Conventional treatment in the removal of microcontaminants

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ABSTRACT

Water treatment plants have been commonly designed to promote high removal of particulate matter and microorganisms, with a significant predominance of conventional potabilization technology, comprising the stages of coagulation, flocculation, sedimentation or flotation, filtration and disinfection in different tanks.

Keywords: Treatment, Removal, Microcontaminants.

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INTRODUCTION

Water treatment plants have been commonly designed to promote high removal of particulate matter and microorganisms, with a significant predominance of conventional potabilization technology, comprising the stages of coagulation, flocculation, sedimentation or flotation, filtration and disinfection in different tanks (LIMA et al., 2014).

In addition to this treatment setup, other technologies have been applied on a full-scale basis for particulate removal. The clarilockor is one of them used in large water treatment plants around the world. The technology has a flocculation zone in the center and a decantation zone circumscribing it, so the entire flocculation and decantation process is carried out in a single compartment (SAXENA; BRIGHU; CHOUDHARY, 2020).

The sludge blanket clarifier, considered a high-rate clarification technology, is another applied example, considered a solids contact system and also combines flocculation and decantation in one unit. Sludge blanket clarifiers maintain a large volume of flocculated solids within the unit, which improves flocculation by stimulating collisions between particles (JOHNSON, 2014).

The concern with different contaminants present in water bodies has led to comparative studies regarding the efficiency of these processes. The presence of natural organic matter (MON) is an example due to the potential for the formation of toxic chlorinated compounds and the possible development of other toxic compounds if the coagulation process is not efficient. Emerging contaminants are also evaluated in conventional clarification processes, mostly finding the inefficiency of coagulation in removal (HUANG et al., 2019; LIMA et al., 2014). Different mechanisms can be addressed from these researches, including varying treatment techniques, and with this information evaluate possible proposals for the removal of these pollutants.

OBJECTIVE

To carry out a brief discussion on water clarification using the conventional clariloculator and sludge blanket clarifier, comparing them with bench scale analyzing the mechanisms and then evaluating their potential characteristics in the removal of the emerging contaminant, diclofenac. To support the discussion, the main article chosen was by Saxena et al 2020 and other pertinent articles were searched in the Web of Science, Scopus and ScienceDirect databases.

DISCUSSION

CLARIFICATION IN TURBIDITY REMOVAL, TOC, DOC – USE OF CLARILOCULATOR AND SLUDGE BLANKET CLARIFIER

In a recent study, Saxena et al, (2020), evaluated two pilot plants, a conventional clarichlorinator and a sludge blanket clarifier for the removal of turbidity and TOC in synthetic waters prepared using kaolin and humic acid as a source of turbidity and organics, respectively. In addition, parameters such as DOC, zeta potential, pH and alkalinity, and UV

254 were measured before and after treatment to compare the removal efficiencies and mechanisms of the two pilot plants. Studies were tested for inlet turbidity ranging from 0 to 20 NTU and inlet TOC ranging from 0 to 10 mg. $^{L-1}$ to check its efficiency for the variable characteristics of the raw water. The performance of the pilot plants was also compared with the bench-scale jar tests.

High basicity polychloride (PAC) was used as the coagulant. Optimal doses were obtained by performing pitcher tests for each combination of inlet turbidity and OCD. The pH of the synthetic waters was alkaline, to simulate the raw water in a region of India that has 17 UN, TOC of the surface waters usually ranges from 2 to 10 mg/L and average pH of 8.40, alkalinity 180-205.

The rapid mixing system consisting of a mechanical impeller for rapid mixing is designed for a detention time (td) of 1 min and a gradient value (G) of 400 s $^{-1}$. In the conventional clarichlorinoculator (CC) the flocculation zone is designed for slow mixing through a radial flow impeller designed for a detention time (td) of 30 min, G-value of ~30 s

$^{-1}$ and surface overflow rate of ~30m3 /m2 /day. **The sludge blanket clarifier (CML)** designed with a much smaller base area and more depth. The clarifier is designed for a detention time of 30 minutes and rate of ~70 m3 /^{m2}/day and a G value of ~2.5 s $^{-1}$.

