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COAGULATION–FLOCCULATION PRETREATMENT OF HIGH-LOAD CHEMICAL–PHARMACEUTICAL INDUSTRY WASTEWATER: MIXING ASPECTS

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The selection of a coagulant-flocculant agent which, based on the maximum chemical oxygen demand removal, warrants the best performance of the removal system for a very complex high-load chemical-pharmaceutical industry wastewater, is described. A total of 23 coagulants/flocculants was tested, including salts, poly-hidroxyaluminates, synthetic polymers as well as natural gums. In a second stage, some mixing aspects were studied. The effects of the specific impeller, the agitation speed during the coagulation and flocculation stages, and the absence or presence of baffles were evaluated in a six-place agitation system. The conventional impellers were replaced by the following types of propellers: Rushton, marine, A310 (Lightning), three flat blades, 45° inclined six blades, and conventional flat blade propeller. It was demonstrated that the appropriate coagulation-flocculation system is capable of diminishing the COD, the apparent color and the dissolved solids up to 40.6, 25.6 and 39.4%, respectively. The best results were observed when using BL-5086, guar gum, Niad II-3, Niad II-4 and locus beam gum. The impeller performance was highly dependent on the agitation speed for each fixed system. With respect to the mixing aspects, it was shown that the selection of the right propeller for the coagulation and flocculation stages is crucial in determining the quality of the treated water, as well as the quantity and quality of the residual sludges generated in the process. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Coagulation-flocculation, high-load wastewaters, mixing, impellers, pretreatment.

INTRODUCTION

The explosive growing of the Mexican industry during the last decades has originated a considerable increase in wastewater complexity and variability. The organic synthesis industry comprises different sectors, such as polymers and synthetic resins, pesticides, paints and pharmaceutic chemistry (Ramírez *et al.*,1994). These industries' wastewaters present high organic loads and toxicity. Many of the present compounds are toxic, even at very low concentrations with an accumulative effect over the biological treatment systems. The activated sludge system is an option employed very frequently for treating municipal as well as industrial wastewaters in México. These systems are often inhibited by industrial high-load and toxic wastewaters. This fact makes the application of a pretreatment necessary. This can be achieved by sedimentation, coagulation-flocculation, filtration or a combination of them, among other systems.

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A very drastic case of high-load toxic industrial effluent is the one coming from the chemical-pharmaceutic industry that produces mainly antihelmintics, the principal gastroenteric disease aid in México. The typical physical-chemical characteristics of the effluent are shown in table 1. Besides the tremendous organic load, some of the specific organic compounds detected by gas chromatography were: benzene, phenol, dimethyl-disulphide, toluene, dimethyl-o-methyl cyclohexanone, methylprophyl disulphide, dimethyl-trisulphide, propoxy-bencene, diisopropyl-disulphide, diisopropyl-phenol, Cl-nitro-anyline and isobutyl-isopropyl-tiophene, acetone and hexane (Ramírez *et al.*, 1994). All these compounds are considered toxic even at low concentrations. The coagulation-flocculation process was proposed as the best pretreatment in order to lower the organic load and salinity levels.

MATERIAL AND METHODS

The wastewaters coming from the antihelmintic production plant were characterised before and after the pretreatment process (Ramírez *et al.*,1994). See table 1 for a typical sample characterisation. The samples were stored at room temperature for a week, before use.

Table 1. Physical-chemical characterisation of the industrial wastewater

Parameter	mg/l	Parameter	mg/l	Parameter	mg/l
TSS	40.4	Tl	0.05	Mg	4.94
VSS	26.4	Al	0.05	Cu	0.05
VDS	11,945	Hg	0.05	V	0.05
TDS	44,555	Se	0.05	Be	0.05
P_T	1.48	Pb	0.05	Ca	274
$N\text{-}NH_3$	1,077	Co	0.05	Ti	0.05
N_{org}	2,240	Cd	0.05	K	13.84
$N\text{-}NO_3$	0.22	Ni	0.10	Na	133.5
$N\text{-}NO_2$	0.015	Si	22.45	Ba	0.05
COD_S	60,671	Mn	0.90	Ag	0.05
COD_T	63,650	Fe	0.40	SO_4	63.61
Alkalinity	490	Cr	0.05	MBAS	3.82

