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Effect of the chemical coagulation on the outlet of the refinery effluent

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ABSTRACT

Effluent of the Zawiya Refinery was analyzed for the estimation of oil and organic matter contents, suspended solid and biological oxygen demand. For reducing the level of above mentioned pollution parameters in the effluent, some chemical coagulants and coagulation aids were tried. From the experiments it was found that the Aluminum Sulphate Octadecahydrate in combination with either activated silica or bentonite clay, each in the ratio of 5 mg/L when added in the effluent samples, brings reduction in the concentration of oil and organic matter contents, suspended solid and biological oxygen demand up to 90%, 80%, 70% respectively. All the above experiments were carried out at the laboratory scale.

INTRODUCTION

The principle contaminants in the refinery effluent are organic substances produced during the refining operation such as (phenols, nitrocompounds, aromatic and aliphatic sulphur and oxycompounds), some fractions of distilled petroleum products, salts of alkaline and alkaline earth metals, transition metals and their salts, some color and odor producing substances, and other pollutants which increases the biochemical oxygen demand of the receiving water. Some of the above defined pollutants are extremely toxic and having mutagenic and carcinogenic properties[1,8,15,16,18], and some are less toxic. The substances which have less toxic effect, when present in large quantity produce undesirable effect on the marine life. Ultimately ecological implications of pollutants are dependent on their concentration, in the final industrial discharge or effluent. These hazardous substances have also affects directly or indirectly on the human beings either by direct contact with the pollutants or by consuming the marine products by them as food (like fishes)[17]. The occurrence of the above mentioned contaminants in food, in drinking water and in air are responsible for the abort term and loge term toxicity. The aquatic pollutants, affects the reproduction process of the marine living organisms, and have embryotoxic and taratogenic effect on the aquatic life[2].

The oil films over water disturb the photosynthesis process of the plant kingdom by reducing the available sunlight and also cut off the oxygen supply from the atmosphere to the marine life. Generally the oily products of low boiling point found to be more toxic than the heavier fuel oils, while the crude itself has intermediate toxic effect. Heavier oils are physically more hazardous than lighter ones. The oil and dispersant mixtures are more toxic than either of them alone. Low boiling hydrocarbon includes, benzene, toluene, xylene, naphthalene, phenanthrene etc. are water soluble to some extant and are known to be toxic to a wide variety of marine organisms. Higher boiling crude oil fractions include polycyclic aromatics which are proved to be seriously damaging long term poisons[6,9,10].

Mineral oils and other plant cuticles, which encourage the adhesion of oil to the vegetation. Oily substances obstruct the leaves pores (stomata) and prevent completely or partially gas exchange to the roots and shoots of plants. Some constitutions of crude oil affects directly on the metabolic processes of marine life. Plants with large underground vegetation system (the perennials) survive oiling better then those without (the annuals), as new growth can occur from these systems, after shoots and leaves have been destroyed. Destructions of vegetation system of the receiving water directly influence its ecology[3,7].

Our work mainly concern to find out suitable economical and efficient coagulants and coagulation aids which have ability to coagulate efficiently the above mentioned pollutants, which normally are present in the effluent in microfine droplets or particles, in order to prevent the ecological system of the receiving water from their toxic effects. The mentioned pollutants are responsible for biochemical oxygen demand, which reduces the available oxygen for the living organisms present in the surrounding. So by decreasing the concentration of the mentioned pollutants in the final effluent, either physically or chemically, helps to preserve the ecological system of the receiving water. We will also try to find out the optimal concentration of the used coagulants and coagulation aids, in order to achieve maximum results from the minimum concentration of the used substances.

Reagents and materials

The following ACS Grade chemicals (conforms the specifications of the Committee on Analytical Reagents of the American Chemical Society) were used through out in our work. Sulphuric acid (sp. gr. 1.84), diethyl ether (99%), aluminum Sulphate octadecahydrate, sodium silicate ($Na_{20}.xSiO_2$ where x = 3-5), bentonite clay, mono potassium dehydrogen phosphate, dipottasium hydrogen phosphate, disodium hydrogen phosphate ammonium chloride, magnesium Sulphate heptahydrate, calcium chloride and ferric chloride hexahydrate, sodium hydroxide, sodium iodide, sodium azide and sodium thiosulphate. Reagent water conforms the specification given in the ASTM standard D-1193, was used throughout the work.

Sampling and preservation

The samples of the effluent were collected at different time from the final discharge of the oil refinery, in the clean amber colored 2.5 L capacity glass bottles. For preventing any change in the composition of the effluent, 6 ml of conc. Sulphuric acid was added in each sample bottle at the time of sampling. The pH of the effluent after the addition of acid was below 2.