The scheme used by Saxena et al, (2020) is presented in Figure 1. A more detailed scheme using the same processes was presented by Srivastava; Brighu; Gupta (2020) for different parameter conditions, rapid mixing with G of 600 s-1 and td of 30s, flocculation zone *td* of 20 min and G of 40 $^{s-1}$ and CML designed to treat of 8000L/d (Figure 2). The objective focused on evaluating the efficiency of technologies for low turbidity waters, simulating raw water with pH 7.5 and alkalinity of 228. Therefore, the samples for evaluation ranged from 0-10 UT. In addition, the post-filtration efficiency on 20 µm filter paper was also evaluated.

Figure 1- Process schematic and accessories of pilot plant, (a) conventional clarifier and (b) sludge blanket clarifier (SAXENA; BRIGHU; CHOUDHARY, 2020)

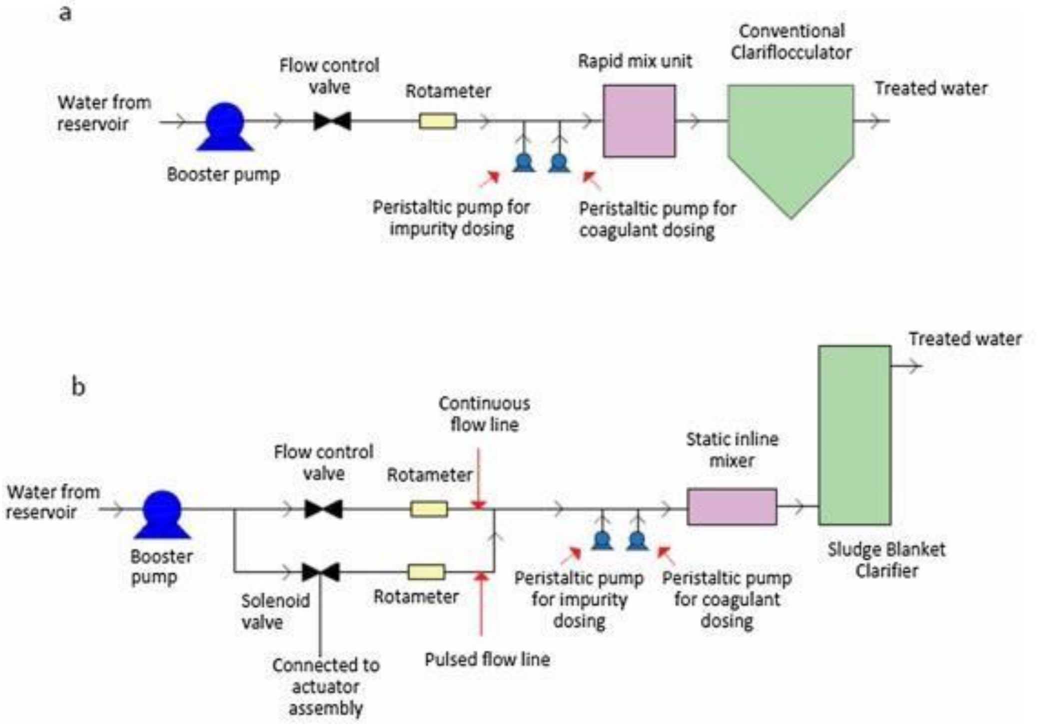
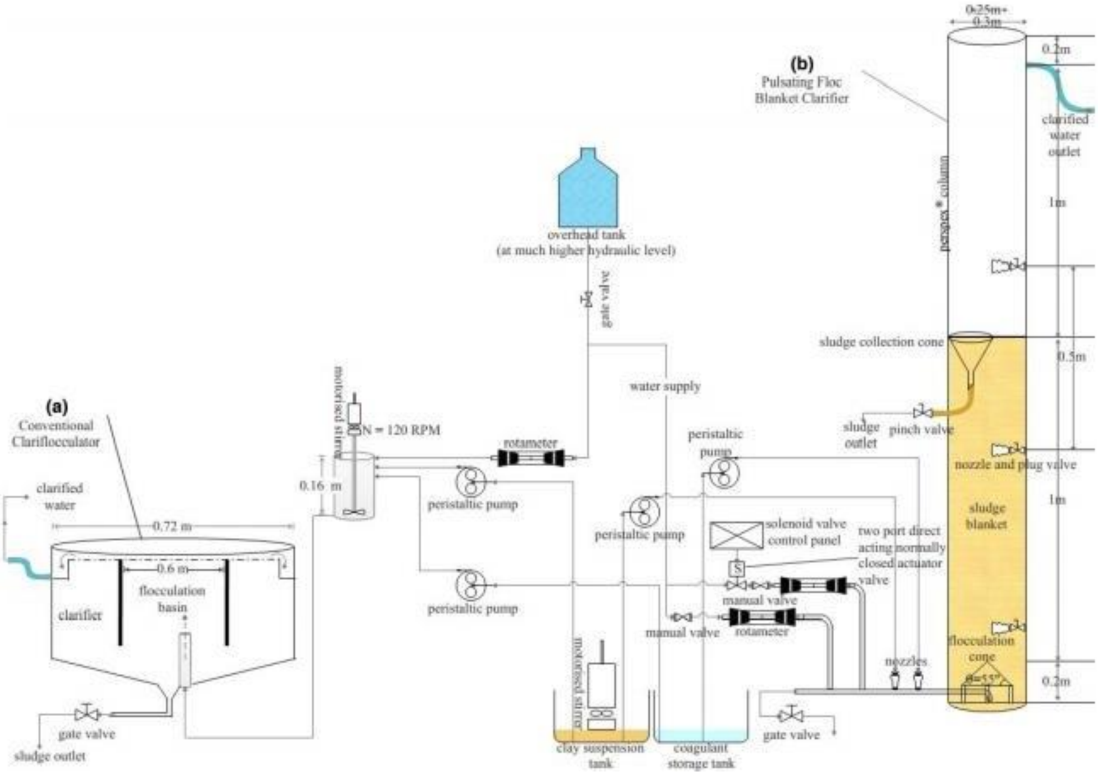


