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Assessment of Coagulant Synergy for the Depollution of Binder Emulsion Plant Effluent

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Abstract
Binder emulsion plant effluent is a source of intense pollution when discharged into the environment without proper degree of treatment due to its strong color as well as higher total suspended solids (TSS) and chemical oxygen demand (COD) contents. An empirical study was conducted to optimize the effect of the coagulants used for the removal of Color, Turbidity, TSS, and COD from binder emulsion effluent. The coagulants, used with and without the induction of Powdered Activated Carbon (PAC) to enhance the decrease in pollution concentration, included Ferrous Sulfate, Ferric Chloride, Alum and Lime. Ferric Chloride used in combination with PAC produced a synergistic effect in terms of effluent depollution and transpired into efficient removal of effluent COD (83%), Color (98%), Turbidity (97%) and TSS (96%). Induction of PAC with all the coagulants combined proved highly effective as well in decreasing the effluent COD, color, Turbidity and TSS by 91%, 99%, 99% and 97% respectively. In a combined process of coagulation and adsorption, combination of ferric chloride and PAC gave effective results in terms of pollutants removal by around 90% as compared to combination of PAC with other coagulants, yielding removal percentages of lower than 50%.

***Keywords*:** Binder Emulsion; Effluent treatment; Coagulation; Powdered Activated Carbon; Adsorption.

Introduction

Binder Emulsion plant effluent, generated in the range of around 800 m^3/day, is the result of cleaning of plant equipment, packing machines and plant floors as well as operation of various units like mixers, reactors, blenders, etc [1]. The effluent is composed of free and emulsified oils, surfactants and co-surfactants, emulsifying agents, antifoaming agents, bactericides, rust inhibitors and solvents [2]. The concentration of effluent parameters such as chemical oxygen demand (COD), total suspended solids (TSS), turbidity and color is normally in higher range due to varying degree of chemicals present in the effluent streams [3-4]. Hence, the effluent disposal with high COD values is a serious environmental problem, as its continuous discharge into receiving water bodies would ultimately choke the aquatic life by changing the water characteristics [5]. High concentration color of this effluent impedes light penetration resulting in the decline of photosynthetic activity by coral reefs and other flora thereby affecting the survival of aquatic life including various food chain organisms [6]. Various physicochemical and biological processes are applied for the removal of TSS, COD, turbidity and color from industrial effluents [7-8]. They include chemical coagulation [9], ultra-filtration [10], nano-filtration [11], reverse osmosis [12], adsorption [13], electro-chemical [14], bioremediation techniques [15] and membrane technology [16, 17]. Most of these treatment methods are either expensive such as ultra and

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nano filtration, membrane technology or ill-suited to treating large volumes of wastewater such as electrochemical process. Whereas, chemical coagulation is comparatively economical than the other methods and could be as effective as the other expensive methods with required maneuvering of the process such as if carried out in conjunction with adsorption phenomenon [18-20]. In case of wastewater treatment via coagulation process, suitability of both the coagulant as well as its dosing are the important considerations in order to accrue good treatment efficiency. Previous research suggests that various coagulants have been used for industrial wastewater treatment via coagulation process such as alum [21], ferric chloride [22], magnesium chloride [23], poly aluminum chloride [24], lime [25] and ferrous sulfate [26] for the removal of color [26, 27], COD [28, 31], turbidity [29] and TSS [30]. The review of these studies suggests that the application of individual coagulants for wastewater treatment resulted in the inefficient removal of the polluting substances from wastewaters thus requiring further treatment of the parameters of concern [32]. However, effective multi-parameter removal of the pollutants would probably require applying suitable combination of the relevant coagulants with their optimized proper doses.

The aim of this research study was to investigate the viable coupling and dosing of the coagulants used with and without PAC adsorbent in order to optimize successful combination that can be applied for the effective treatment of refractory type of binder emulsion effluent, which shows the highlight point of this research study.

