Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2021.27597

235 (2021) 135–140
September

Evaluation of porcelanite and bentonite performance as an effective coagulant agent for petroleum contaminated wastewater treatment

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Received 19 January 2021; Accepted 10 July 2021

ABSTRACT

One of the major problems in the petrol industry is water contamination. This study deals with the treatment of contaminated waters of the North Gas Company in Kirkuk province north of Iraq. There are many different processes and additive materials that can be used to treat contaminated water. In this study, different materials were added to give a coagulated layer that can help in the treatment of the contaminates in polluted water which then can be removed through filtration. The combined mixture of 80% porcelanite and 20% bentonite additives were applied as a coagulation agent in the present work. A comparison treatment performance was also made with aluminum sulfate. Milling and grinding to a fine powder using a ball mill was adopted to produce a homogeneous bed of porcelanite and bentonite as new flocculants, results revealed that higher treatment efficiencies can be obtained using the new flocculent. Removal efficiencies of 93%, 94%, 91%, and 85% were achieved respectively for turbidity, COD, BOD_5, and conductivity, compared with removals efficiencies for the same parameters using the aluminum sulfate (500 ppm), 91, 62, 59, and 51. Using the new flocculate, the turbidity of wastewater was completely removed, and insignificant differences were observed in the pH parameter. The chemical treatment ability of the porcelanite-bentonite mixture was improved based on removal efficiencies, compared with other chemicals such as alum which are currently widely used. The importance of this topic lies in using natural materials abundant, locally available and environmental friendly, to treat the water leaving the North Gas Company filtration station before sending it to the river, reuse of treated water in the industry contributes significantly to lowering the cost of water production required for utility units.

Keywords: Porcelanite; Bentonite; Flocculation; Wastewater treatment

1. Introduction

Contaminated water causes serious environmental problems due to the presence of a very large amount of suspended solids, high chemical oxygen demand, and also its color.

Therefore, wastewater must be treated before it is released into the environment [1].

The pollutants in the wastewater include different types of salts, mineral oils, surfactants, heavy metals, etc.

Coagulation is a major process that is used in drinking water, wastewater, and industrial wastewater treatment. It is one of the important chemical and physical

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processes used in water treatment. Other industrial water and wastewater treatments can be made by electrical and chemical means [2].

Coagulation and flocculation take place in successive steps aimed at destabilizing the suspended particles, allowing particle collision and growth of floc. The coagulation term is defined as the addition of a positively charged ion from a polylactolite or salt catalyst, which will produce particle instability as it targets particles whose diameters fluctuate between 7–10 and 10–14 cm. Adding any positive electric charge will neutralize the negative electric charge.

Marey's [3] study successfully proved the effectiveness of the combination of chitosan and bentonite as a coagulating agent in the Ismailia canal as a water treatment plant. The optimal conditions were determined based on the turbidity removal. In this research, the optimum conditions of the synthesis of composite chitosan-bentonite were at a weight ratio of bentonite/chitosan 5:1 and time 30 min and an optimal pH of 8. Coagulation with chitosan-bentonite successfully removed the turbidity with an efficiency of 97.7%. On these conditions, more chitosan can interact with the matrix of bentonite to form a chitosan-bentonite composite. The chitosan is located on the outer surface of the bentonite and does not enter the layer structure of bentonite.

Rozainy's [4] study also successfully proved the effectiveness of the combination of chitosan and bentonite as a coagulating agent in a DAF tank for the raw water treatment process. The optimal conditions were determined based on turbidity removal. In addition, the principal factors affecting coagulation were determined throughout the study, including optimal coagulant dosage, mixing time, pH, and mixture ratio of primary coagulant and coagulant aid in the treatment of raw water. Coagulation with chitosan-bentonite had successfully removed the turbidity with an efficiency of 97%. The coagulants performed well (97% removal of turbidity) when the chitosan-bentonite ratio of 30:70, the concentration of 1,000 mg/L (300:700 mg in 1 Liter of raw water), optimal pH of 7.3 and 30 min of mixing time during flocculation.

Ranga [5] concluded that bentonite provides a cheaper, safe, effective, and economic method for wastewater treatment before disposal to the water stream. Clay minerals are effectively used for the removal of organic matter, toxic metals, and nutrients. Modified betonies showed higher adsorption as compared to raw bentonite. It provides an ecofriendly and economic method for the treatment of wastewater as compared to chemical based methods.