Figure 2- Process schematic and accessories of pilot plant, (a) conventional clarifier and (b) sludge blanket clarifier (SRIVASTAVA; BRIGHU; GUPTA, 2020).



Turbidity Removal

According to Saxena; Brighu; Choudhary (2020), in general, the percentage of turbidity removal increased with the inlet turbidity (Table 1).

Table 1 – Turbidity removal as a function of inlet turbidity.

Input turbidity	CC	CML	In Test (JT)
5 UNT	43–54%	20–57%	- DC 30% less efficient than JT - CML 39% less efficient than JT
10 UNT	52–75%	36–77%	
15 UNT	63-79%	57-72%	
20 UNT	76-84%	60-81%	

For COT at entry, the decrease was more significant for CML than for WC (Table 2). Overall, the percentage of removal was higher for CC than CML; and for both systems there was a decrease in turbidity removal efficiency as the input TOC increased, but again it increased because the TOC was too high. On average, compared to the test jar result, the removal efficiency was 30% lower for CC and 39% lower for CML.

Table 2 – Percentage of turbidity removal as a function of inlet TOC

COT	CC	CML	In Test (JT)
0	50 a 76%	20 a 76%	- DC 30% less efficient than JT - CML 39% less efficient than JT
2	46-77%	22-66%	
4	48-71%	31-65%,	
6	43-84%	43-81%	
8	51-79%	57–77%;	
10	54-81%	42–75%	

Residual turbidity ranged from 2.32 to 8 NTU and 2.13 to 8.63 NTU for CC and CML, respectively. In the case of CC, the sludge is collected at the bottom and remains undisturbed. However, in the case of CML, the blanket expands and contracts at intervals. It is possible that the pulsed flow of water is not evenly distributed throughout the cross-sectional area of the blanket which can cause differential flow of water through narrow channels in the blanket while increasing the upward flow velocity in that particular area during expansion. This could be a possible reason for marginally higher residual turbidity in CML than CC.

The results of Srivastava's research; Brighu; Gupta, (2020) (Figure 3) for turbidity removal show that the CML was more efficient in the face of the lowest turbidity residuals. Another interesting point in his research was the post-filtration analysis in a 20um filter (Figure 3), observing that the CC technology presented lower turbidity values and, therefore, the water clarified with particles > 20um in its majority, thus favoring greater retention in the filtration stage.