T : total, S : soluble

Jar tests. Conventional jar tests were developed in order to determine the most appropriat coagulant-flocculant agent and dose, in terms of the organic load removal. The products tested were : CaO, $FeCl_2$, $FeSO_4$.$7H_2O$ (J.T. Baker, México) and $Al_2(SO_4)_3$ (Prosisa, México), BL-5086, BL-5029, Bubond 60, Bubond 63, Bubond 65, Bufloc 528 (Buckman Laboratories, México), Niad II-3, Niad II-4 and Niad II-5 (Diaztech, Canada) as well as natural gums: sodium alginate (Kelco, SA), food grade xanthan gum (Sigma Chemicals, USA), guar gum (Sigma Chemicals, USA), food grade locus bean gum (Química Hércules, México), dextrane (Sigma Chemicals, USA) and industrial grade carboxy-methyl celulose (Goodrich, UK). All the products were diluted in distilled water at 1% (w/v); 200-1200 ml of the 23 product solutions were tested. The selection of the best products was carried out with 1000-ml graduated flasks, mixed with the conventional flat-blade propellers. Chemical oxygen demand (COD), apparent color and total dissolved solids TDS (*i.e.* salinity) as well as final pH were determined, in order to characterise the coagulation-flocculation efficiency, as described by APHA, AWWA and WPCF (1989). In addition, the amount and

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volume of sludge produced were determined and the apparent density was calculated. The sludge volume was determined at the Imhoff cones and the dry weight of the sludge, by filtration of a portion of the sludge in preweighed filter paper. After drying at room temperature, the filters with the sample were kept in a silica disicator overnight and re-weighed. The standard conditions for these tests were: 1 minute at 100 rpm; 25 minutes at 25 rpm and 25 minutes for sedimentation time.

Modified Jar tests. A Phipps and Bird jar test equipment was modified as follows: 2000-ml graduated flasks were fitted with four aluminium baffles. These baffles had a width of 1/10 the flask diameter and were separated 45° among them. The standard flat impellers were replaced by the following impellers : Rushton (RT), marine (MP), A310 Lightning (LA310), three flat blades (3FIB), 45° inclined six blades (P45), and conventional flat blade (CONV) with impeller diameter/tank diameter ratios of around 0.4. Different coagulation and flocculation speeds were employed for every impeller experience: 10, 100, 150, 200, 250 and 300 rpm, and 10, 25, 50 and 100 rpm, respectively. Some experiences were developed without baffles, in order to assess their effect over the coagulation-flocculation performance.

RESULTS AND DISCUSSION

Coagulant-flocculant selection. As shown in figure 1, nine of the 23 tested products showed remarkable results in terms of developed COD, color or salinity removals. The alum sulphate did not show a good performance (9.37, 13.38 and 2.16% removal of COD, color and salinity, respectively). On the other hand, BL-5086, guar gum and Niad II-3 were the best products with COD removals of 40.6, 40.6 and 37.5%, respectively. The corresponding color removals were as high as 14.12, 5.94 and 13.61%. Color removal could not be considered as an important feature if this process is considered as a pretreatment. Yet, the color in this case could be related to the presence of color-forming compounds, as the anyline derivatives, which are known to be toxic compounds. Finally, this top-products achieved 6.5, 5.2 and 9.2% of TDS removal, which are not negligible. The calcium chloride was not efficient at all in removing COD or color, but salinity. The total salinity removal was as high as 39.31%, thus this was the only efficient product for salinity reduction. The possible mechanism for this removal is not the coagulation-flocculation, but the chemical precipitation of some specific ions. Other noticeable products were ferric chloride and Niad II-4. These results are partially summarised on table 2, together with the final pH values and the optimum doses. From this table, it is interesting to remark that the salts of alum and ferrum diminished the solution's pH-values, which implies an additional neutralisation step, and its related cost.

