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Effect of New Generation Coagulants on Properties of Industrial and Municipal Waste Water: An Overview

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Abstract: **-- Normally, industries and municipalities discharge the wastewater into open land or in water bodies without ample treatment due to which the ecosystem gets disturbed. For the treatment of wastewater, chemical coagulation is intended primarily to remove color, turbidity and chemical oxygen demand (COD) of the wastewater. For increasing the efficiency of primary treatment of industrial and municipal wastewater, better and more effective coagulants are necessary. This paper includes review of comparative studies of various coagulants such as Aluminum Chloro-Hydrate (ACH), Magnesium chloride (MgCl2), Poly-Glu, Poly-Aluminium Chloride (PACl) on laboratory scale, which can prove to be effective in enhancing the coagulation thus rendering primary treatment process of wastewaters more effective.**

***Index Terms*:- Aluminum Chlorohydrate, Coagulation, Magnesium Chloride, Poly-Glu.**

I. INTRODUCTION

The rapid increase in population due to which the increasing establishment of industries to meet the global demand degraded our environment in various ways, leading to pollution of land, air, and water. Industries use the huge volume of water and varieties of complex chemicals during the different steps of processing, and therefore industries are considered major polluter of potable water. The unused materials from each processing step of industries are discharged as wastewater which possesses various types of hazardous chemical and organic matter, which carry high biochemical oxygen demand (BOD), chemical oxygen demand (COD), turbidity, color in it. Due to the presence of various unwanted matter in water, the receiving water bodies not only become aesthetically unacceptable but also the discharge of these effluents can be carcinogenic, mutagenic and generally detrimental to our environment.

The available literature shows a large number of well-established conventional decolorization methods involving physico-chemical, chemical and biological processes, as well as some of new emerging techniques like sono-chemical or advanced oxidation processes. However, there is no single economically and technically viable method to solve this problem and usually two or three methods have to be combined in order to achieve an adequate level of color removal [1]. Additionally, biological processes are generally cheap, simple and environment-friendly, which can be used effectively to remove the biodegradable organics but to a very lesser extent for removal of color due to less biodegradable nature of the textile dyes. Almost all advanced oxidation processes are associated with high cost of operation and may produce toxic by-products. Nowadays, the need for high-quality drinking water is increasing, but the non-polluted water sources are continuously decreasing. Additionally, the discharge criteria of wastewater are becoming stricter, according to the new legislation, in order to prevent environmental pollution and infection of drinking water sources. It is clear that more effective water and wastewater treatments are needed. The coagulation/ flocculation process is a very important step in water and in wastewater treatment which is widely used, due to its simplicity and cost-effectiveness. Regardless of the nature of the treated sample (e.g. various types of water or wastewater) and the overall applied treatment scheme, coagulation/flocculation is usually included, either as pre-treatment or as post-treatment step. The efficiency of coagulation/ flocculation strongly affects the overall treatment performance and hence, the increase of the efficiency of coagulation stage seems to be a key

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factor for the improvement of the overall treatment efficiency. The efficiency of coagulant is normally understood by comparing effluents' characteristics before and after application of coagulants. These characteristics include COD, TSS (Total Suspended Solids), color, pH, etc. Also, effectivity is studied by determining the concentration of the target pollutant in the wastewater after the treatment with the coagulant. This paper is intended to present an overview of the effectiveness of the different coagulants on various industrial and municipal effluents.

II. DECOLORISATION OF TEXTILE WASTEWATER

A. General

The treatment of textile wastewater containing various toxic chemicals that are released from textile industries along with the mixture of different classes of dyes is complex. Also, very limited data are available to assess the quantity and nature of sludge production [1]. Therefore, Verma A. K. et al investigated the effectiveness of Ferrous Sulfate (FeSO4.7H2O), Magnesium chloride (MgCl2.6H2O), Poly-Aluminium chloride (PACl) as well as Aluminium chloro-hydrate (ACH) as coagulants. Lime was used for the adjustment of desire pH as the coagulant aid for the decolourization and COD reduction of synthetic textile wastewater containing different classes of new generation dyes along with the various other chemicals. The study was focused on evaluating comparative effect of pH and coagulant dosage on color removal efficiency and amount of sludge production for each of the combinations of synthetic dyes.