Material and Methods

Raw effluent samples of binder emulsion plant were collected from the discharge point of Binder Emulsion Processing Plant located in Jamshoro, Sindh, Pakistan. Most of the research work was conducted at the effluent treatment plant laboratory of the plant. Physico-chemical analysis (Table 1) of the effluent was conducted according to the standard laboratory protocols [33]. Commercial chemical coagulants of analytical grade such as ferric chloride, ferrous sulphate, alum and lime along with powdered activated carbon (PAC) were purchased from Al-Mehran Chemicals Limited, Karachi, Pakistan.

Table 1. **Characteristics of the binder emulsion plant effluent**

Effluent Parameters	Concentration
Temperature, ^{0}C	28
pH	9
TDS, mgL^{-1}	1200
Conductivity, uS-cm^{-1}	554
COD, mgL^{-1}	7025
BOD, mgL^{-1}	3100
Color, Ptco	7160
Turbidity, FTU	1340
TSS, mgL^{-1}	820

The experimental work was conducted via coagulation and adsorption techniques using jar test method. The effluent quality parameters were measured before and after the treatment according to the methods prescribed in APHA [34]. Total dissolved solids and electrical conductivity of effluent samples were measured by conductivity meter (Hach Company, U.S). COD of the samples was determined via dichromate method and color, turbidity and TSS at their specific wavelengths were analyzed using Spectrophotometer (DR-2000).

The coupling protocol of the coagulants applied for the treatment comprised of ferric chloride-lime, ferrous sulfate-lime and alum-lime with a fixed dosing of 1.2-0.80 g/L. The operational parameters of the process were kept constant during all the treatment drills including mixing time (30 min), agitation speed (150 rpm), temperature (25ºC) and settling time (1 hr.). After settling of the effluent flakes, coagulated samples were filtered through filter paper (125 µm) before their analyses. Total sample volume taken for each treatment run was 500 mL.

Simultaneous coagulation - adsorption technique for the effluent treatment was carried out via Jar testing method. In this method coagulant dosing was kept the same, i-e 1.2 g/L, while PAC dosing was fixed as 1.0 g/L. Both the coagulant and adsorbent were introduced into the effluent test samples separately and the process was carried out under similar conditions as observed in the earliest method. The effluent samples treated via this method were filtered through vacuum filtration before being analyzed for the parameters such as COD, color, turbidity and TSS. All the results were obtained in triplicate to estimate the error formation before the results being presented as a mean value.

Results and Discussion

Effluent treatment using combined dosing of ferric chloride and lime

The effluent treatment with combined dosing of coagulants ferric chloride and lime yielded in removal rates of 34%, 35%, 61%, 45%, 46% and 29% for TDS, EC, COD, color, turbidity and TSS respectively, giving an overall average reduction of 45% for all the pollutants (Fig. 1). Lime was used as a flocculent as well as pH maintaining agent in coagulation process thus aiding in the settlement of suspended impurities. During the course of effluent coagulation chemical reaction would likely have taken place between water and substances added into it resulting in the possible formation of multiple forms of metals hydroxide precipitates such as $Fe(OH)^{2+}$, $Fe(OH)_2^{+}$, $Fe(OH)_4^{2+}$, $Fe_3(OH)_4^{5+}$, neutral $Fe(OH)_3$ as well as negatively charged $Fe(OH)_4^{-}$. This formation of precipitates probably accounted for the reduction in the pollutional characteristics of the effluent in terms of the given parameters. However, the lower removal of the pollutant's concentration obtained during this treatment cycle may well be hinting at increasing the dosing of the coagulants used to enhance the treatment efficiency of the process. Joo *et al.* reported the reduction of turbidity (66%) and COD (73%) from an effluent sample of relatively lower pollution loading using similar coagulants [35]. Compared to this, our results for the main pollutant COD with higher loading also showed the similar efficacy of the coagulants used in reducing pollution concentration, which is probably subject to the magnitude of original characteristics of the effluent sample.