Procedure

Estimation of oil and other organic matter contents

Four portions of effluent, 2.5 L each, have been taken from the samples collected the first day and marked them as A1, A2, A3, and A4. Sample A1 was analyzed for the estimation of oil and organic matter contents, according to the ASTM standard procedures[11], immediately, without any treatment. A mixture of 12.5 mg hydrated aluminum Sulphate and 12.5 mg of activated silica was added in the sample A2. Similarly a mixture of 12.5 mg hydrated aluminum Sulphate and 12.5 mg of bentonite clay was added in the sample A3. Sample A4 was processed without addition of any chemical. Samples A2, A3, A4 were stored for the settlement of the aggregated particles for the period of 24 hours. After the expiry of this period, the supernatant fluid of all the samples was analyzed for oil and other organic matter contents, according to the ASTM standard procedure[11]. Similarly the samples which collected after three months and six months were processed and analyzed by the procedure mentioned above for the estimation of oil and other organic matter contents.

Estimation of suspended solid

Four portions of effluent, each of one liter volume, have taken from the samples collected the first day and marked them as A1, A2, A3, and A4, in four volumetric flasks. The suspended solid contents of the sample A1 was estimated immediately according to the ASTM standard procedure[12]. A mixture of 5 mg of hydrated aluminum Sulphate and 5 mg of activated silica was added in the sample A2, Similarly a mixture of 5 mg hydrated aluminum Sulphate and 5 mg of bentonite clay was added in the sample A3. The sample A4 processed without addition of any above mentioned chemicals. Samples A2, A3, A4 were stored for the period of 24 hours, for the sedimentation of aggregated particles. After the expiry of this period supernatant fluid of the stores samples were analyzed for the estimation of suspended particulate matters according to the ASTM stan-

TABLE 1 : Effect of coagulants on the concentration of oil and other organic matters in refinery effluent after 24 hours sedimentation

Sample no.	Concentration of oil and other organic matters in mg/l			Reduction in concentration of oil and other organic matters in wt%, in treated samples type	
	In fresh samples without treatment	In the samples containing 5 mg/l hydrated aluminum Sulphate & 5 mg/l activated sodium silicate (treated sample type A)	In the samples containing 5 mg/l hydrated aluminum Sulphate & 5 mg/l bentonite clay (treated sample type B)	(A)	(B)
1	3.9	0.4	0.4	89.7	89.7
2	4.1	0.5	0.5	87.8	87.8
3	3.9	0.4	0.4	89.7	89.7
4	4.0	0.4	0.4	90.0	90.0
5	4.0	0.4	0.4	90.0	90.0
6	4.0	0.4	0.4	90.0	90.0
Average reduction, wt% = (89.9) (89.9)					

TABLE 2 : Effect of coagulants on the concentration of suspended matters in refinery effluent after 24 hours sedimentation

Sample no.	Concentration of suspended matters in mg/l			Reduction in concentration of suspended matters in wt%, in treated samples type	
	In fresh samples without treatment	In the samples containing 5 mg/l hydrated aluminum Sulphate & 5 mg/l activated sodium silicate (treated sample type A)	In the samples containing 5 mg/l hydrated aluminum Sulphate & 5 mg/l bentonite clay (treated sample type B)	(A)	(B)
1	4,478.0	913.5	976.2	79.6	78.2
2	4,720.0	939.3	1,014.8	80.1	78.5
3	3,186.0	627.6	681.8	80.3	78.6
4	4,184.0	853.5	907.9	79.6	78.3
5	4,445.0	897.9	960.1	79.8	78.4
6	3,316.0	646.6	696.4	80.5	79.0
Average reduction, wt% = (79.98) (78.50)					

TABLE 3 : Effect of coagulants on the biochemical oxygen demand in refinery effluent after 24 hours sedimentation

Sample no.	Biochemical Oxygen Demand (5-days), in mg/l			Reduction in Biochemical Oxygen Demand (5-days), in wt%, in treated samples type	
	In fresh samples	In the samples containing 5 mg/l hydrated aluminum Sulphate & 5 mg/l activated sodium silicate (treated sample type A)	In the samples containing 5 mg/l hydrated aluminum Sulphate & 5 mg/l bentonite clay (treated sample type B)	(A)	(B)
1	79.3	23.7	24.5	70.1	69.1
2	83.4.	25.0	25.8	70.0	69.1
3	83.0	25.0	25.8	69.9	68.9
4	77.8	23.5	24.3	69.8	68.8
5	77.9	23.2	24.0	70.2	69.2
6	77.6	23.4	24.3	69.8	68.7
Average reduction, wt% = (69.70) (68.97)					

dard procedure[12]. Similarly the samples which collected after three months and six months were processed of suspended matters, according to the procedure mentioned above.