B. Experimental Procedure

Synthetic textile wastewater was prepared as per the reported chemical constituents of real textile wastewater [1], with a total dye concentration of 200 mg/L. The total dye concentration was prepared either with a single dye or mixing three different dyes in equal ratio along with the various chemical additives used during textile processing for various purposes such as starch, acetic acid, sucrose, sodium carbonate, sodium hydroxide, sulphuric acid, detergent, and sodium chloride. The synthetic wastewater was prepared by using Reactive Black 5 (RB5), Congo Red (CR) and Disperse Blue 3 (DB3) in the tap water. Dyes were procured from Sigma-Aldrich, Germany [1].

Using jar test procedure, the optimum pH value and coagulant dosage required for efficient color removal were determined. For the coagulation experiments 1 L beakers, containing 500 mL of wastewater were used. For pH adjustment, Lime or 1.0 M H2SO4 was added to each beaker. Chemical coagulant was added and mixed for 3 min under rapid mixing condition at 80 rpm. The solution was mixed at slow flocculation for 15 min at 30 rpm. After sedimentation for 20 min, supernatants from the top of the beaker were taken for the analysis.

C. Analysis and Results

Colour measurement was carried out after filtration of supernatant through Whatman No. 5 filter paper. Then, the pH of the liquid was adjusted to about neutral. The absorbance of liquid was measured. COD was analyzed as per closed reflux calorimetric method after digestion of the samples in COD reactor (Model DRB 200, HACH, USA) and then absorbance measurement was carried out by COD spectrophotometer at 600 nm (Model DR 2800, HACH, USA) [1]. The COD standard curve was developed based on the absorbance. All the methods used for the analysis of wastewater characteristics were as per Standard Methods [1] and performed at room temperature (25±5°C).

The experiments were designed for finding the optimum pH for all the combinations of synthetic textile wastewater that allowed for maximum decolorization and COD reduction. The effect of pH on the treatment efficiency was examined using the fixed amount of coagulant at various pH conditions (4, 6, 8, 9, 10, 11, and 12) for all the coagulants. Lime and H2SO4 were used for the adjustment of the desired pH.

Percentage color removal increases with the increase in pH from 4.0 to 11.0 or 4.0 to 12.0 when FeSO4.7H2O and MgCl2.6H2O, respectively was used as coagulants. For 1000 mg/L doses of MgCl2.6H2O /Lime the wastewater containing RB5 the color removal efficiency was found above 99%. FeSO4.7H2O /Lime was also found to be effective which gave more than 96% color removal efficiency at a coagulant dosage of 1200 mg/L. However, the considerable decrease in color removal efficiency was observed at an even higher dosage of ACH, which still showed better efficiency as compared to PACl (Fig. 1a).

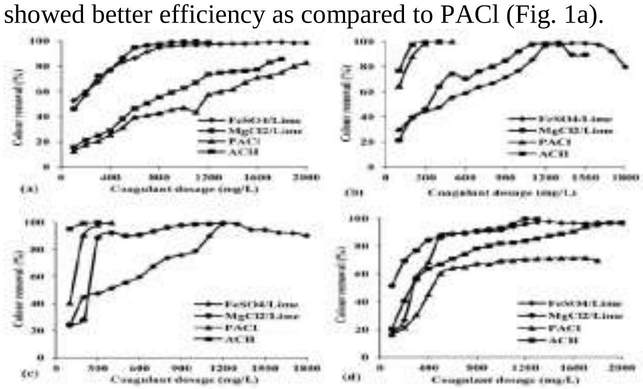

Fig. 1. Effect of coagulant dosage on the color removal

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for synthetic textile wastewater containing (a) RB5 (b) CR (c) DB3 (d) RB5+CR+DB3

Similar trends of COD reduction were observed with increasing coagulant dosage as obtained in case of color removal for all the combinations of synthetic textile wastewater using $FeSO_4.7H_2O$/Lime, $MgCl_2.6H_2O$/Lime, PACl and ACH (Fig. 2). A maximum of 62.02% COD reduction was observed 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. Significant COD reduction was also obtained for remaining combinations of synthetic textile wastewater using $FeSO_4.7H_2O$/Lime and ACH as shown in Fig. 2.