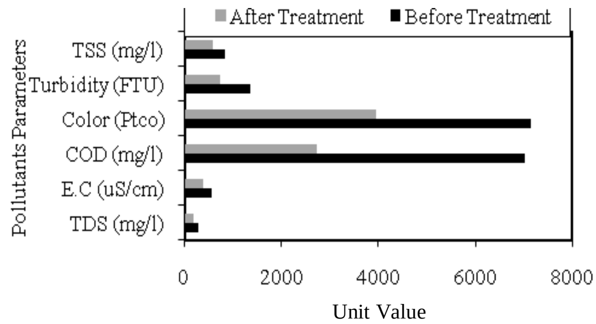

Figure 1. **Effluent characteristics before and after treatment using combined dosing of ferric chloride and lime.**

Effluent treatment using combined dosing of ferrous sulfate and lime

The effluent treatment with combined dosing of coagulants ferrous sulfate and lime yielded in reduction of TDS, EC, color and turbidity by 21%, 20%, 29%, and 29% respectively indicating lower concentration removal by around 15% in terms of the given parameters when compared to the results obtained using ferric chloride and lime. Whereas, COD and TSS values were increased by 28% and 7% under the influence of this combined dosing of coagulants, implying towards the inefficacy of ferrous sulfate as an effective coagulant for the treatment of this particular effluent (Fig. 2). This could be the case as the induction of this coagulant did not result in the formation of precipitates during the process of coagulation probably due to the different chemical nature of the substance. Apparently when there was no enough formation of metal hydroxides, reduction rate of effluent pollutants was lowered [36]. In addition, upon increasing the dose of Ferrous sulfate would also not increase the coagulation efficiency for proper treatment of emulsion effluent.

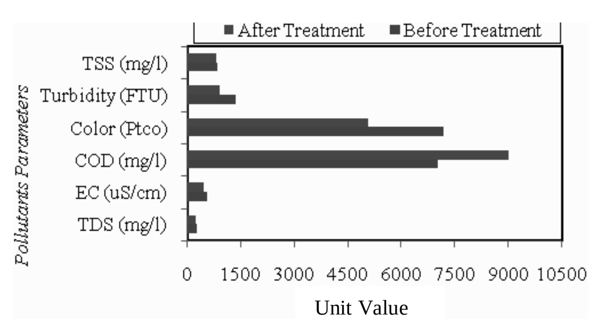

Figure 2. **Effluent characteristics before and after treatment using combined dosing of ferrous sulfate and lime.**

Effluent treatment using combined dosing of alum and lime

Effluent coagulation using combination of alum and lime resulted in the decrease of concentration for COD, color, turbidity and TSS by 48%, 58%, 24% and 21% respectively (Fig. 3). This treatment yielded better results as compared to the previous combination of coagulants in terms of accruing pollution reduction as to COD and color. Again, better results were probably related with the formation of aluminum metal hydroxide precipitates observed during the course of this treatment. Ahmad *et al*. and Guida *et al*. reported TSS (65%) and COD (80%) reduction from the respective effluent samples at a dosing rate of 8 g/L of alum, which was eight times higher than the dosing rate that we have used in this study [37, 15]. This implies that alum when used as a consortium can result in higher removal efficiency of the pollutants in contrast to that when it is used alone.

