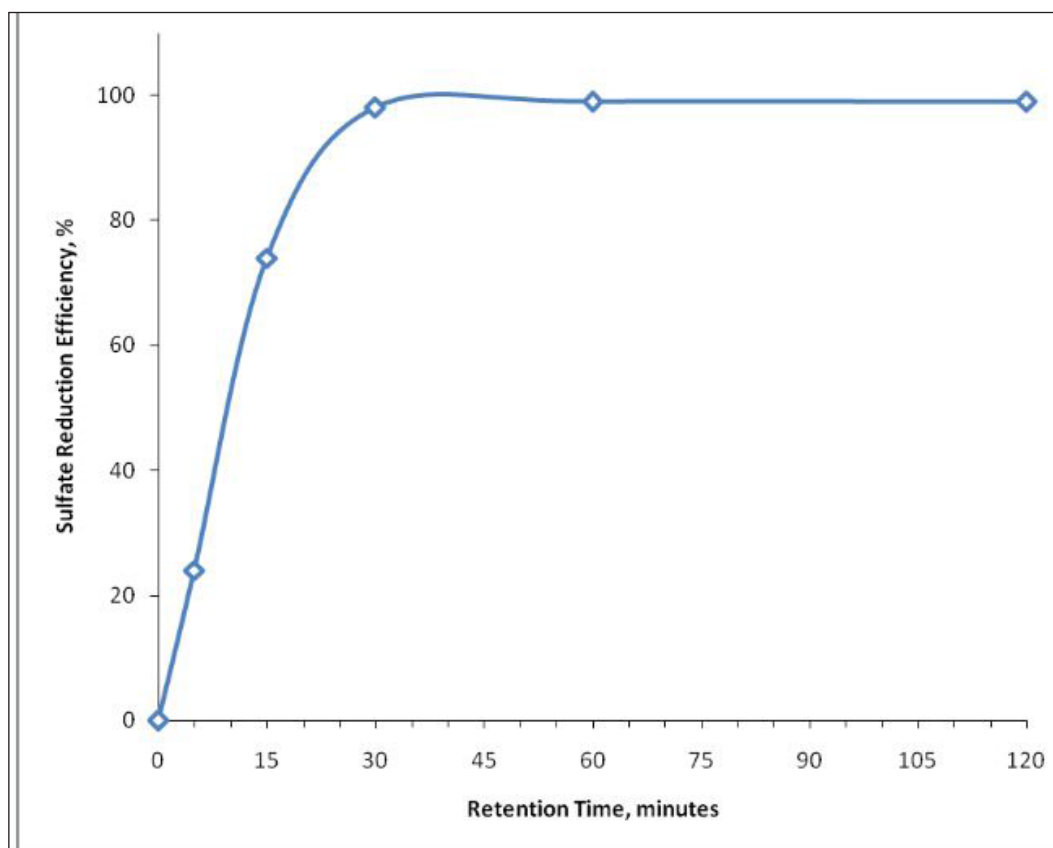


Figure (10): Optimization of Retention time

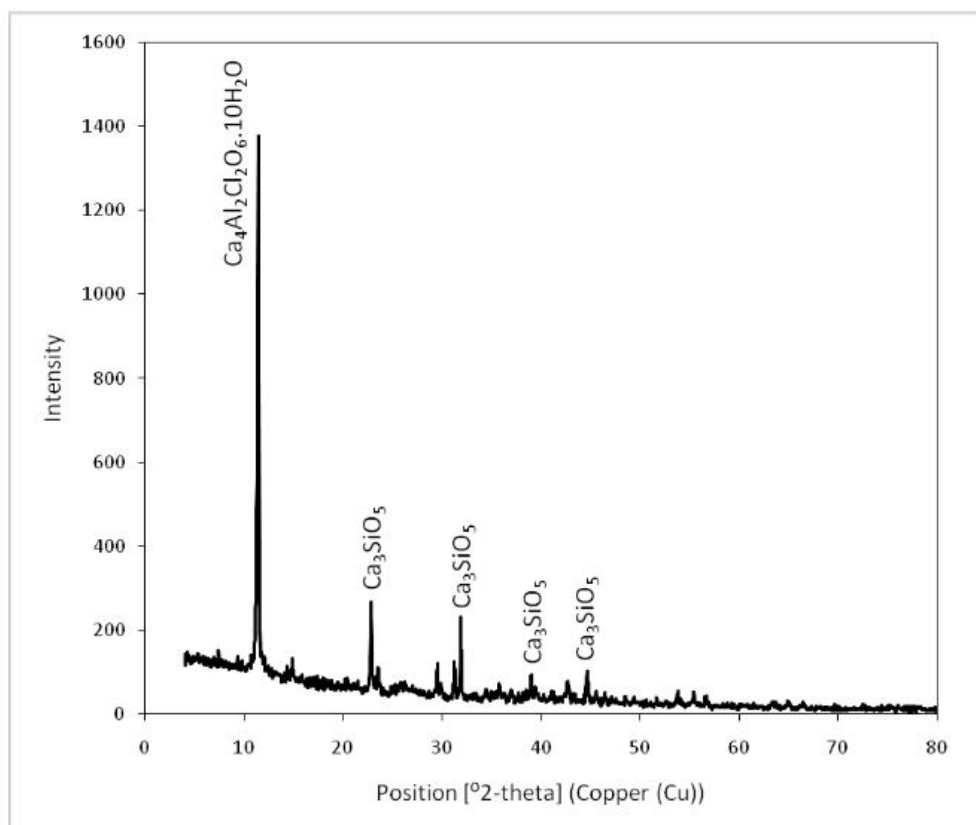


Figure (11): XRD: Tetra-calcium Di-aluminum oxide dichloride decahydrate, $\text{Ca}_4\text{Al}_2\text{Cl}_2\text{O}_6 \cdot 10\text{H}_2\text{O}$