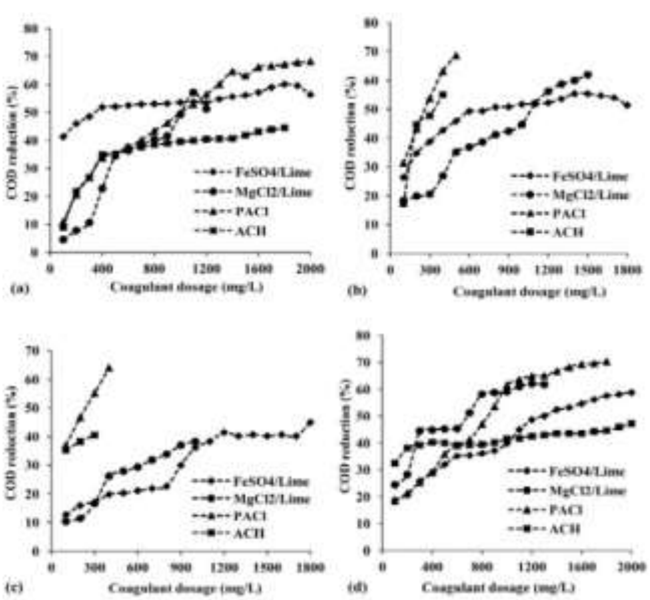

Fig. 2. Effect of coagulant dosage on the COD reduction for synthetic textile wastewater containing (a) RB5 (b) CR (c) DB3 (d) RB5+CR+DB3

III. DECOLORIZATION OF SILK DYEBATH EFFLUENT

General

The number of studies has been carried out for the treatment of synthetic dye wastewater using magnesium and aluminum-based hydrated and pre-hydrolyzed coagulants. In addition to these metallic coagulants, the effectiveness of natural coagulant such as guar gum (GG) for the treatment of dye solutions has also been investigated in the recent years [2]. However, very limited studies have been carried on the effectiveness of these coagulants for the treatment of real dyebath effluents.

B. Experimental Procedure

For the conducting experiments, analytical-grade MCl [$MgCl_2·6H_2O$, purity 99.99% w/w], industrial-grade PACl [$Al_2(OH)_3Cl_3$, purity 30% w/w] and industrial-grade ACH [$Al_2(OH)_5Cl$, purity 30% w/w] as coagulants were used. Although both PACl and ACH are pre-hydrated aluminum salts belonging to the class of polyaluminium coagulants, in practice, ACH is more hydrated and has a higher alumina content than PACl [2]. Analytical-grade GG was used as a coagulant aid, and 1.0M H_2SO_4 and NaOH were used to adjust the desired pH. From a local textile hand mill, the real silk dyebath effluents are obtained.

By performing a jar test the optimum pH value and coagulant dosage required for efficient color removal is determined. 500 mL of wastewater were used in one-liter beakers for the coagulation experiments. For the adjustment of pH H_2SO_4 (1.0 M) was added to each beaker. Chemical coagulant was added and mixed for 3 min under rapid stirring at 80 rpm. The solution was then mixed at slow flocculation for 15 min at 30 rpm. After sedimentation for 30 min, supernatants from the top of the beaker were removed for the analysis. All runs were performed in duplicate, and the results are presented as the averages of two values each [2]. The filtration of the supernatant is carried out by Whatman No. 5 filter paper for the determination of color measurement. The pH of the filtrate was adjusted to about neutral before the absorbance was measured. COD was analysed according to the closed reflux colorimetric method after digestion of the samples in a COD reactor (model DRB 200, Hach Company, Loveland, CO), and then absorbance measurements were carried out on a COD spectrophotometer at 600 nm (model DR 2800, Hach Company, Loveland, CO) [2]. The percentage color removal efficiency is determined.

C. Analysis and Result

The effect of pH on the treatment efficiency was examined at a constant coagulant dose and varying pH (4, 6, 8, 10, 11, 12, and 12.5) for all coagulants. No significant increasing or decreasing trends in treatment efficiency were observed during variation of the pH when PACl (100 mg L^{-1}) or ACH (50 mg L^{-1}) was used as the coagulant. However, a continuous increase in the treatment efficiency was observed as the pH was increased from 4.0 to 12.0 when MCl (800 mg L^{-1}) was used as the coagulant (Fig. 3). Beyond pH 12, slight decreases in the decolorization and COD reduction were observed. The optimum pH for MCl was observed to be as high as 12.0 in the alkaline

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region, whereas for PACl and ACH, the optimum values were 6 and 4, respectively (Figure
3 a,b). The results of this study are in good agreement with the findings reported by Gao et. al [5].
The low optimum pH conditions for PACl and ACH can be attributed to these mechanisms. Therefore, it can be said that the principal removal mechanism for ACH is adsorption and charge neutralization, whereas, for PACl, it is sweep flocculation [2]. Although almost the same high decolorization efficiencies were observed for ACH at pH values of 4 and 10 (Fig. 3a), the flocs formed at pH 10 was appeared to be light and fragile and did not settle by gravity for a substantial period of time of more than 2 h. However, the sludge thus formed could be removed very easily by filtration using filter paper. The sludge formed at pH 4 was bulky and dense and settled very easily by gravity within a 30-min settling time. Therefore, pH 4 was considered to be the optimum pH for ACH.