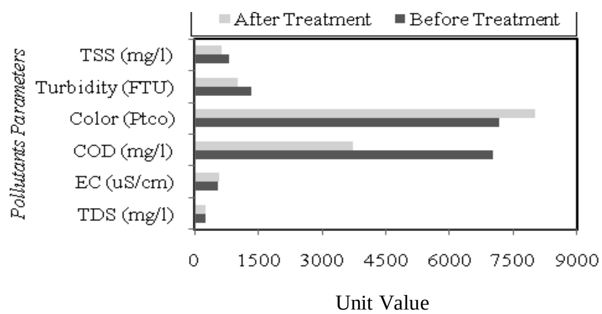

Figure 3. **Effluent characteristics before and after treatment using combined dosing of alum and lime.**

(Fig. 4) shows comparison of the treatment protocols using different combination of coagulants employed for reduction in the concentration of pollutants present in the binder emulsion effluent. It clearly shows that effluent coagulation with ferric chloride yielded in higher removal of pollutants' concentration by around 18% as compared to other coagulants. This suggests towards higher affinity of this particular coagulant for the dissolved and suspended particulates present in the effluent to be associated with the resultant precipitates formed. This was in contrast to the other coagulants used, in which precipitate formation was not effective enough to influence enough decrease in the pollutants' concentration. This condition might have occurred due to non-conducive nature of the chemical composition of the coagulants applied as it was likely not in conformity with the characteristics of the effluent in terms of particulate colonization with the coagulants.

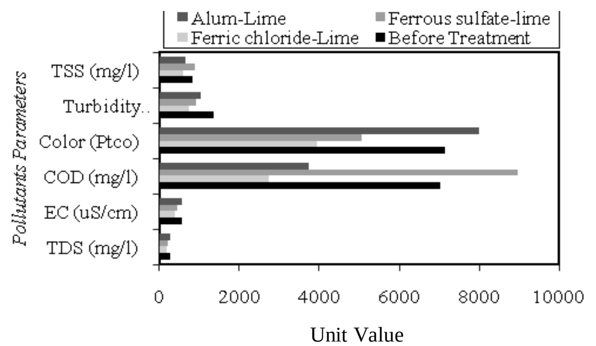

Figure 4. **Treatment efficiency comparison of different coagulants.**

Effluent treatment with combined dosing of coagulants and powdered activated carbon

Ferric chloride being an effective coagulant, as observed in the earlier experiments, was also applied in conjunction with powdered activated carbon (PAC) with a dosing rate of 1.2 – 1.0 g/L to further optimize the treatment efficiency. The results showed that the induction of PAC along with the coagulants transpired into the enhancement of the treatment efficiency. Overall, 82%, 98%, 98% and 99% reduction in the concentration of COD, color, turbidity and TSS, respectively, was effected which implied towards better removal of the pollutants in terms of COD by 20% as well as color, turbidity and TSS by more than 60% than the values obtained via coagulation without using PAC (Fig. 5). This also hinted at the PAC contribution towards almost complete elimination of the suspended pollutants present in the effluent. In addition, during the course of this run and aside from the generation of chemical precipitates, there was little sludge formation, which meant that apparently all the suspending polluting substances were probably captured by the combined technique of coagulation and adsorption. These results were in agreement with those reported elsewhere in the literature [35].

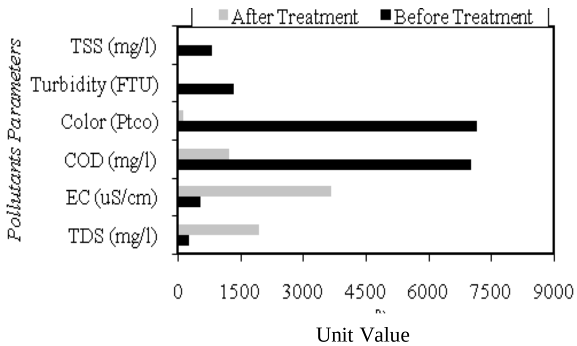

Figure 5. **Effluent characteristics before and after treatment using combined dosing of ferric chloride and PAC.**

In contrast, the induction of coagulants ferrous sulfate and alum with PAC adsorbent did not prove viable as with ferrous sulfate 11% and 3% reduction occurred in COD and turbidity, respectively; whereas, color and TSS values were rather increased by 18% (Fig. 6).

