Effects of New Era Coagulants on Properties of Industrial Wastewater: An Overview

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Abstract - *Production of alcohol from starchy material is employed to certain extent in India. However, most of the alcohol is produced from molasses alone. Besides use for beverage, medicinal, pharmaceutical, alcohol is also used as ingredients for organic chemicals, which are used in producing a wide variety of intermediates, drugs, rubbers, pesticides, solvents, etc. This all leads to heavy production of spent wash, particularly from distilleries. This paper deals with the review of comparative study of performance of new era coagulants viz. poly aluminium chloride(PAC), aluminium chlorohydrate(ACH), magnesium chloride and poly-glu which can contribute to make primary treatment more competent.*
KEYWORDS: PAC, ACH, $MgCl_2$, Poly-Glu, pH, COD, turbidity, TSS.

Key Words: Chemical oxygen demand(COD), Total suspended solids(TSS), turbidity, pH, jar test, optimum dose.

1. INTRODUCTION

The speedy rate at which the population is increasing has led to rapid increase of industries to fulfill our demands and this has degraded our surroundings and environment in numerous ways leading to pollution of air, water and land. Industrial establishments deploy different types of chemicals and huge amount of water during different stages of processing and therefore they are the main sources of polluted water. Each stage of processing in those industries is responsible for contaminating the potable water as unused material is discharged as waste water and that waste water carries higher chemical oxygen demand, turbidity, higher biological oxygen demand. Due to addition of unwanted matter in water, the water of receiving water body becomes carcinogenic, mutagenic and aesthetically undesirable. The available literature displays numerous long established decolourisation methods involving chemical biological and physic-chemical process besides new techniques like advanced oxidation process. But as none of the methods are technically and economically feasible as individual methods so in general two or more than two methods have to be adopted in combination to achieve desired results. Moreover biological processes are inexpensive, ecofriendly and simple which can be used effectively to remove the biodegradable organic matter. However the colour removal efficiency will be less due to lesser biodegradable nature of colour dyes. In upcoming days the need of potable water will be increasing but the availability of non-polluted sources water is decreasing. So discharge limits of waste water are made stringent in order to reduce the pollution and contamination of drinking water sources. It is clear that more effective and efficient methods of waste water treatment are required. The flocculation and coagulation process which is very simple and inexpensive is widely used in water and waste water treatment. These methods are included in initial stage or final stage of treatment. The overall treatment performance is affected by the efficiency of coagulation and flocculation. Characteristics of effluent such as COD, total suspended solids, colour, pH helps to understand the efficiency of coagulant. Also the concentration of main pollutant after treatment helps to study the efficiency. This paper deals with an overall effectiveness of the different coagulants on various industrial and municipal effluents.

2. DECOLOURISATION OF TEXTILE WASTEWATER

2.1 General

Textile industries release wastewater in large quantity. This wastewater contains high amount of toxic chemicals along with mixture of different types of chemical dyes. The treatment of such wastewater is a very complex process. Moreover the data regarding the quantity and quality of generated sludge is very limited. Therefore *A. K. Verma et al* investigated the efficacy of magnesium chloride, poly aluminium chloride as well as aluminium chlorohydrate as coagulant. The desired pH was obtained using lime[1]. It also served the purpose of coagulant for decolourisation and COD reduction of synthetic textile wastewater containing various other chemicals. The main purpose of this study was evaluation of relative effect of pH and coagulant requirement on colour removal efficiency and quantity of sludge production for each combination of synthetic dyes.