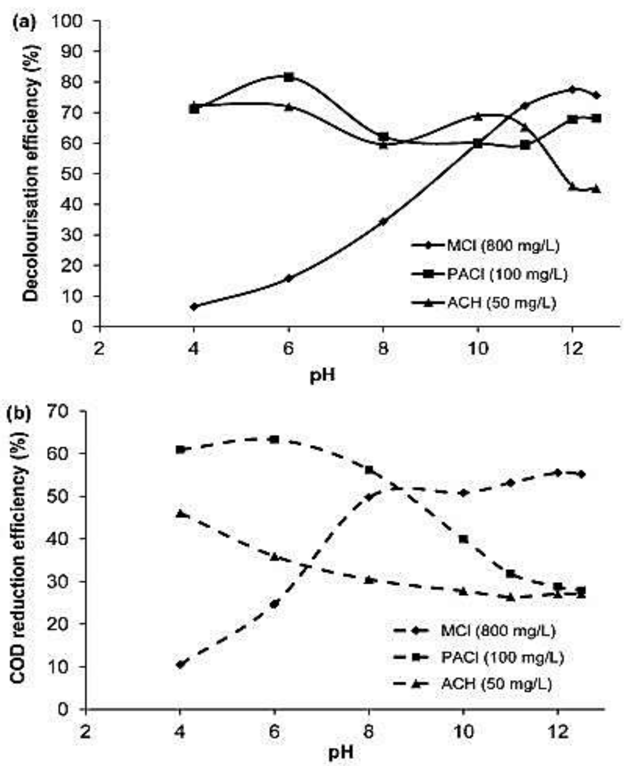

Fig. 3 Effect of pH on treatment efficiency of different coagulants for real silk dyebath effluents: (a) decolorization efficiency, (b) COD reduction efficiency.

The optimum coagulant dosage for the treatment of dyebath effluents was determined by varying the coagulant dosage and maintaining a constant optimum pH. Treatment efficiency results for various coagulants in terms of color, COD, and turbidity reduction as functions of coagulant dosage are shown in Fig. 4.
By using MCl as a coagulant, it was observed that the percentage color, COD, and turbidity reductions increased with increasing coagulant dosage. Color, COD, and turbidity reductions of 97.42%, 61.47%, and 98.34%, respectively, were obtained at a very high dosage of 1800 mg L−1 MCl. Excellent color removal of close to 97% was also obtained at a slightly lower dosage of 1600 mg L−1 MCl (Fig. 4a).