Table 2. Summary of the coagulant-flocculant selection tests

Product	Optimum dose, mg/l	$COD_{removal}$ %	$Salinity_{removal}$ %	Final pH	$COD_{removal}/dose$
Alum sulphate	400	9.37	2.16	6.49	1.71
BL-5086	800	40.6	6.50	6.94	5.07
Guar gum	600	40.6	5.26	6.98	6.76
Locus bean gum	1000	28.1	5.10	7.07	2.81
Ferric chloride	1000	33.4	8.66	5.88	3.34
Niad II-3	800	37.5	9.22	6.71	4.60
Niad II-4	1200	27.7	10.4	NE	2.30
Niad II-5	400	18.7	2.67	NE	4.67
Calcium chloride	200	-	39.31	7.09	-

NE: Not evaluated

In the last column, the arbitrary unit $COD_{removal}/dose$ was calculated for every product. This dimensionless parameter takes into account the capability of every miligram of product to coagulate-flocculate a defined quantity of COD. The higher the value of this parameter, the more efficient the product. The best figures were obtained for guar gum, BL-5086 and Niad II-5. Since the BL-5086 product reached 40.6% COD

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removal, 14.2% color removal and 6.5% salinity removal, as well as the second best $COD_{removal}$/dose value, it was chosen for the forthcoming mixing studies.

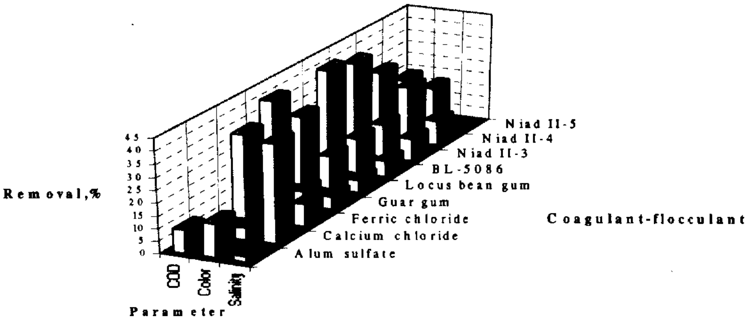

Figure 1. COD, apparent color and salinity removal values for the various products employed

Effect of the baffles. The effect of the baffles presence was studied through a coagulation-flocculation experiment in which coagulation speed was 25 rpm and rapid mixing was 200 rpm. The differences between removal values for the baffled and non-baffled systems was as high as 10 to 53% for COD, 2 to 3% for color and 4 to 88% for salinity. It is noticeable that the baffles effect is not the same for the different impeller configurations. As it is known, the behaviour of the radial-flow impellers (*i.e.* RT, CONV, 3FIB) in the presence of baffles is quite different from that of the axial-flow impellers (*i.e.* MP) and of the mixed-flow impellers (*i.e.* the rest of configurations). Figure 2 shows the particular differences for the COD removals.

With respect to sludge production and quality, it can be said that differences among the sludge production for each type of impeller were more pronounced for the non-baffled system than for the baffled one. High sludge production of 400-450 ml (data not shown) were observed in the non-baffled system, while in the baffled system the sludge production was about 350-400 ml. In what refers to the sludge apparent densities, these were higher for the baffled system, which in turn is beneficial for the full scale process (because of the lower volume requirements and better sedimentation rates).