2.2 Experimental procedure

The actual textile wastewater was studied and then synthetic textile wastewater was prepared with dye concentration of about 200 mg/l[1]. The dye concentration was prepared with a single dye or combining more than two dyes in equal ratio besides different chemical constituents used during textile processing such as sulphuric acid, sodium chloride, starch, acetic acid, sodium carbonate detergent. Reactive black 5 (RB5), Disperse blue (DB3), Congo Red (CR) were used in tap water to prepare the synthetic wastewater. Sigma-Aldrich, Germany provided dyes[1]. The optimum pH value and coagulant dosage required for efficient colour removal were determined from jar test. Experiment was performed using 1 L beakers, containing 500 ml of wastewater. pH was adjusted using lime or 1 M H_2SO_4 in each beaker. Chemical coagulants were added and mixed for 3 min under rapid mixing condition at 80 rpm. Slow flocculation was deployed for 15 min at 30 rpm. Supernatants were taken for analysis from the top of the beaker after 20 min of sedimentation.

2.3 Analysis and results

Supernatant was filtered out through Whatman No. 5 filter paper. After that its colour measurement was done. The pH of that liquid was brought to near 7. The absorbance of liquid was measured. After the digestion of samples in COD reactor (Model DRB 200, HACH, USA), COD was analysed as per closed reflux calorimeter method. The COD spectrophotometer (Model DR 2800 HACH USA) was used at 600 nm to measure the absorbance. The COD standard curve was plotted based on the values of the absorbance obtained. All the methods employed were as per standard procedures and performed at room temperature (25±5 ° C)[1]. The experiments were aimed at finding out the optimum pH for all the groups of synthetic textile wastewater that allowed for the maximum decolourisation and COD drop. The effect of pH on treatment efficiency was examined using the fixed amount of coagulant at different pH conditions. As stated earlier H_2SO_4 and lime were used to obtain the desired pH. As pH increased from 4.0 to 11.0 or 4.0 to 12.0, percentage colour removal increased when $FeSO_4.7H_2O$ and $MgCl_2.6\ H_2O$ were used as coagulant respectively. For 1gm/l dose of $MgCl_2.6H_2O$/lime in wastewater containing RB5, the efficiency of colour removal was observed to be above 99%. 96% colour removal efficiency was also found by using $FeSO_4.7H_2O$/Lime at a coagulant usage of 1200mg/l. Also, as ACH concentration was increased, the colour removal efficiency also increased. which still showed better efficiency as compared to PACl(Fig. 1a).

CR (c) DB3 (d) RB5+CR+DB3

COD reduction style was seen with increasing dose of coagulant as obtained in case of colour removal for all the combinations of synthetic textile wastewater employing $FeSO_4.7H_2O$/Lime, MgCl2.6H_2O/Lime, PACl and ACH (Fig. 2). A maximum of 62.02% COD reduction was seen at the optimum coagulant dosage of 1200 mg/L $MgCl_2.6H_2O$ /Lime for the wastewater containing all three dyes together (Fig. 2d). Highest COD reduction of 70.32% had been observed at the extreme PACl dosage of 1800 mg/L. Considerable COD reduction was also seen for remaining combinations of synthetic textile wastewater using $FeSO_4.7H_2O$/Lime and ACH as shown in Fig. 2

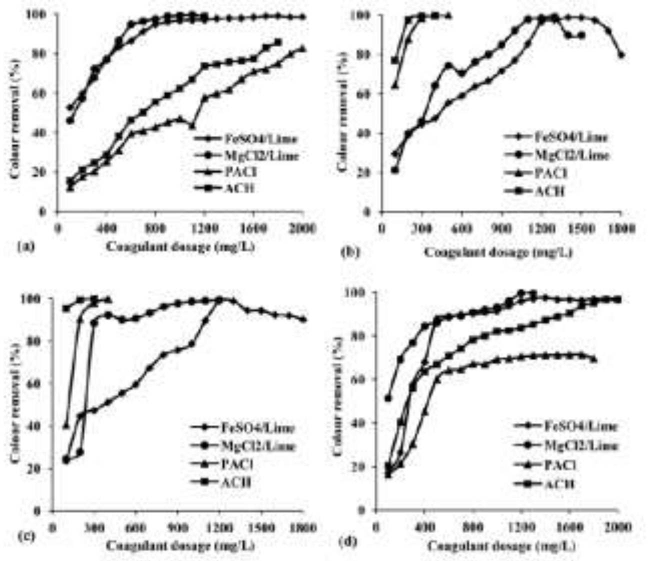

Fig. 1: Effect of coagulant dosage on the colour removal for synthetic textile wastewater containing (a) RB5 (b) CR (c) DB3 (d) RB5+CR+DB3