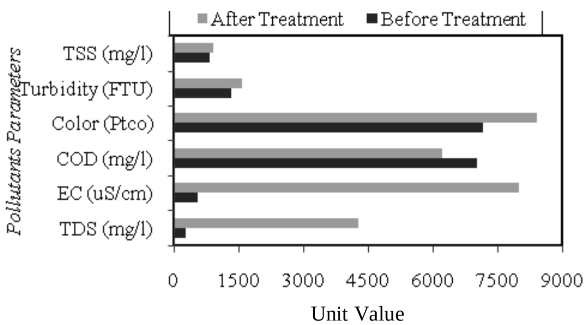

Figure 6. **Effluent characteristics before and after treatment using combined dosing of ferrous sulfate and PAC.**

In case of Alum when used with PAC, slightly better results were possible only for COD (41%) and color (15%), while TSS and turbidity values were instead showed increase by 49% and 40% respectively, suggesting that even the combination of these coagulants with PAC was still not viable in terms of efficient removal of the pollutants from the effluent (Fig. 7). It was thought that perhaps due to inefficient formation of coagulant precipitates, the pollutant particulates were not stabilized thus resulting in poor trapping of these particles leading to their lower removal.

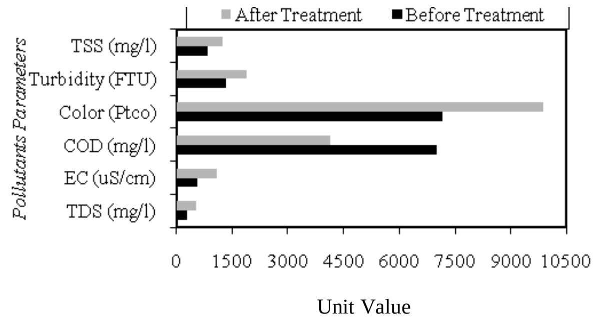

Figure 7. **Effluent characteristics before and after treatment using combined dosing of alum and PAC.**

PAC was also used in association with all the three coagulants and the results suggested that combined effect of all the coagulants particularly ferric chloride and alum influenced the formation of precipitates to the maximum as well as adsorption of the impurities. This synergistic effect on the effluent characteristics almost resulted in complete removal of the concentration of parameters such as COD, color, turbidity and TSS (Fig. 8).

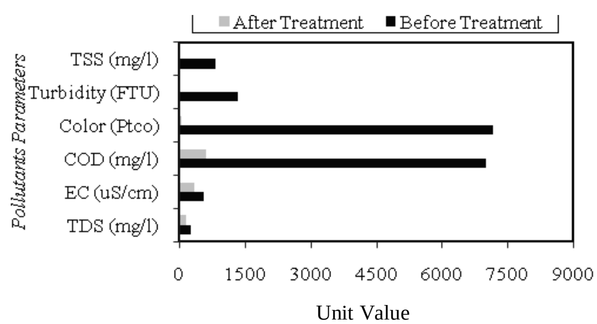

Figure 8. **Effluent characteristics before and after treatment using combined dosing of mixed coagulants and PAC.**

Comparison of all the treatment protocols applied is shown in (Fig. 9), which clearly shows that induction of PAC along with all the selected coagulants proved highly effective as compared to other treatment options used. It is likely that under the influence of multiple effect coagulation, all the coagulants introduced into the process behaved individually forming characteristic metal hydroxide precipitates thereby increasing the potential for the removal of the pollutants from the effluent. Combination of ferric chloride and PAC also showed good performance during the course of effluent treatment, but still it was lesser when compared to the joint induction of multiple coagulants and PAC. The induction of separate combinations of ferrous sulfate-PAC and alum-PAC did not yield in better results due to ineffective formation of characteristic precipitates in these runs resulting in lesser removal of pollutants.