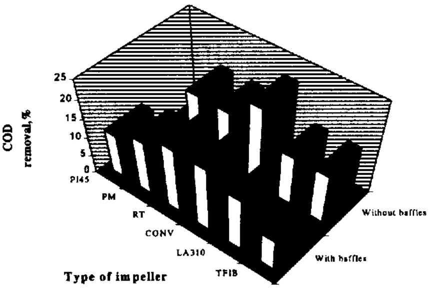

Figure 2. Effect of the baffles on the COD removal

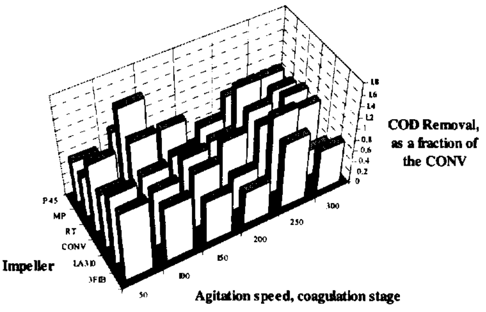

Figure 3. COD removal as a fraction of the CONV impeller, coagulation stage

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Coagulation and flocculation speeds for the different impellers. Regarding to the effect of the speed in the coagulation stage (when flocculation speed was set at 25 rpm) for the different impellers the following was observed: COD removal was affected strongly by the agitation speed, but this effect was not the same for all the tested impellers. In figure 3, the COD removal, as a fraction of the COD removal reached by the CONV impeller, can be observed for the rest of the impellers. The best overall COD removals were obtained at 50 and 300 rpm. The worse results were observed when working at 100 rpm. The best results, related to the type of impeller were found when using the RT, LA310 and 3FIB (at 50 rpm), and RT and CONV (at 300 rpm). Some differences were observed for the COD removal values at the same agitation speed for the different impellers. The fact that many impellers developed in higher COD removal values in comparison with the CONV impeller, means that in many conventional jar tests the coagulation-flocculation systems are underestimated.

Regarding to the color removal values (plot not shown) the same trend was observed, but the differences among the operation at different speeds were less significant. With the exception of the highest testing speed (300 rpm), where the color removals were six-fold compared to those observed at 50 rpm, the rest of the agitation speeds gave very similar results. The salinity removal was practically the same, regardless of the coagulation stage speed.

The sludge production resulted a mild function of the coagulation stage speed. In the figure 4, the sludge production was plotted for the different agitation speeds and tested impellers. As it can be seen, the maximum sludge production was reached when working at 100 rpm in average, while the minimum sludge production was observed at 300 rpm (half of the sludge produced at 100 rpm). Sludge production at 50, 150, 200 and 250 rpm was quite similar. With respect to the type of impeller used, the trend is not very clear, but the LA310 was the impeller with highest sludge production in three of the six agitation speeds. In contrast, the 3FIB was the impeller with the lowest sludge production in four of the six agitation speeds. The quality of the produced sludges was affected by the agitation speed, as predicted. The highest sludge apparent densities were observed for the 150 rpm experiments (specially for the CONV impeller, data not shown), while the lowest densities were observed for the 300 experiments (particularly for the 3FIB and LA310 impellers).

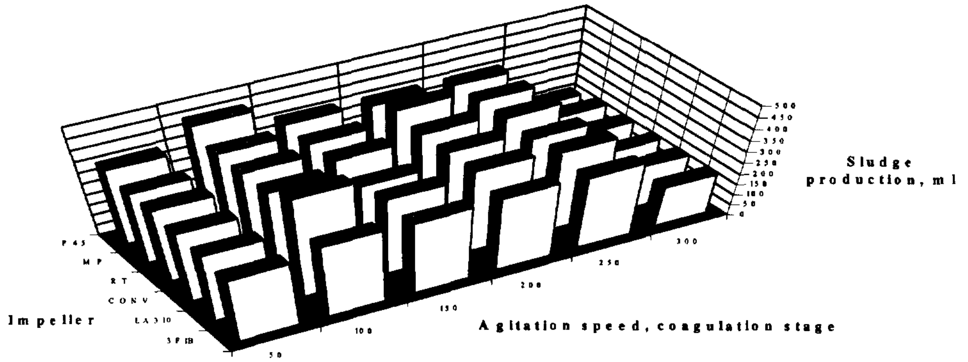

Figure 4. Sludge production, coagulation stage

The effect of the agitation speed on the flocculation stage (when the coagulation speed was set at 300 rpm) was less important if compared with that observed in the coagulation stage. For the different impellers and speeds, the trends were as follows: the COD removals were higher at 25 rpm in the average. The best results were reached when using the PM, RT and CONV impellers; the worse, when PI45 was employed. At figure 5, the COD removal as a fraction of that reached with the CONV impeller is shown for the six different impellers and the four flocculation speeds. With respect to the color removal, the best results

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were observed at 25 rpm (plot not shown). The salinity removal was higher at 10 rpm, but the effect of the impellers is not very clear.