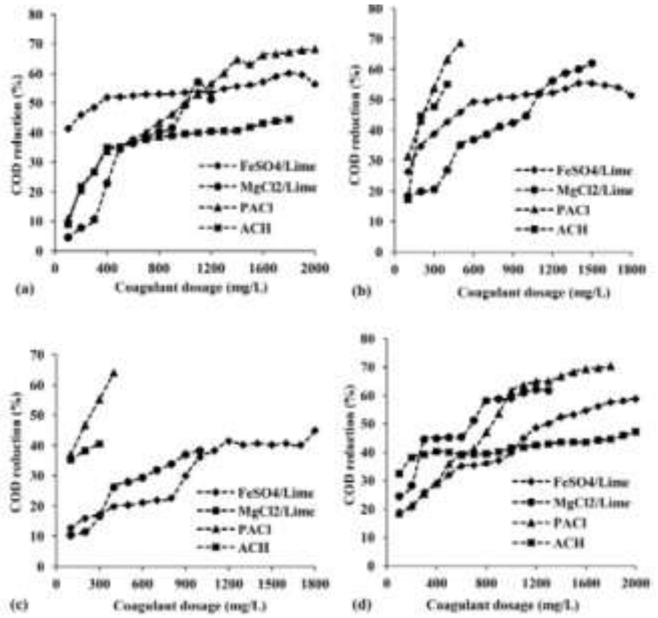

Fig. 2: Effect of coagulant dosage on the COD reduction for synthetic textile wastewater containing (a) RB5 (b) CR (c) DB3 (d) RB5+CR+DB3

3. DECOLOURISATION OF MOLASSES SPENT WASH BY COAGULATION

3.1 General

In India, there are about 300 distilleries generating about 2.75 billion litres of alcohol annually[2]. India is the fourth largest manufacturer of ethanol in the world and second largest in Asia. Indian distilleries utilize mostly sugarcane molasses as raw ingredient. 4-10 kg of molasses produces about one litre of alcohol. Distillery has been identified as one of the most polluting industries among 17 polluting industries by Ministry of Environment and Forests, Govt. of India. The anaerobically treated spent wash released by distillery does not meet Central Pollution Control Board's (CPCB) criteria for discharge into streams or land disposal. Ground water colourisation is problem for areas having disposal of spent wash on land. *Migo et al* studied colour removal of molasses based distillery effluent using a commercial inorganic flocculant[2]. For decolourisation of anaerobically digested spent wash, collective chemical and biological methods were also adopted. This paper deals with pretreatment studied by *M. S. Chauhan et al* in the form of cost effective option of coagulation of anaerobically digested molasses spent wash so that biological treatment can be adopted with dilution.

3.2 Experimental setup

Wastewater produced by 30KLD distillery producing rectified spirit using sugarcane molasses as raw material was used for study. Anaerobically digested molasses spent wash was procured from overflow of the anaerobic digester and was stored at 4°C. Closed reflux method was employed for measuring COD using HACH COD Digester (Model DRB 200, USA) as directed in standard methods(APHA-AWWA-WEF,2005)[2]. Distilled water was added for diluting samples

3.3 Colour measurement

Colour intensity was measured in terms of absorbance at 475 nm[2]. Samples were diluted in 1 M phosphate buffer to maintain neutral pH. Before absorbance determination, samples were centrifuged at 10,000 rpm for 10 min for removing hindrance due to suspended particles in the sample, the supernatant was diluted 100 times and the absorbance was measured using Thermo Spectronic visible spectrophotometer. Colour reduction was judged in terms of reduction in absorbance with reference to that of the original.