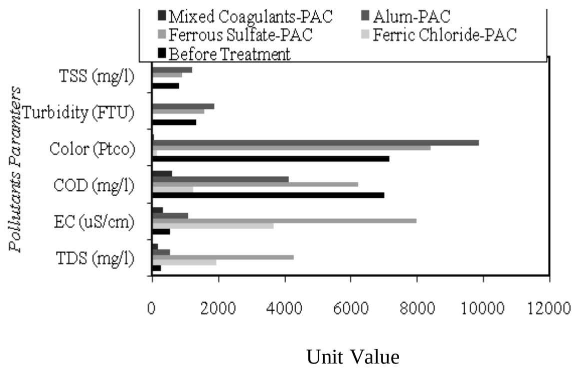

***Figure 9*. Comparison of treatment efficiency obtained using different coagulants and PAC.**

Statistical analysis of treatment processes

The statistical analysis was carried out for the coagulation as well as combined process of coagulation and adsorption in order to replicate the efficiency of the optimized treatment protocol via statistical predictions. Experimental data as obtained from the applied treatment protocols was interpreted via polynomial function at order 4. The statistical results transpired that polynomial function was suitable giving higher values of R^2.which are presented in (Table 2), while the statistical results for both coagulant and combined treatment protocols are shown in (Fig. 10) and **(**Fig. 11), respectively.

***Table 2*. R^2 values determined from coagulation and combined process of coagulation and adsorption**

Mate-rials	$FeCl_3$-Lime	$FeSO_4$-lime	Alum-Lime	$FeCl_3$-PAC	$FeSO_4$-PAC	Alum-PAC	Mixed Coagulant-PAC
R^2 Values	0.959	0.894	0.855	0.989	0.800	0.813	1.0