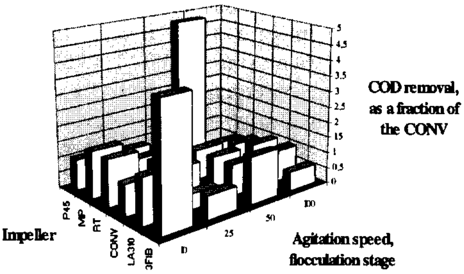

Figure 5. COD removal as a fraction of the CONV impeller, flocculation stage

The sludge production was relatively influenced by the flocculation speed. The maximum sludge productions was observed at 10 rpm, but the lower productions were found, curiously, at 25 rpm. The effect of the type of impeller was negligible for all the agitation speeds. Figure 6 shows the sludge production in ml for every modified jar test. The quality of the produced sludges was also influenced by the agitation speed. The higher sludge apparent densities were observed for the 100 rpm experiments (specially for the RT and the LA310), while the lower densities were obtained consistently at 25 rpm (for CONV, LA310 and 3FIB). The densities of the sludges obtained working with CONV, LA310 and 3FIB at 25 rpm were 50% lower than those obtained when working with the PI45 impeller.

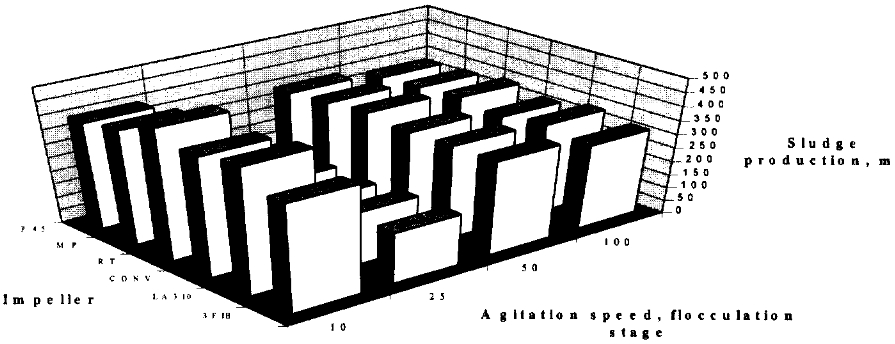

Figure 6. Sludge production, flocculation stage

Reynolds number versus impeller performance. Figure 7 shows the COD removal against the Reynolds number (Re) for every impeller operating on the coagulation stage, calculated as

$$Re = N*D^2*\rho / \mu \qquad (1)$$

where

N agitation speed,
D impeller diameter,
ρ fluid density and
μ fluid viscosity

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As shown, all the curves depicted the same behaviour. For 1,000 < Re < 11,000, the COD removal *vs.* Re can be modeled by means of a quadratic equation. The lines were different in each of the impellers, but all the curves showed a minimum of around 4,000-7,000. The flatter curves were those resembling the RT and the MP, while the more pronounced minimum was found for the PI45 impeller. The color and salinity removal *vs.* Re plots (figures not shown) were less complex. In the case of the color removal, it was found to be a direct function of the Re, but the lines for all the impellers were quite parallel. The salinity *vs.* Re curves were very flat, almost independent of the Re-values.

For the different impellers working on the flocculation stage, the trends were quite different from those depicted in the coagulation stage. Most of the behaviour was well described by means of a quadratic equation, but with rather different constants. With the MP, the COD removal was increased as the Re was increased, until a maximum value at Re around 2,000. 3FIB and LA310 showed less pronounced behaviours with a minimum value of around Re of 3,000. The PI45 decreased as much as the Re was increased, and in the case of the RT was quite independent of Re. Figure 8 shows the COD removal against the Reynolds number for every impeller operating on the flocculation stage.