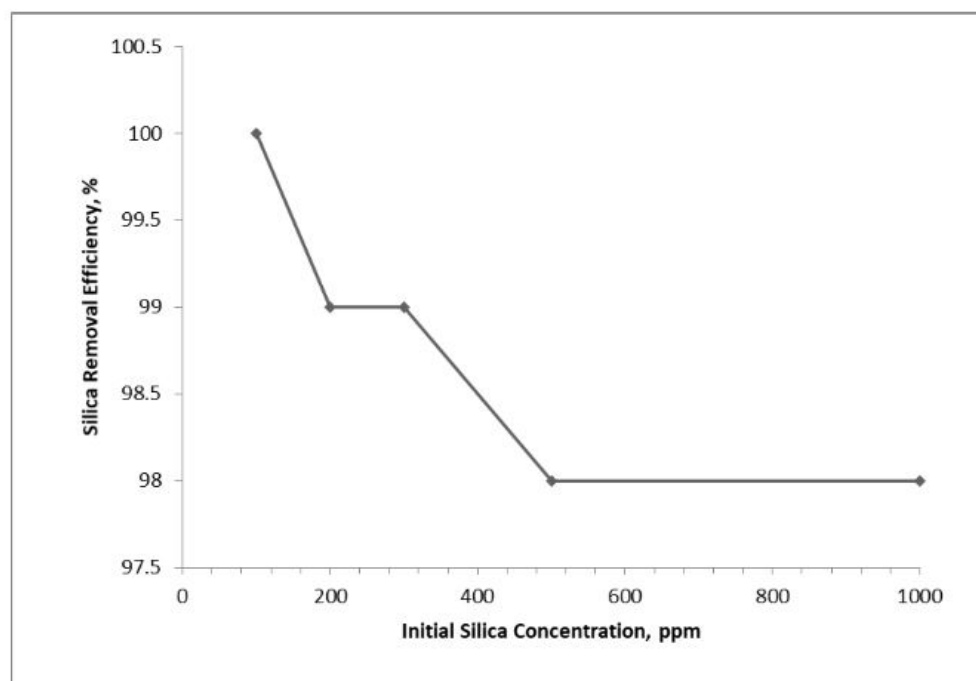


Figure (12): Silica removal Efficiency with different initial concentrations

TABLE 1. Characterization of raw and treated industrial wastewater *

Parameters	Unit	Results			Notes
		Raw WW	Treated WW	% R	
pH	==	7.9	8.0	==	
Turbidity	NTU	306	75	85%	
TDS	mg/L	3880	200	98.5%	
TSS	mg/L	765	30	97%	
COD	mg/L	7000	2400	79%	
T-PO ₄ ³⁻	mg/L	175	ND	100%	
SO ₄ ²⁻	mg/L	600	20	96.7%	
Cl ⁻	mg/L	190	114	40%	
SiO ₂	mg/L	3.6	ND	100%	

* Average of three successive results

TABLE 2. EDS basic data of Ettringite

Element	Weight (%)	Atomic (%)	Net Int.	Error (%)
O	62.47	78.56	50.99	11.81
Al	6	4.48	23.98	10.19
S	9.11	5.71	42.38	6.2
Ca	22.42	11.25	69.57	4.52

TABLE 3. Heavy metals removal efficiencies

Element	Unit	Results				
		Raw IWW	Treated IWW			
			Lime	% R	Lime + Aluminum	% R
Cr	mg/L	12	0.13	99.9 %	< 0.01	99.9 %
Cd	mg/L	20.5	< 0.01	99.9 %	< 0.01	99.9 %
Ni	mg/L	19.7	< 0.01	99.9 %	< 0.01	99.9 %
Pb	mg/L	24.7	1.0	99.9 %	< 0.01	99.9 %
Fe	mg/L	16	99.9 %	< 0.01	< 0.01	99.9 %
Mn	mg/L	18	99.9 %	< 0.01	< 0.01	99.9 %
Zn	mg/L	20	97.5 %	4.84	0.5	97.5 %
As	mg/L	19	99.8 %	0.02	< 0.01	99.8 %

TABLE 4. Analyses of the yield from sulfate reduction

Parameter	Unit	Results	
		Inlet	Outlet
pH*	==	12.8	8.0
TDS**	ppm	1800	200
Calcium	ppm	360	95
Sulfate	ppm	20	20

reduce pH* and TDS**. This process performed by purging of carbon dioxide, CO₂ into treated water. Residual Calcium can be reduced by precipitating as Calcium Carbonate, CaCO₃.