3.4 Coagulation studies

Commonly available coagulants viz. ferric chloride, ferric sulphate, ferrous sulphate, calcium chloride, calcium oxide, calcium hydroxide, potash were examined in this study for their efficiency of decolourisation and COD reduction. To replicate field conditions, all the coagulants used were of laboratory grade. On undiluted samples of anaerobically digested molasses spent wash, jar tests were carried out with coagulants. 1 litre samples were taken in six beakers, each of 1 litre volume and flash mixed at 100 rpm for 2 minutes followed by slow mixing at 20 rpm for 30 minutes. After leaving the solution undisturbed for 1-8 hours, the supernatant samples were further analysed. The optimum pH was found on the basis of reduction in absorbance in the pH range 2-12. Hydrochloric acid or lime was u0sed for pH correction[2]. By altering the dose of coagulant, the optimum dose was found at optimum pH.

3.5 Results and discussion

Results of pH and dose optimization for various coagulants and spectra of 100 times diluted ADMS and coagulant treated ADMS are given below. The optimum pH for ferrous sulphate was 11 and its dose of 26 gm/l offered 71 % and 36% colour and COD reduction respectively(Fig. 3).

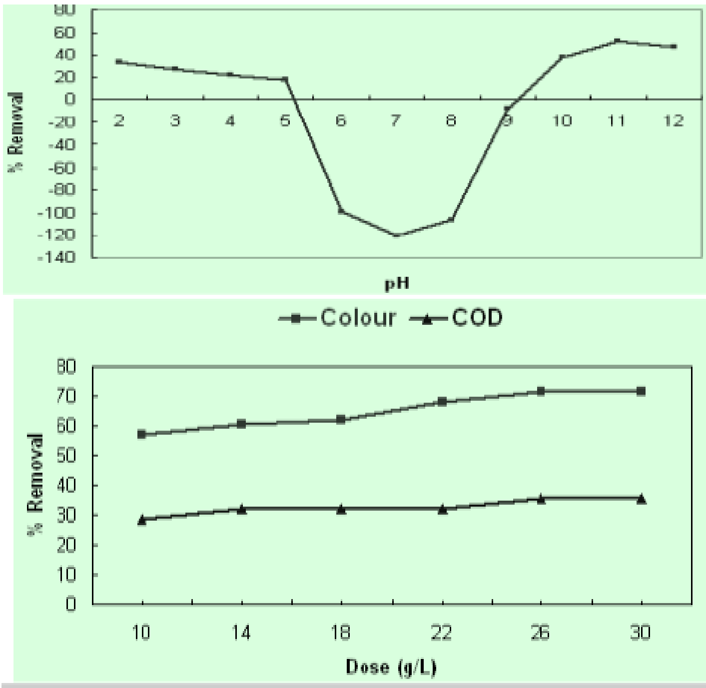

Fig. 3: Colour removal by coagulation with ferrous sulphate

Ferric chloride is active coagulant as this gives Fe^{3+} ions. Ferric chloride did well at pH of 4, giving 50 % and 39 % colour and COD removal respectively at 8 gm/l. Optimum pH for ferric sulphate which was also 4 and addition of 8 gm/l could gain 43 % reduction in colour with 28 % reduction in COD. However, both the ferric salts were found to impose greenish colour to the treated sample. Even at lesser doses, although absorbance at standard wavelength(475 nm) was reduced but overall colour of spent wash was poor than control. Results of pH and dose optimisation for various compounds are shown in Table 1[2].