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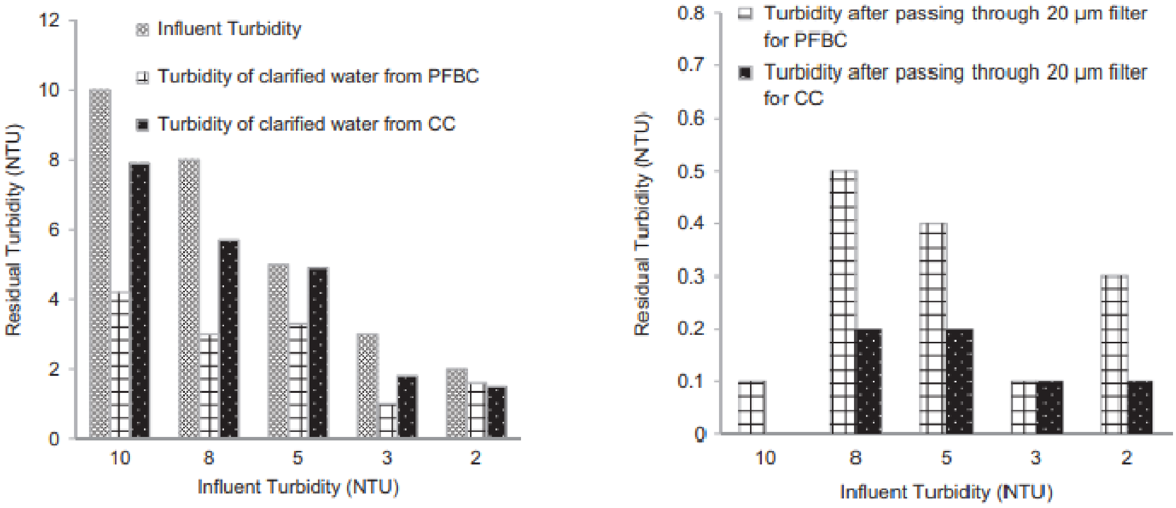
Figure 3 – Residual turbidity after clarification (a) and after additional filtration (b)



TOC and COD Removal

The percentage of OCD removal increased as incoming OCD increased, and then stagnated as incoming OCD increased for all three systems (Figure 4).

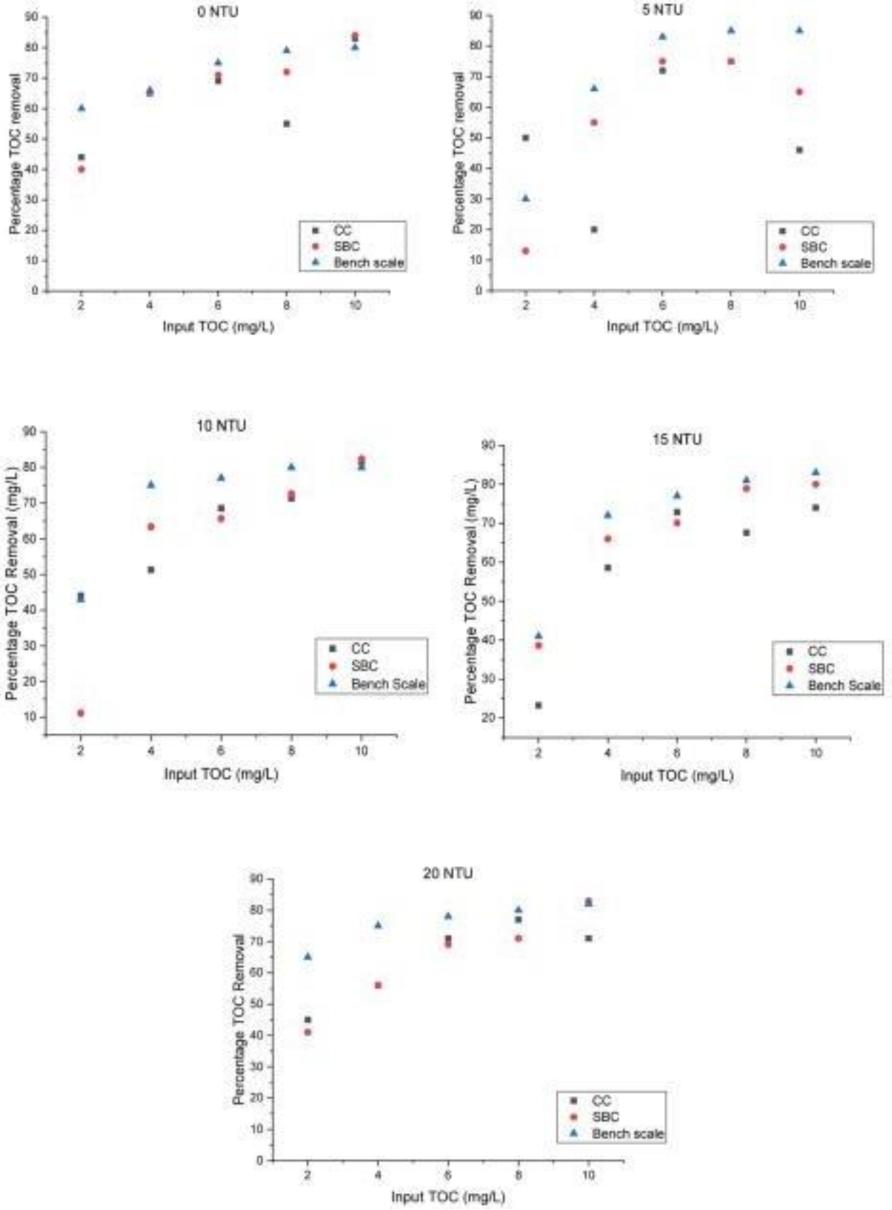
Table 3 - TOC removal percentages as a function of the variation in incoming TOC.