In another study, Jassim [6] tested both the raw and the water purified by produced ceramic for a number of water quality parameters, that the ceramic disc purifier could remove, as an average percentage of removal, 99.98% of turbidity, 78.86% of the electrical conductivity, 81.61% of the total dissolved solids, 73.45% of Ca^{++}, 49.69% of Na^+, 55.63% of NO_3^-, 37.54% of HCO_3^-. Their results showed that CP has excellent adsorption ability for solutes of seven heavy metals, Mn, Fe, Pb, Cd, Co, Cu, and Zn, at the concentrations of 1 mg/L each and 10 mg/L each. The adsorption capacities of each filter to adsorb seven heavy metals were computed according to Langmuir and Freundlich models. The results showed a variety in adsorption capacities for each heavy metal.

In another study, Abdullah [7] found that the bentonite-limestone mixture produces less sludge volume index and showed lowest zeta potential values. The zeta potential of treated bentonite and bentonite mixed were –26.7 mV for bentonite-alum, −20.7 mV for raw bentonite, −19.9 mV for bentonite-zeolite, and −17.6 mV for bentonite-limestone which demonstrated the coagulation and adsorption process occurred. On the other hand, the effects of contact time indicated that the adsorption capacity of combination bentonite was higher than raw bentonite.

Bourliva [8] studied the removal of suspended solids (SS), chemical oxygen demand (COD), nitrate ion, ammonium ion, phosphate ion, and toxic metals. The treatment gave overflowed clear water improved concerning the quality parameters. The bentonite adding before flocculation resulted in effective removal of heavy metals such as chromium and copper. Additionally, the bentonite removed nitrogen compounds with relatively high efficiency, while the clay presence highly improved the COD removal.

Coagulation or successful flocculation refers to the successful collision that will occur when unstable suspended particles are pushed towards each other by the force of the characteristic hydraulic shear force inside the flocculation or coagulation basin. Here, the colloids will clump and then bond with each other to form a small mass and then turn into visible masses (Fig. 1).

The most common type of coagulating is achieved with aluminum salt, the salt is more common and economical for aluminum called alum ($Al_2(SO_4)\cdot nH_2O$) as it is widely used as a coagulant in the field of water and wastewater treatment. The aqueous chemistry of aluminum is very complex, as when adding any coagulant to aluminum in hydrotherapy, many interaction pathways will be found, and this is the mechanism by which aluminum works to remove colloids or contaminants [10].

The destabilizers containing the aluminum monomers are neutral charge or coagulation of colloidal particles in the presence of $Al(OH)_3$ and are called the sweep mass here, the organic materials are removed by the adsorption method on the deposition of aluminum. Many different methods have been used for unstable pollutants using coagulation materials or chemical flocculation, for example, aluminum salts. The coagulation method is controlled by different types of hydrolysis [11]. Fig. 2 illustrates the reaction schematics of coagulation.

Mineral clay has been used widely and is considered to be one of the most common uses as an absorbent and ion exchange for water treatment uses in general and wastewater

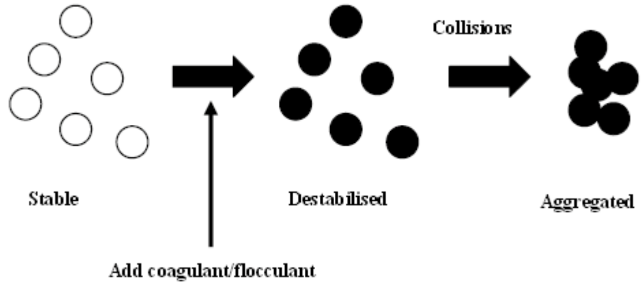

Fig. 1. Mechanism of coagulation [9].