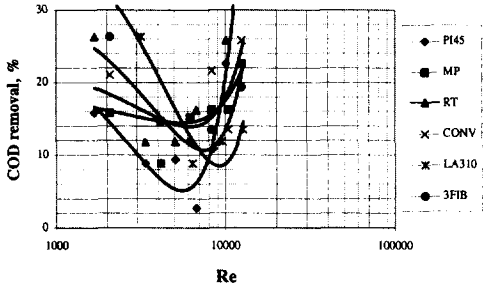

Figure 7. COD removal as a function of Re, coagulation stage

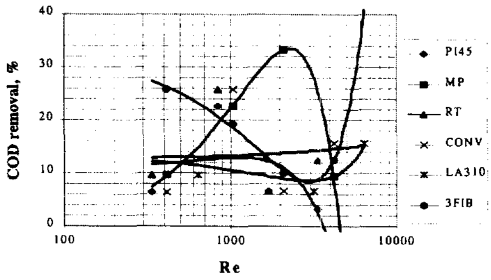

Figure 8. COD removal as a function of Re, flocculation stage

Some mixing cost considerations. The power consumed by the coagulation-flocculation system is highly dependent on the dimensionless power number (Po), according to the equation

$$P = Po*\rho*N^3*D^5 \qquad (2)$$

where

P power consumed by the system
Po dimensionless power number

The rest of the parameters are defined in equation 1. This equation is normally used for scaling-up the process. The values for Po are reported for water and some two-phase and even three-phase systems as a function of Re (Sánchez *et al.*,1992, Velasco *et al.*, 1993, Albíter *et al.*, 1994). The measurement of the real Po numbers for a given system is always preferable to using the value reported for a similar system, but this is not always technically possible. The Po for the PM in water is about 0.35-0.45 for the Re corresponding to the coagulation speeds, and 0.4-0.6 for the Re range related to the flocculation stage. On the other hand, the Po for the CONV impeller is about 2, quite constant for the whole Re range. Finally, the RT has Po values of 4-5.4 for the coagulation Re, and 3.1-4.8 for the flocculation Re. These Po-values can be used as indicator when deciding which of the studied impellers could be the best for the treatment of the high-load wastewater, based on their particular performances and energy costs.

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CONCLUSIONS

It was demonstrated that the appropriate coagulation-flocculation system is capable of diminishing the organic load (as COD), the apparent color and the dissolved solids (salinity) up to 40.6, 25.6 and 39.4%, respectively, of a very complex high-load chemical-pharmaceutical industry wastewater. The best results were observed when using BL-5086, guar gum, Niad II-3 and Niad II-4. The BL-5086 was chosen for subsequent mixing experiments, since 40.6, 14.2 and 6.5% removal efficiencies were reached when using it. Furhtermore, a $COD_{removal}$/dose index of 5 was observed, the second best from the group. Guar gum is a very promising product, which will be further characterised for its application in the coagulation-flocculation process. In addition, more experiments should be carried out assessing the effect of the COD load over the coagulation-flocculation development.

With respect to the mixing aspects, it was shown that the selection of the right propeller for the coagulation and flocculation stages is crucial in determining the quality of the treated water, as well as the quantity and quality of the residual sludges generated in the process. Another interesting conclusion is that the conventional jar test is a quite rapid and simple test in order to determine products and doses. However, if only these tests are developed, the system can be under or overestimated. A modified jar test (including different types of impellers, *i.e* conventional and non-conventional) could warrant the right selection of the product, dose and agitation speed, as well as the best suited impeller. In addition, other kinds of experiments can be developed in the same system, to study the effect of the impeller diameter to tank diameter ratio (R/T), the height of the impeller with respect to the tank bottom, and the position of the shaft, coupled to the impeller (*i.e.* eccentric, concentric).

The results obtained in this stage of the project are quite promising, but many other works must be carried out. The effect of more than one impeller in the shaft, and even the combination of different kind of impellers (*i.e* one radial impeller in the upper part of the tank and one axial impeller pumping downwards) must be studied. On the other hand, the use of more than one product for the coagulation or flocculation stages, must be analysed. For instance, the use of ferric chloride plus BL-5086 could be successful. The treatment of the wastewater with any of the best products found, followed by calcium chloride precipitation, would reach, possibly, the best organic load, apparent color and salinity removals. One of the weak points of the paper is, undoubtedly, the small scale where the experiments were carried out, but the scale-up of the process will not be hard with the Power-Reynolds numbers relationship.

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