TOC	CC	CML	In Test
2	23-50%	11-41%	- DC 11% less efficient than JT - CML 9% less efficient than JT
4	20-65%	55-66%	
6	69-73%	66-75%	
8	55-77%	71–79%;	
10	46-83%	65-84%	

Only at low TOC intake of 2 mg/L, CC had better performance. For higher OCD concentrations, CML performed better. Overall, the percentage of TOC removal for pilot-scale reactors was lower than for bench-scale system. Residual OCD ranged from 1.01 to 5.36 mg/L for CC and 1.21 to 3.53 mg/L for CML.

DOC removal did not show any particular trend with increased TOC input or turbidity. Removal to the bench scale system, CC, and CML was 30–89%, 27–87%, and 38–92%, respectively. The residual DOC for bench scale, CC, and CML ranged from 0.5 to 1.4, 0.46-4.39, and 0.43 to 3.24 mg/L, respectively. The removal of DOC has been improved in CML than the other two systems. This improvement in DOC removal was seen in lower entry COTs that can be attributed to the increased collision rate in CML.

Figure 4 - Percentage of TOC removal as a function of incoming TOC at different turbidity values (Saxena et al, 2020).



UV254 Removal

The UV 254 portion of the DOC is understood to be the macromolecular hydrophobic portion, composed mainly of organic aromatic compounds. Intensified coagulation has been reported to act on both NOM fractions (hydrophobic and hydrophilic) when pH is optimized and removal occurs predominantly by load neutralization and lower by sweep coagulation (SAXENA; BRIGHU; CHOUDHARY, 2020). In the research presented by saxena; Brighu; Choudhary (2020), the pH was alkaline and therefore the removal of hydrophobes may have been favored at high pH and the dominant mechanism may be adsorption and coagulation by sweep.

UV254 removal increased with the increase in input TOC for both processes (Table 4).

Table 4 – UV254 removal as a function of the incoming TOC.