Table 1: Results of pH and dose optimisation

Sr. No	Compound used	Optimum dose(in gm/l)	Optimum pH	Colour reduction(%)	COD reduction(%)	Remarks
1	Ferrous sulphate	26	11	71	36	Imparts greenish colour to treated sample
2	Ferric chloride	8	4	50	39	
3	Ferric sulphate	8	4	43	28	
4	Calcium chloride	14	10	46	32	
5	Calcium hydroxide	18	12	49	21	
6	Calcium oxide	18	6	48	28	

Based on above observations, alum and ferrous sulphates were selected for double coagulation study in permutation with lime. Later it was found that high coagulant dose, excess sludge formation and high retention time due to poor sludge settling were limitations of double coagulation. Therefore it was not recommended for pre-treatment option. Also coagulation with the help of ferric salts was discarded as they imparted greenish colour. Similarly poor settling characteristics were displayed by calcium salts. Also it was found that all options for coagulation are economically feasible with range varying between Rs. 0.05/l to Rs. 0.5/l.

4. TREATMENT OF PULP & PAPER MILL FFLUENT BY COAGULATION

4.1 General

The manufacturing of paper has numerous adverse effects on the environment. The paper production industry is one of the main industrial polluters of surroundings and precious natural resources. This industry consumes huge amount of water which then produces large quantity of wastewater. It takes up to 60 m^3 of freshwater for production of one ton of paper. The wastewater generated by paper production industry releases pollutants when this water is discharged into recipient water without any treatment. Most of the pollutants include heavy metals, suspended solids, colour compounds, organic and inorganic substances, cyanide, sulphides. Because of these pollutants various environmental problems occur which include increase in slime level, thermal impact and loss of aesthetic beauty of the environment. They are also responsible for increase in level of toxic substances in water which then cause death of plankton and fish. Therefore it becomes necessary to treat wastewater generated from paper and pulp industry before discharging it into water bodies. Also new technologies need to be developed and adopted so that the all stringent rules and regulations on the quality of wastewater released into the environment can be complied with. Numerous methods are present to carry out the treatment of effluent of this industry. They include catalyzed ozonation, solar photo-fenton process, advanced oxidation, adsorption, coagulation and flocculation. The main constituent of the wastewater generated by paper and pulp industry is fibre. This wastewater also contains high level of BOD, COD and pH. Coagulation/flocculation can be used to remove these pollutants besides toxicity and turbidity. This treatment will also help in reducing the cost incurred in secondary treatment as well as proper removal of toxic compounds and colour. Thus, the removal of chemical oxygen demand (COD) and colour of paper mill effluent is studied using coagulation process as discussed by P. *Kumar et al*. The batch coagulation process was performed using various coagulants like aluminium chloride, poly aluminium chloride and copper sulphate.

4.2 Experimental procedure

Black liquor was procured from a local combined craft pulp and paper mill. This liquor had a COD of about 7 x 10^5 mg/l. This black liquor was diluted with distilled water to obtain a synthetic sample having a COD value of about 7000 mg/l. The average characteristics of the synthetic wastewater are presented in Table 2.

Table 2: Characteristics of diluted black liquor

Parameter	Values
Chemical oxygen demand (COD) (mg l-l)	7000
Biochemical oxygen demand (BOD) (mg l-l)	1400
pH	10.45

Total solids (TS) (mg l-l)	7240
Total dissolved solids (TDS) (mg l-l)	6680
Total suspended solids (TSS) (mg l-l)	560
Conductivity (µmhos cm-l)	51760
Colour	Dark brown