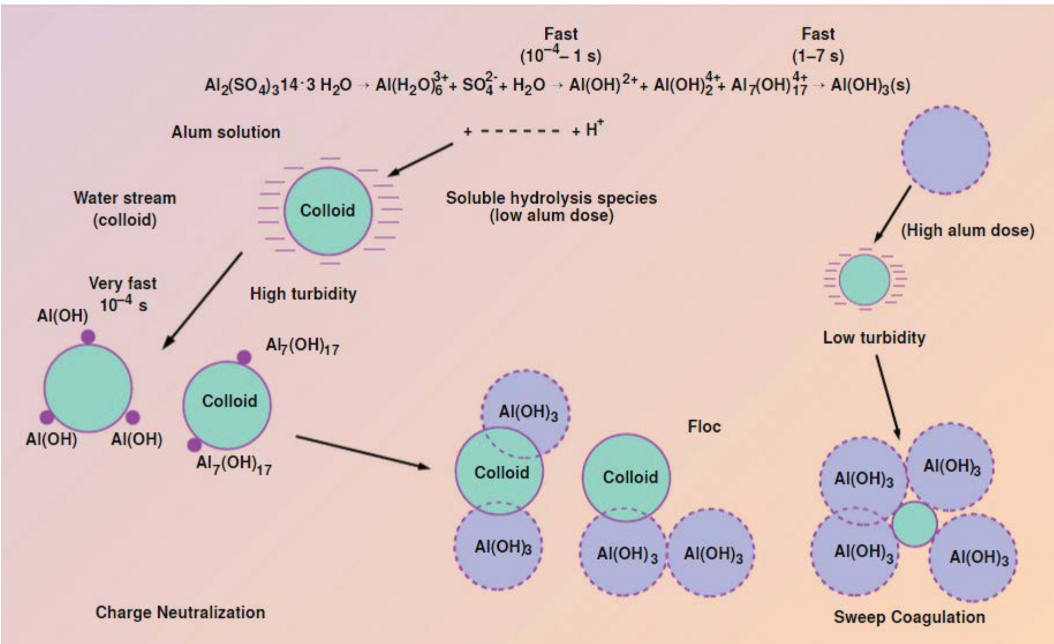

Fig. 2. Reaction schematics of coagulation [12].

treatment, in particular, to remove organic pollutants, heavy metals, and nutrients electrically, through organic and inorganic cations from the environment to polyaluminum chloride, where its ability to absorb from its high surface areas and its high interchangeability and it is considered one of the highly effective natural clay minerals, especially in the form of granules that are used to treat wastewater [13].

In the present work, a mixture of 80% porcelanite and 20% bentonite was used as a coagulation agent. The study aimed to use porcelanite as a source of silica and alumina. Porcelanites (siliceous rocks) as coagulation agents in treating wastewater. Porcelanites were brought from the western part of Iraq in the Rutba region. The matter had a thickness of (0.5 to 1.3 m) layer in Al-Sufra, and Al-Trafwi site, and it consists of opal-CT (crystal layers – three layers) and are derived from biogenic amorphous opalline silica, associated with shale. Pocelanites – siliceous rocks – are the part of the phosphorene in the western Digme and Akashat formations respectively.

2. Materials and methods

Raw contaminated wastewater samples were collected from the treated effluent of the equalization basin in the central processing plant of the outfall of a North Gas Company in Kirkuk, Iraq. The purpose of floatation (coagulation plus dissolved air floatation) is to reduce fats and suspended solid contents and to remove oil from wastewater coming from the equalization basin [14].

The aluminum sulfate is already used for water purification as a coagulation agent, in the present work, a local porcelanite mineral found in large quantities in the western area of Iraq was used as coagulation and flotation in combination with bentonite, (80/20 wt.%) which is also found in large quantities locally.

The porcelanite and bentonite with a chemical analysis as given in Tables 1 and 2, respectively were used as coagulation agents also.

All raw materials used were brought from the Ministry of Industry and Minerals Geological Survey, porcelanite was in the form of rocks meanwhile the bentonite was as powder. Grinding those raw materials (the rocks) to very fine particles was achieved by the porcelain ball mill, also the ball mill is used to achieve a homogeneous mixture of 80% porcelanite and 20% bentonite.

The study applied different concentrations of coagulation agents as shown in Table 3 .

The process is based on pressurizing a recycle stream and saturating it with air, to form bubbles. These bubbles formed on the surface of suspended particles and they are attracted to the particles by surface energies then scraped from the floatation basin surface.

Turbidity, COD, BOD_5, and conductivity were analyzed according to the methods given by ASTM standards, v.11.01 Water D1889-88A, and ASTM standards part 31, ASTM standards D5847, and the conductivity using the standards ASTM D1125-14. The conductivity is measured in the process and then the values are obtained directly, so that they can be controlled and used to monitor the process.

3. Results and discussion

The removal efficiency (% removal) was calculated from the following formula:

$$\text{Removal efficiency}\left(\%\right)=\left[\frac{\left(C_i-C_f\right)}{C_i}\right]\times 100 \quad (1)$$

where C_i and C_f are the initial and final concentrations for each parameter (Turbidity, COD, BOD_5, and Conductivity) of petroleum wastewater, respectively. The initial value of each selected parameter was listed in the below table.