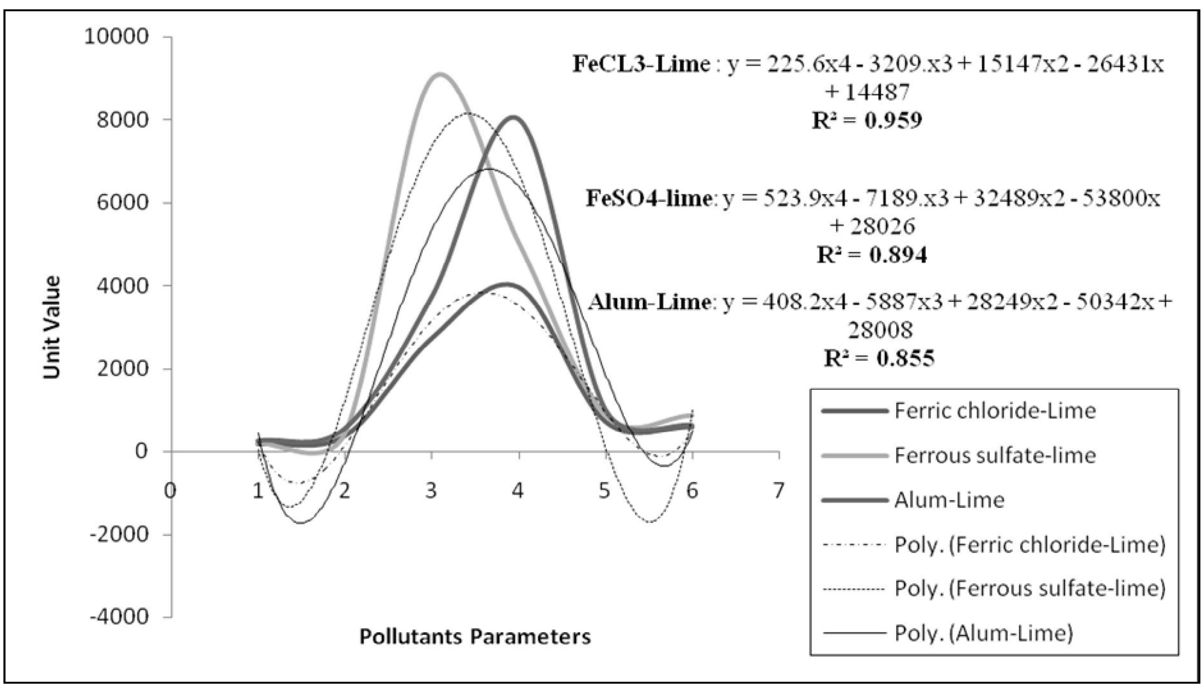

***Figure 10*. Statistical analysis in polynomial function for various coagulant for effluent pollutants reduction.**

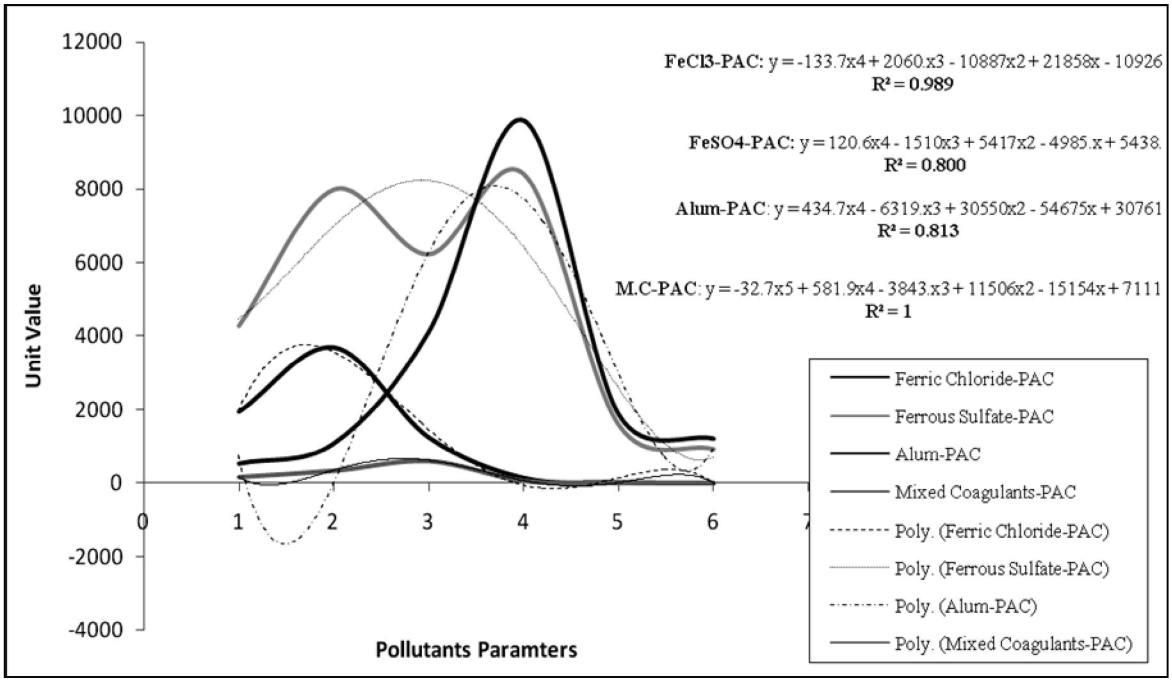

Figure 11. **Statistical analysis in polynomial function for various hybrid materials for effluent pollutants reduction.**

Conclusions

The synergy of coagulants ferric chloride, alum and lime was investigated to influence reduction in the pollution concentration of binder emulsion effluent. The results showed that ferric chloride and lime yielded in better combined effect of removing the pollutants than the other combinations. In a combined process of coagulation and adsorption, combination of ferric chloride and PAC gave effective results in terms of pollutants removal by around 90% as compared to combination of PAC with other coagulants, yielding removal percentages of lower than 50%. However, combination of all the selected coagulants and PAC produced even better results when the concentration of pollutants was reduced by 98%.

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