4.3 Results & analysis

When aluminium chloride ($AlCl_3$), PAC and copper sulphate are dissolved in water, the metal ions hydrate and hydrolyse to form monomeric and polymeric species : $M(OH)^+$, MOH^{2+}, $M_2(OH)_2^{4+}$, $M(OH)_4^{5+}$, $M(OH)_2^0(s)$ and $M(OH)_4^-$ etc. At low pH (pH < 7), both Al^{3+} and Cu remain in the solution and form precipitates of CuOH or $Al(OH)_3$ as the pH is increased or as the coagulant dosage is increased[4]. Fig. 4 shows the effect of pH on the COD reduction and colour removal of the wastewater having an initial COD value of 7000 mg/l at ambient temperature (25 °C) using different coagulants. The coagulant mass loading was kept consistent as 5 gm/l for $AlCl_3$ and $CuSO_4.5H_2O$ and 5 ml/l for PAC. The readings were noted at different initial pH (pH_0) values i.e. at 2.0, 4.0, 5.0, 6.0, 7.0 and 8.0. The COD of supernatant was then measured. For aluminium chloride, the COD reduction was found significant at $pH_0 \leq 5$ and maximum at the pH of 4.0 resulting in a COD reduction of 74 %. At $pH_0 > 5$, the COD reduction is found to reduce. For the coagulation by PAC, the maximum COD reduction (70 %) is reported at $pH_0 = 5$. After increasing or decreasing initial pH from 5, the COD reduction was found to decrease in both the cases. Similar COD reduction phenomena was noted for coagulation of biodigester effluent of an alcohol distillery plant using $AlCl_3$ and PAC. For 5 gm/l of $CuSO_4$ the COD reduction was increased from pH_0 1.5 to 6.0, then decreased as pH_0 was increased from 6 to 8. The maximum 80 % COD reduction was achieved using this coagulant at pH_0 6. $CuSO_4.5H_2O$ gave better results (80%

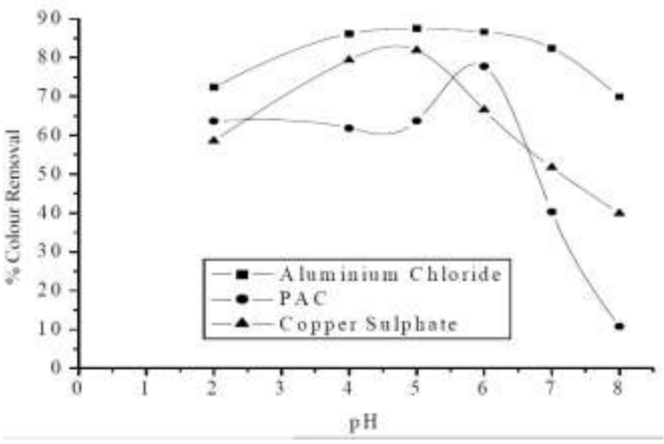

Fig. 4: Effect of pH on %COD removal for different coagulants($CuSO_4.5H_2O$ = 5 gm/1, $AlCl_3$ = 5 gm/1, PAC = 5 ml/1)

COD reduction). The colour reduction was also studied, it was found to be in order of COD reduction for all the coagulant. The decolourization is expressed as the percent decrease in the absorbance of the biodigester effluent sample from the untreated sample at absorbance = 263 nm. The optimum colour reduction is found to be 86 %, 78 % and 82 % for $AlCl_3$, $CuSO_4.5H_2O$ and PAC treated effluent at their optimum pH_0 : $pH_0 = 4$ for $AlCl_3$, $pH_0 = 5$ for PAC and $pH_0 = 6$ for $CuSO_4.5H_2O$. It may be concluded that the COD and colour reduction of pulp and paper effluent is a strongly dependent on the pH_0 value. For different coagulants, the effect of mass loading on the COD reduction of the synthetic wastewater (COD_0 = 7000 mg/l) was studied at ambient temperature of 25 °C at their optimum pH_0 (Fig. 5). The coagulant mass loading was varied from 1 to 9 gm/l for $AlCl_3$ and $CuSO_4.5H_2O$ and 1 to 9 ml/l for PAC. From the figure, it is observed that as PAC coagulant dose is increased, the COD reduction is increased till 8 ml/l coagulant dose, after which, the COD reduction is almost unchanged. Thus, the 8 ml/l of PAC dose is optimum, resulting in 84 % COD reduction. For $CuSO_4.5H_2O$ coagulant, the COD reduction has been found to increase till 5 gm/l dose, giving maximum COD reduction of 76 %. After increase in coagulant loading, the COD reduction decreases, indicating, 5 gm/l as optimum dose to $CuSO_4.5H_2O$. For $AlCl_3$ coagulant, the COD reduction has increased considerably till its loading of 5 gm/l, giving 74 % COD reduction, After an increase in its loading, the COD reduction increased marginally till 7 gm/l and beyond which, the COD reduction has decreased. The colour reduction at optimum pH of coagulation for different coagulants is presented in Fig 6. For optimum mass loading of $CuSO_4.5H_2O$ (5 gm/l), $AlCl_3$ (5 gm/l) and PAC (8 ml/l) at optimum pH_0, the colour reductions are found to be 75 %, 88 % and 92 %, respectively.