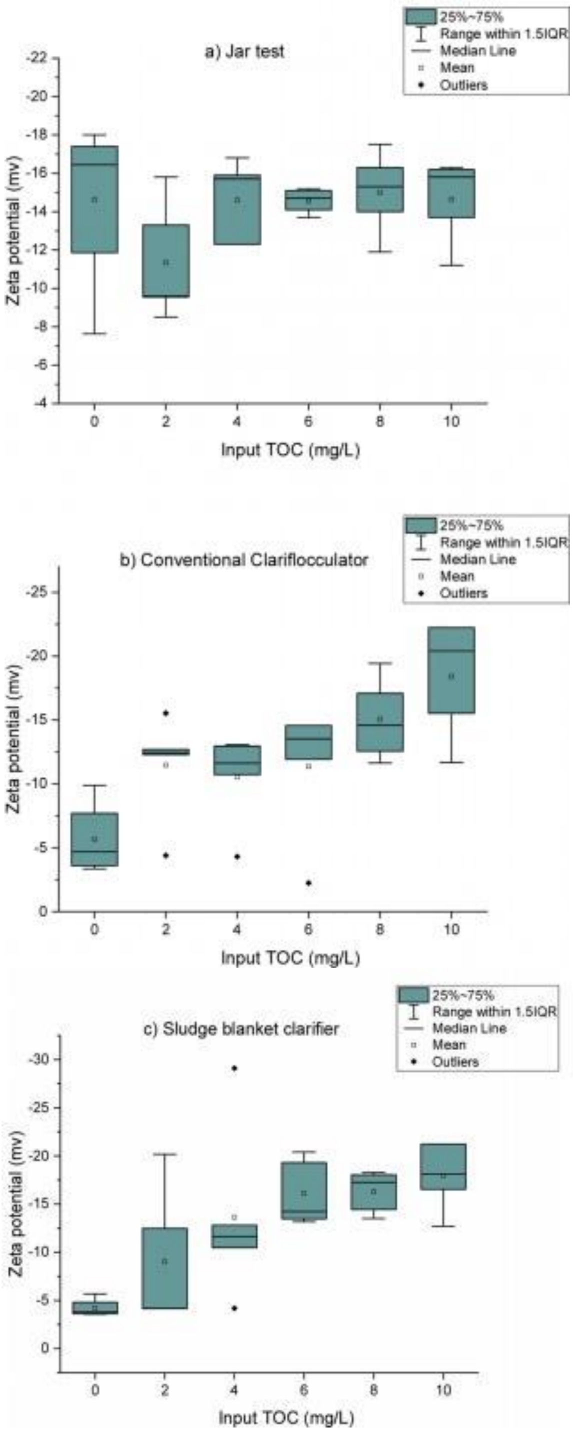
Input COT	CC	CML	In Test
2	72-80%	75-80%	- DC 8% less efficient than JT - CML 7% less efficient than JT
4	80-82%	79-85%	
6	86-89%	79-91%	
8	79-88%	86-89%;	
10	82-89%	77-90%	

Zeta potential

Zeta potential measurement is important to the coagulation process as it is indicative of the surface potential of the colloidal system and can be used effectively to measure changes in impurity load in water or coagulation destabilization efficiency (SAXENA; BRIGHU; CHOUDHARY, 2020). The Zeta potential also provides insights into prevalent mechanisms. After coagulation, the zeta potential of the jar, CC and CML tests ranged from −7.63 to −18.00, −3.36 to −22.23 mV and −3.57 to −21.23 mV, respectively.

In the case of the jar test, the zeta potential is quite similar with the increase in the input TOC. However, it can be seen that the zeta potential is more negative for the samples with high TOC input for both pilot plants (Figure 5). This indicates that the effect of the concentration of the incoming particle is more pronounced in the case of pilot plants. At lower particle concentration, the charge neutralization mechanism was dominant and resulted in a decrease in the negative charge of impurities. However, no full load neutralization was observed. The charge neutralization mechanism is known to occur at low colloidal concentrations and low coagulant doses. As TOC input increased, the load neutralization mechanism decreased, as evidenced by the higher negative zeta potential of the treated water, denoting other mechanisms involved.

Figure 5- Zeta potential after treatment for (a) Jar test, (b) CC and (c) CML;



REACTION MECHANISMS

The removal mechanisms in the coagulation and flocculation process may depend on pH/alkalinity, type of impurities (hydrophobic/hydrophilic colloids), particle concentration (high or low turbidity or TOC), type of coagulant (conventional/pre-polymerized) and its dose. A number of mechanisms are at play simultaneously in a system. The aggregation mechanisms through which particles are removed are essentially a combination of charge neutralization, trapping

In a study by Saxena; Brighu; Choudhary (2020), the impurities were mainly hydrophobic inorganic turbidity, hydrophobic organic matter, and hydrophilic organic matter. The pH was alkaline and the coagulant used was pre-polymerized PACl with relatively stable speciation when compared to conventional coagulants, which is not impacted by variable pH conditions.

The mechanisms of removal of organic and inorganic impurities were studied using four isotherms by linear as well as nonlinear modeling: Langmuir, Freundlich, Temkin and BET isotherms. Determination coefficient R2 closer to 1 and lower RSME (Root Mean Square Error) were used to evaluate the best fit, linear and nonlinear, respectively.