Note than Calcium Carbonate, CaCO₃ can dissolve in excess from Carbon dioxide, CO₂, and yield Calcium bicarbonate, Ca(HCO₃)₂ which can dissolves, so, we must take care to reach TDS to the minimum Dissolved solids.

The optimal experimental conditions for Ca/SO₄²⁻ ratio, 2:1; Al/SO₄²⁻ ratio, 1:3; solution temperature, 25°C; and reaction time, 30 min were determined and the efficiency of the removing of sulfate was 98%. Yu et al., 2018 reached to the optimum operation condition for removing of sulfate with the molar ratio of Ca/SO₄²⁻ of 2.0, the reaction time 20 min, and the reaction temperature 55 °C, and the efficiency of the removing of sulfate was 82.6% [38]. Finally, the produced amount of precipitated sludge can be removed as solid material after the completion of the reaction.

Feasibility and Application Prospect of the Method:

The removal of sulfate ions and other ions in actual Sugarcane wastewater by using the advanced Calcium-aluminate precipitation method was evaluated. The composition of wastewater and the results of purification various ions are shown in Tables 1. The results indicate that the advanced Calcium-aluminate precipitation method had high reduction efficiencies for Sulfate ions and heavy metal ions, with average reduction efficiencies of more than 98% and 99%, respectively. In addition, Cl⁻ could also be removed minimally by the method. The results show that the reduction of high-concentration sulfate ions from the Sugarcane wastewater is feasible by using the advanced Calcium-aluminate precipitation method. The Sulfate concentration in the treated wastewater met the requirements for reuse of water; meanwhile, heavy metal ions were effectively removed. As displayed in Table 1, the pH of the treated wastewater was 8.0; thus, the water could be reused. In addition, the solid sediment produced by wastewater treatment can be used as a raw material for ceramics and other building materials production. Therefore, considering pollutant removal efficiencies, and resource reuse, the advanced Calcium-aluminate precipitation method has the potential to be a

commercial application in the field of reduction of high-concentration sulfate ions from the industrial wastewater in the future. The Advanced Calcium-aluminate precipitation method has become a preferred method due to its high removal efficiency, many studies have used this method to treat industrial wastewaters, such as aluminum anodizing, textile industries, and mine water [28], [35], and [37]. The Product of treatment process can be used as a highly efficient sorbent material for removing hydrogen sulfide (H₂S) from air Stream [39].

Conclusions

In this paper, the advanced calcium-aluminate precipitation method was used to reduce the sulfate ions, and the influences of experimental parameters on sulfate removal were investigated. The advanced calcium-aluminate precipitation method can effectively reduce Sulfate ions concentrations, and heavy metal ions with reduction efficiencies of more than 98%, and 99%, respectively. In addition, Cl⁻ can be removed minimally by the same method. Aluminum, NaAlO₂ dosage, Calcium, Ca(OH)₂ dosage, pH, reaction time, have remarkable effects on the sulfate ions reduction. The optimal experimental conditions Ca/SO₄²⁻ ratio, 2:1; Al/SO₄²⁻ ratio, 1:3; solution temperature, 25°C; and reaction time, 30 min were determined. The advanced Calcium-alumina precipitation method is feasible for treating real wastewater with high sulfate concentration and has the potential to be a commercial application in the high-concentration sulfate wastewater treatment field in the future.

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خفض الكبريتات وإزالة العناصر الثقيلة من الصرف الصناعي بطريقة الترسيب الكيميائي المتقدم

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المعالجة المتكاملة لمياه الصرف الصناعي أصبحت ضرورة ملحة خاصة في هذا الوقت الراهن وذلك لمواجهة العجز المائي الذي تعاني منه الدول خصوصا في المناطق التي لا تمر بها أنهار. في هذا البحث تم استخدام نظام متكامل لمعالجة مياه الصرف الصناعي المحتوي على تركيزات عالية من الكبريتات. يتميز هذا النظام بإزالة الكبريتات بكفاءة عالية تصل الى ٩٨٪. في هذا النظام تم استخدام بعض أنواع المخترات كمعالجة كيميائية مثل أكسيد الكالسيوم CaO والومينات الصوديوم NaAlO₂ حيث أجريت دراسة لمعرفة الكمية المناسبة لكل منهم. للوصول الى اعلى كفاءة للمعالجة يجب ان يكون نسبة الكالسيوم : الألومنيوم : الكبريتات هي 6 : 1 : 3 . تم تصنيع وحدة معالجة كيميائية لاجراء التجارب كنموذج لتطبيقه في احدي المصانع. تم عمل فحص على المادة المترسبة بواسطة SEM-EDAX & XRD تبين ان هذه المادة هي Ettringite. هذا النظام يستخدم أيضا في إزالة عناصر ثقيلة بكفاءة عالية وبعض الايونات الخري مثل السيليكات والفوسفات بكفاءة عالية. وإزالة المتبقي من الكالسيوم وضبط pH تم ضخ غاز CO₂.