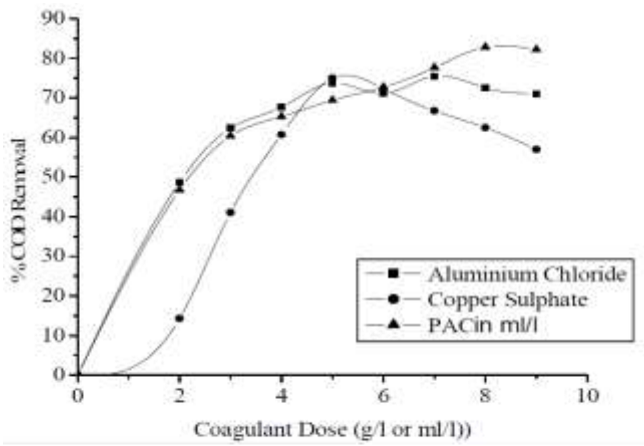

Fig. 5: Effect of coagulant dose on % COD removal at their corresponding optimum pH_0 ($pH_0 = 6$ for $CuSO_4.5H_2O$, $pH_0 = 4$ for $AlCl_3$, $pH_0 = 5$ for PAC)

Fig. 7 shows the variation of pH after addition of different dose of coagulants.

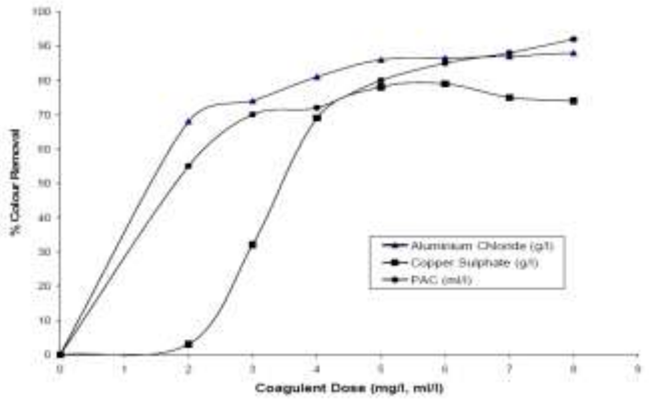

Fig. 6: Effect of coagulant dose on colour removal at their corresponding optimum Ph

(pH_0=6 for $CuSO_4.5H_2O$, pH_0= 4 for $AlCl_3$, pH_0=5 for PAC)

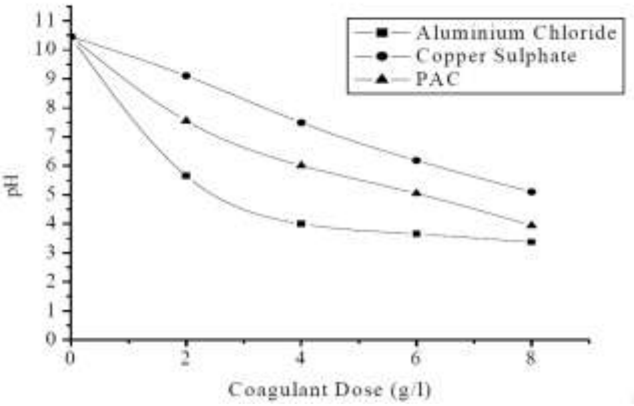

Fig. 7: Effect of coagulant dosing on pH of effluent

The effect of different coagulants, such as PAC, aluminium chloride and copper sulphate on the COD and colour reduction are presented in Fig. 10.