Parameters	Initial concentrations
Turbidity	16.095 NTU
COD	53.86 ppm
BOD_5	22.43 ppm
Conductivity	924.55 µs/cm

The dose of alum from 100 to 500 mg/L gave the pH value of 7.5, the results indicate the efficiency of the COD ranged from 30% to 62% with a highly efficient result. The predominant removal method at lower doses of alum is adsorption. Thus, when high doses of coagulant were taken, and whenever the dose of alum was increased, the percentage of the COD was high, so the appropriate dose of alum was taken which gave the highest removal of COD rate of 500 mg/L as shown in Fig. 3.

Meanwhile using the mixture of 80% porcelanite and 20% bentonite as a coagulation agent gave an enhancement of treating and removal efficiency as illustrated in Fig. 4.

The highest doses of flocculation or coagulation were obtained with the addition of coagulants, longer coagulation times, lower flotation rates, as well as sedimentation, filtration aids, and filtration rates required for the production of treated water that is low in turbidity in complete plants. The coagulant should be mixed uniformly in wastewater.

The removal of organic matter was determined according to the COD parameter. Higher treatment efficiencies were obtained when the mixture of porcelanite and bentonite was used as flocculants. Removal efficiencies of 93%, 94%, 91%, and 85% were achieved for turbidity, COD, BOD_5, and conductivity, respectively when porcelanite and bentonite

Table 1
Mineral analysis of as received Porcelains [13]

Compound	wt.%
SiO_2	62.02
CaO	11.55
MgO	7.2
Al_2O_3	2.71
Fe_2O_3	0.87

Table 3
Concentrations of coagulation agents used in the present work

Coagulation agent / Concentration %	wt.%	wt.%	wt.%	wt.%	wt.%
Aluminum sulfate	100	200	300	400	500
Porcelanite	500	1,000	1,500	2,000	3,000

Table 2
Chemical composition of bentonite

Materials	SiO_2 %	Fe_2O_3 %	Al_2O_3 %	CaO %	MgO %	SO_3 %	Na_2O %	K_2O %
Bentonite	50.05	6.26	16	7.94	3.14	0.85	1.01	0.47

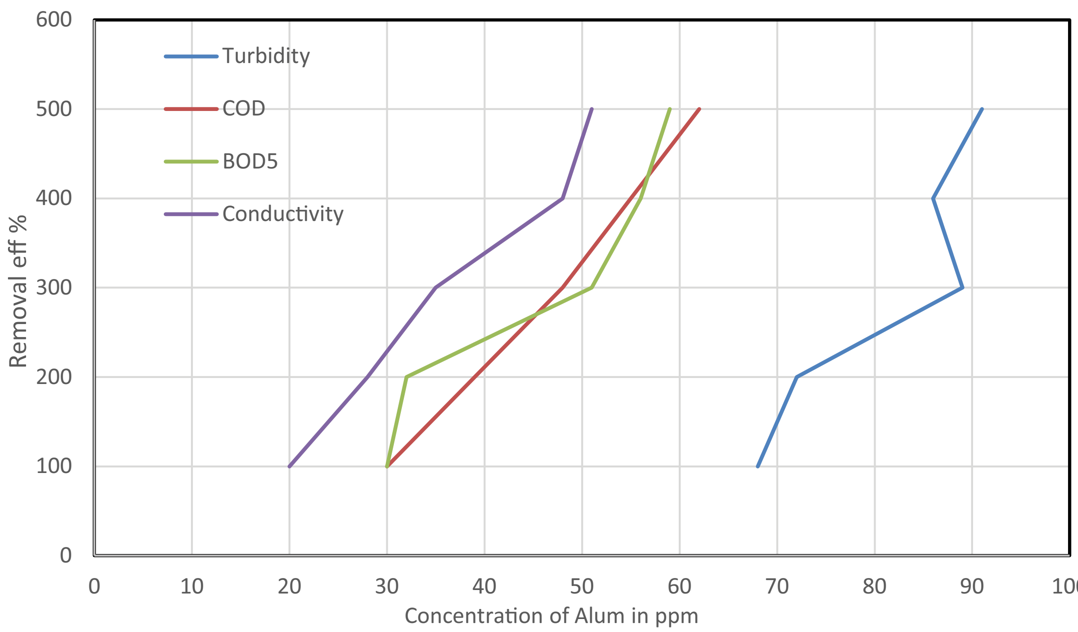

Fig. 3. Removal efficiency of turbidity, COD, BOD_5, and conductivity with the concentration of aluminum sulfate.