Estimation of biochemical oxygen demand

Dilution water

Ten liters of the highest quality distilled water was aerated at 20°C with clean compressed air. 10 ml of each of phosphate buffer, magnesium sulphate, calcium chloride and ferric chloride solutions (method of preparation are available in the literature[5], were added in the above prepared aerated distilled water with continuous stirring.

Seeding

100 ml domestic sewage was collected in a 150 ml capacity beaker and stored it over night at room temperature for the sedimentation of suspended particles. 20 ml of settled sewage was transferred from the beaker into above mentioned treated dilution water.

Preparation of samples

400 ml of seeded dilution water was transferred in each of the three one liter capacity marked cylinder A, B and C. 65 ml fresh refinery effluent from the samples collected the first day was transferred in each cylinder A, B and C. After careful mixing, the volume was made 650 ml by the addition of more dilution water. A mixture of 3.25 mg of hydrated aluminum Sulphate and 3.25 mg of activated sodium silicate was added with continuous stirring in the sample cylinder A and similarly a mixture of 3.25 mg of hydrated aluminum Sulphate and 3.25 mg of bentonite clay was added into sample cylinder B with continuous mixing and sample cylinder C was processed without addition of any chemical substance. A separate blank solution was prepared by mixing 13 ml settled sewage with sufficient dilution water to made total 650 ml and marked this solution as D. Each of the prepared solution A, B, C and D was equally distributed into two cleaned, dried and tight covered BOD bottles, marked A1, A2, B1, B2, C1, C2, D1 and D2. The sample bottles A2, B2, C2 and D2 were incubated at 20°C ± 1°C for 5 days. The dissolved oxygen was estimated immediately in the sample bottles A1, B1, C1 and D1accordind to the procedure given in literature[4]. Similarly after the incubation period, the dissolved oxygen was estimated in the sample bottles A2, B2, C2 and D2. BOD values were calculated by computation as mentioned in the procedure given in the literature[5]. The same steps were performed for the estimation of BOD in the effluent samples collected after three and six months.

RESULTS AND DISCUSSION

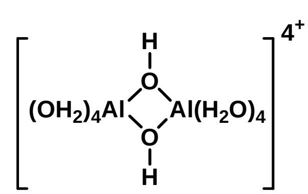
Aluminum Sulphate, calcium hydroxide, calcium oxide, ferric chloride and sodium aluminate have coagulating properties. Activated silica, bentonite clay and polyelectrolyte are classified as coagulation aids[14]. For obtaining better results, both coagulant and coagulation aid are used in combination.

In our work we have chosen hydrated aluminum Sulphate as coagulant and activated silica and bentonite clay as coagulation aids. From the experiments it has been found that hydrated aluminum Sulphate in combination with either activated silica or bentonite clay (in concentration 5 mg/l each) in the refinery effluent, reduced the concentration of oil and organic matter contents, suspended solid and biological oxygen demand up to 90 wt%, 80 wt%, 70 wt% respectively as shown in table (1, 2 and 3).

The coagulation mechanism of hydrated aluminum Sulphate as mentioned in the literature[13] is based on the equation written below:

$$Al(H_2O)_6^{3+} + 3HCO_3^- \longleftrightarrow Al(OH)_3 \text{ solid} + 3CO + 6H_2O$$

In the aqueous medium the aluminum ion (provided by aluminum Sulphate) hydrolyzed as shown in the above reaction, and by doing so, it consumes alkalinity of the medium and convert into insoluble $Al(OH)_3$. This gelatinous precipitate of aluminum hydroxide carries suspended substances (both of organic and inorganic origin), which are responsible for biochemical oxygen demand of the medium (effluent) and settled down under the influence of gravity. The other possible mechanism of coagulation as described in the literature[2], the hydrated aluminum ion dimerises or polymerises in the aqueous medium as shown below:



These dimmers and polymers carry some residual charge which attracts the opposite charged suspended particles present in the medium. The mechanism of action of coagulation aid is not known in detail. But from the available information in the literature[13], activated silica or bentonite clay improves the coagulation by toughening the flock through ionic or electronic bond formation and bridge the smaller coagulating particles into bigger particles which can easily settle down.

CONCLUSION

From this work it has been found that the hydrated aluminum Sulphate, in combination with either activated silica or bentonite clay is an efficient, economical and easy in handling, coagulating mixture, suitable for improving the quality of refinery effluent, industrial discharge and waste water. 5 mg/l was found to be a suitable concentration, in which both coagulant and coagulation aid, can be added in the effluent or in other polluted water for obtaining good results.

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