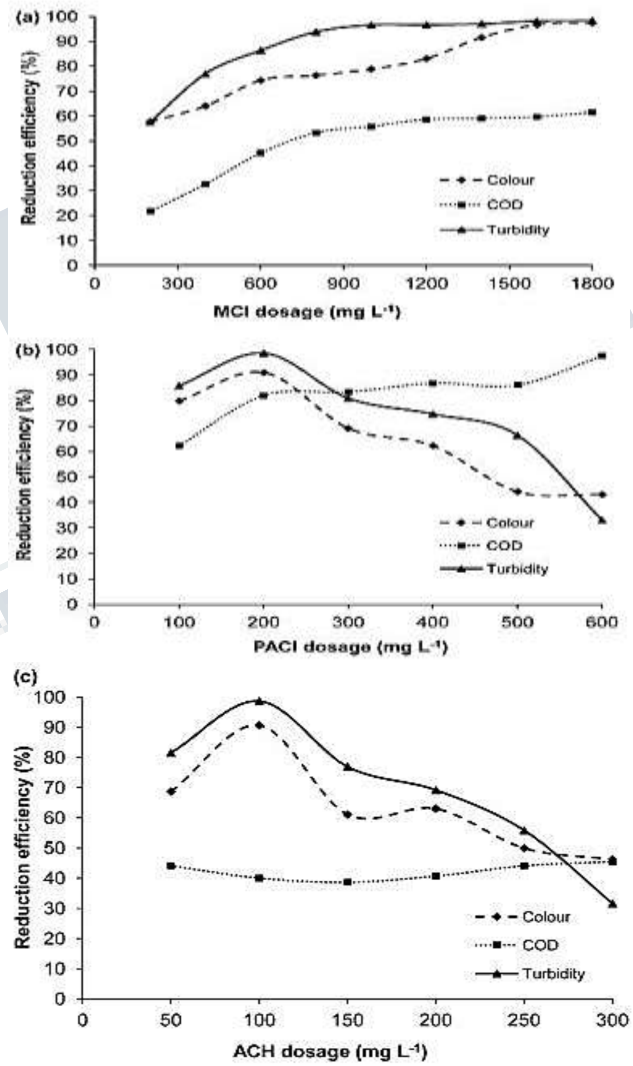

Fig. 4 Effect of coagulant dosage on the treatment efficiency of dyebath effluents with (a) MCl, (b) PACl, (c) ACH.

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The 200 (mg L−1) of PACl dosage gives 91% color removal. Excellent COD and turbidity reductions of approximately 82% and 99%, respectively, were obtained at the same dosage of PACl. At 600 mg L−1, PACl produced a maximum 97.45% COD reduction; however, at this dosage, the decolorization efficiency decreased considerably. A decrease in the color removal efficiency was observed above the optimum dosage of the coagulant (Fig. 4b).

A similar trend as in the case of the PACl was observed for ACH as well. However, the ACH dosage was found to be almost 50% less than that of the PACl (Fig. 4c). A color removal efficiency of maximum 91% was obtained at only 100 mg L−1 ACH. Also, an excellent turbidity reduction of 99% and a significant COD reduction of 40% were observed at the same dosage of coagulant. The result of an analysis shows aluminum salts such as ACH and PACl were found to be very effective in the decolorization of dyebath effluents at a very low coagulant dosage. Although the decolorization efficiency was observed to be greater for MCl, considering both the dosage and the decolorization efficiency, ACH was found to be superior to both MCl and PACl.

IV. COLOR REMOVAL OF REACTIVE DYE

A. General

Textile, paper, dyeing mills and tannery industries use many kinds of artificial composite dyes and discharge large amounts of highly colored wastewater, due to this the self-purification of the stream get disturbed. Therefore, this wastewater must be treated before discharge in stream or water body with the acceptable limit of disposal parameter given by environmental protection laws for the receiving water. For wastewater treatment coagulation and flocculation methods are widely used, as these methods are efficient and simple to operate. Therefore, the aim of Mohamed R. M. S. R. et al research was to determine the effectiveness of the coagulation-flocculation method for the removal of color from textile wastewater using three different types of coagulants.

B. Experimental Procedure

From an equalization tank of textile treatment plant of a dye mill in Batu Pahat, Johor, Malaysia the textile wastewater samples were collected, which contains Remazol Black B (RBB), Remazol Brilliant Blue R (RBBR), and Remazol Brilliant Red F3B (RBRF3B) [3].

Aluminium sulfate (Alum), polyaluminum chloride (PAC) and magnesium chloride (MgCl2) were used as the coagulants, whereas polyelectrolyte, Koaret PA 3230 of commercial grade, was used as the coagulant aid. Sodium hydroxide (NaOH, reagent grade) was used as the pH adjusting agent in the coagulation-flocculation process. Distilled water was used to prepare all the dye solutions, coagulants and coagulant aid solutions.

In the first part of experiment the treatment of 150 mL reactive dye with 3,000 mg/L to 7,000 mg/L of alum, 1,000 mg/L to 5,000 mg/L of MgCl2, and 500mg/L to 4,000mg/L of PAC respectively. Jar test was conducted to determine the effects of solution pH, types of coagulant, coagulant dosage and coagulant aid dosage on color removal.

A six-paddle stirrer with six beakers is used for conducting jar test; each beaker containing 150 mL of the prepared dye solution. For adjustment of desire pH NaOH was added, after mixing for a period of 1 min at 60-65 rpm the initial pH of the solution measured. The coagulant was added to the beakers and the samples were mixed for 3 min at 60-65 rpm and followed by the addition of polyelectrolyte as the coagulant aid. Respective settling time was recorded when the formed flocs get settle and the solution height reached half the beaker. After measuring final pH of the dye solution, the supernatant was taken for analysis.