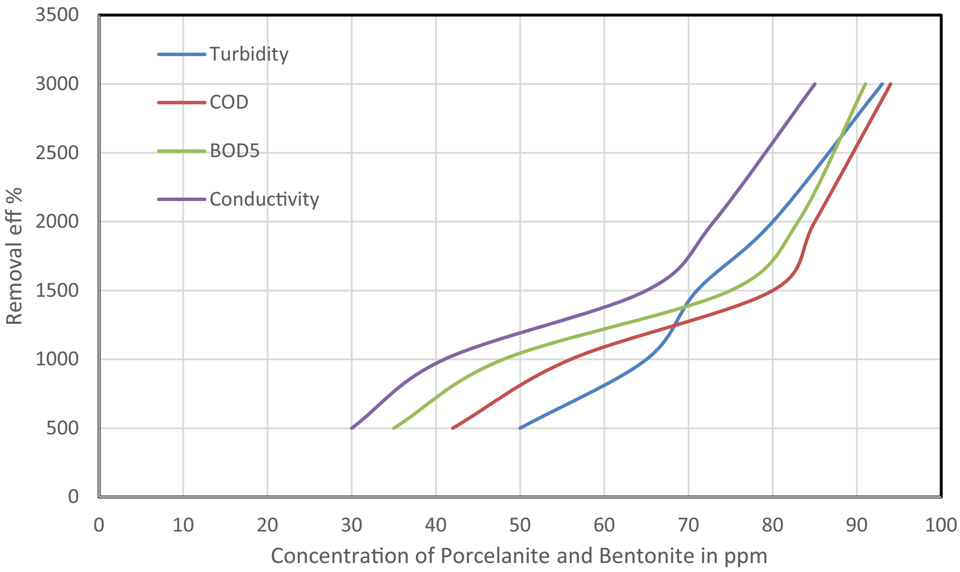

Fig. 4. Removal efficiency of turbidity, COD, BOD_5, and conductivity with the concentration of porcelanite and bentonite.

Table 4
Removal efficiency of turbidity, COD, BOD_5, and conductivity with the concentration of aluminum sulfate

Alum sulfate ppm / Removal eff%	Turbidity	COD	BOD_5	Conductivity
100	68	30	30	20
200	72	39	32	28
300	89	48	51	35
400	86	55	56	48
500	91	62	59	51

Table 5
Removal efficiency of, turbidity, COD, BOD_5, and conductivity, with the concentration of porcelanite and bentonite

Porcelanite and bentonite / Removal eff%	Turbidity	COD	BOD_5	Conductivity
500	50	42	35	30
1,000	65	56	48	41
1,500	71	80	75	65
2,000	80	85	83	73
3,000	93	94	91	85

were used as coagulants and flocculants. The wastewater turbidity is completely removed, and little pH differences are observed. For aluminum sulfate as a coagulation agent, the highest efficiency was obtained in turbidity removal efficiency 95%, using (500 ppm alum concentration).

After sedimentation, the water should be filtered to continue removing suspended matter and germs.

This work illustrates that the porcelanite, bentonite mixture is a promising alternative for petroleum wastewater treatment, the water because of its high efficiency to attach the biological contaminants. Milling and grinding to a fine powder for the mixture get contributed to increase the surface area and enhance the chance of attachment of contaminants also.

4. Conclusion

The petrochemical industry could cause serious environmental pollution as a result of waste and discharges industrial wastewater loaded with many dangerous pollutants resulting from the operation of the units. Source of industrial wastewaters originate from industrial processes and they may contain contaminants that degrade the water quality, such as, suspended sediments, bacteria, oxygen demanding matter, and perhaps toxic substances. Therefore, wastewater must be treated from all these contaminants, so that they are within the limits in accordance with the conditions required by laws.

Adding chemicals (aluminum sulfate) or natural coagulants (porcelanite and bentonite mixture) speeds up the sedimentation process, to remove the contaminants.

The coagulation–flocculation process was improved clearly by using the natural raw mixture of porcelanite and bentonite for reducing the concentrations of contaminants in wastewater samples of the effluents from a North Gas Company in Kirkuk/Iraq.

This was the first time that abundance, environmentally safe, and low price ores have been used, therefore, it could well be suggested as a good alternative for other coagulation agents, moreover, it works in a high removal efficiency as appeared from the study results.

Acknowledgments

Special thanks go to the staff of the Environmental Department of North Gas Company, also thanks and regards to the laboratory staff of Al Israa University for their assistance in achieving this work.

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