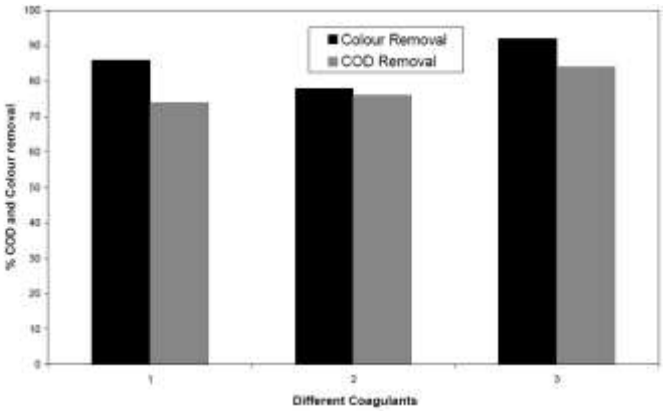

Fig. 8: Comparison of different coagulant for maximum COD and colour removal at corresponding to optimum pH and optimum dose.
1. Copper sulphate 2. Aluminium chloride 3. PAC

From the figure, it may be seen that at their optimum dose, 8 ml/l for PAC and 5 gm/l for $CuSO_4.5H_2O$ and $AlCl_3$, the COD reduction is maximum (84 %) for PAC which is followed by $CuSO_4.5H_2O$ (76 %) and $AlCl_3$ (74 %). The corresponding colour reductions were 92% for PAC, followed by 86 % for $AlCl_3$, and 78 % for $CuSO_4.5H_2O$. The colour reduction increases up to a breakpoint after which it starts reducing due to increase in the coagulant concentration to 86.30% colour removal at 5 gm/l dose in present work. Copper sulphate is used by *Garg et al*[4] for thermal precipitation of pulp and paper mill effluent[4], who have observed 61.4% COD removal. The better result (74% COD removal) in present work (using $CuSO_4$ coagulant) may be due to different process used by *Garg et al*[4]. They have performed thermal precipitation reaction at 95 °C. In the present work, the coagulation is performed at room temperature 25 °C. Poly aluminium chloride offered better result as 82.85% COD removal and 91.81% colour removal.

5. Poly Glu- A new coagulant

Chairman and CEO of Nippon Poly-Glu Co. Ltd. Kanetoshi Oda came up with a new coagulant Poly-Glu(Poly glutamic acid). Poly glutamic acid removes pollutants from water in the form of precipitation, leaving behind clean water. In fact, clarifying agents made from poly glutamic acid are capable of cleaning dirty water faster than agents made from chemicals like poly aluminum chloride or ferric chloride and they offer a number of other advantages. Unlike other chemical products to clean water, the only one clarifying agent containing poly glutamic acid is necessary, which makes it very convenient to use. In addition, poly glutamic acid clarifying agents are made from natural materials like soybean, hence are eco-friendly and affordable. Now a days to clean the dirty water that drains into the surrounding from factories, houses and apartments the poly glutamic clarifying agents are used. They are also used in overseas initiatives realized with the assistance of the Japanese government, such as a project to clean drinking water in Bangladesh[5].

6. SUMMARY

The referred research papers show positive efforts for development of coagulation and flocculation process. ACH and PAC were found to be suitable coagulants for treating textile wastewater. Each coagulant works well within a certain pH range and dose range. Every wastewater too has its own coagulating efficiency. Hence it is essential to work on mechanism of floc formation of these new generation coagulants. However, results may change with different industrial wastewater. They provide with more efficiency as compared with traditional coagulants like alum. They also result in lesser floc formation. Moreover, newly introduced coagulants like poly glutamic acid are most eco-friendly and have non-toxic effects on water being treated. More research on these new generation coagulants will surely make the primary treatment process more efficient.

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