The color removal is measured by using UV visible spectrophotometer. The dye concentrations were determined by color point (pt./Co) measurement using spectrophotometer (HACH DR 2000) [3].

C. Analysis and Result

The color removal efficiency of various coagulation-flocculation treatments on various reactive dyes solution was studied. The analysis carried out, in which the amount of coagulant and coagulant aid dosages was varied and applied to each 150-mL reactive dye solution. From 25% to 62% the percentage removal of dye increased tremendously when the concentration of MgCl2 increased from 1,000 mg/L to 2,000 mg/L. When 3,000 mg/L of MgCl2 was used the maximum dye removal efficiency is obtained which was 97%. According to Fig. 5, if the dosage of alum is increased from 1,000 to 6,000 mg/L simultaneously the color removal also increases, achieving a maximum of 78.5% removal. However, further increase in dosage to 7,000 mg/L the percentage of color removal decrease. This may be due to the restabilization of dye particles by excess alum hydrolysis species [5].

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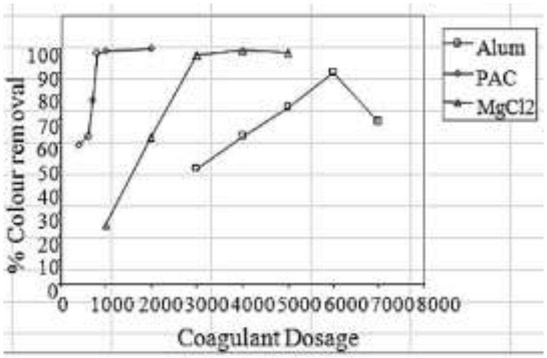

Fig. 5 Colour removal of different dosages of coagulants

Further increase in the MgCl2 dosage could only slightly increase the percentage removal of dye. From the graph, it can be seen that MgCl2 and PAC achieved higher color removal at low dosage. However, with increasing coagulant dosage the difference in color removal efficiency became small. Among the coagulants used, PAC was the most effective coagulant in treating each dye which efficiently removes color up to 100% at the dosage of 800 mg/L. From the analysis, PAC was more effective than MgCl2 and alum, as >99% color removal was attained using the smaller quantity of the coagulant.

V. COAGULATION BY POLY GLU

Kanetoshi Oda, chairman, and CEO of Nippon Poly-Glu Co., Ltd. He invented new coagulant Poly-Glu (Polyglutamic acid). Polyglutamic acid removes pollutants from water in the form of precipitation, leaving the water clean. In fact, clarifying agents made from polyglutamic acid is capable of cleaning dirty water faster than agents made from chemicals like polyaluminum chloride or ferric chloride, and they offer a number of other advantages [6]. Unlike other chemical products, to clean water the only one clarifying agent containing polyglutamic acid is necessary, which make it very convenient to use. In addition, polyglutamic acid clarifying agents are made from natural materials and are environmentally friendly and affordable. Nowadays, to clean the dirty water that drains into the environment from factories, houses, and apartments the polyglutamic 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 [6]. In addition to Bangladesh, including Thailand and Mexico, these clarifying agents are exported to more than 30 countries around the world. They have also been used to clean water for people living in disaster-stricken areas, such as after the recent Great East Japan Earthquake [6]. Actually, polyglutamic acid is coming into use in an increasingly wider range of undertakings. Another recent discovery related to polyglutamic acid is its incredible capacity for absorption, which is bound to be the subject of much more attention in the future [6].

Summary

The referred research papers provide good vision for enhancement of coagulation and flocculation process. Every wastewater sample has an optimum pollutant concentration value which can be reduced using primary treatment process, means coagulation/flocculation due to which the load on tertiary treatment reduces. The result of these new generation coagulants is definitely superior than the normal conventional coagulants. The treatment efficiencies of the coagulants depend significantly on the pH of the wastewater. Aluminium salts such as ACH and PACl were found to be very effective in the decolorization of dyebath effluents at a very low coagulant dosage. Decolourisation of synthetic as well as real textile wastewater has been successfully carried out by using PAC, ACH, MgCl2, which increase the effectivity of primary treatment process. There is no study carried on the application of Poly-Glu on the treatment of textile, dairy or municipal waste water. If the coagulant is applied to different industrial wastewater like dairy, soap or municipal the results may vary.

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