According to Saxena; Brighu; Choudhary (2020), the mechanisms for the bench-scale studies were a combination of charge neutralization, adsorption, and entanglement and the isotherms followed the BET model, which is a multilayer model physical adsorption.

In this study, there are two types of pilot plants, which differ in flocculation mode. In the case of the conventional clarichlorinator, the aggregation happens by mechanical slow mixing by a rotary impeller and in the sludge blanket clarifier the aggregation happens by hydraulic mixing.

The CML at 0-15 UT turbidity fit the BET model, predominantly physical and multilayer NOM adsorption initially; CML at 20 UM fitted the Temkin model, as turbidity increases the adsorbate-adsorbate interactions become dominant indicated by the Temkin model, causing impurity trapping; In the case of a sludge blanket clarifier, there is a high solids concentration rate in the mat at higher turbidity promoting contact opportunities significantly between the particles.

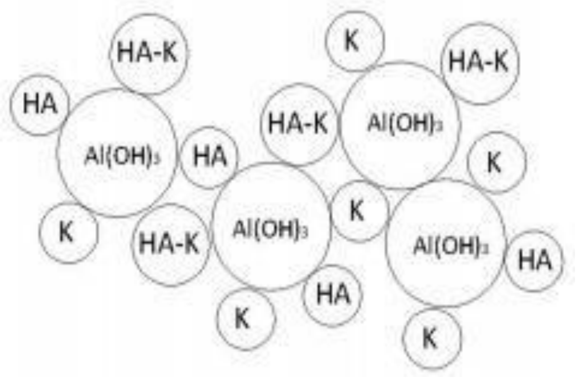
According to Srivastava; Brighu; Gupta (2020), the flake contraction and expansion blanket in a CML provides a fluidized zone of high concentration of solids treatment, which stimulates nucleation, providing surface sites, increases the flake detention time, and excess of Al species may occur, thus reducing the effect of load neutralization by Alb or Ala species and promoting adsorption and entanglement in the growing precipitate in CML. These individual allied/combined processes can help in reducing the turbidity of clarified water.

For CC, the values of R2 <0.9 and were not as high as CML, indicating the prevalence of some other mechanisms that may be load neutralization or complexation by preformed Alb species. The CC RMSE values were lower in the case of the Langmuir model for 5, 10 and 15 NTU, indicating physical and chemical adsorption in monolayer. At 20 NTU, the RMSE was the lowest for the Freundlich model, indicating multilayer physical and chemical adsorption. The prevalence of chemical adsorption indicates the dominance of load neutralization in CC, unlike CML. It is also interesting to note here that more residual DOC was found in the case of CC and the withdrawal of

DOC was better in the case of CML. The prevalence of load neutralization in CC can result in the formation of soluble complexes that could not be established and result in high DOC in CC.

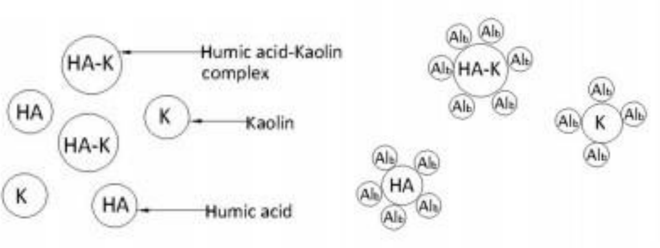
In general, for hydrophobic colloids at alkaline pH, the mechanism may be adsorption followed by entanglement of impurities in the rising precipitate. As the precipitate is formed, it is first adsorbed on the impurities by the Vander Waal forces causing charge neutralization which is also known as the NCP (precipitation load neutralization) mechanism and as the precipitate continues to grow the presence of $Al(OH)3$ species can cause the entrapment of particulate colloids, both organic and inorganic (Figure 6). Not only that, the presence of $Al(OH)4^-$ at alkaline pH can cause bridging between two positive spots of the coagulant absorbed in the impurities.

Figure 6 – Adsorption and entanglement mechanisms favored by the NCP process (SAXENA; BRIGHU; CHOUDHARY, 2019).



At the same time, the removal of dissolved or hydrophilic species can occur by the PNC (precipitation by load neutralization) model. The role of electrostatic forces is vital for the removal of hydrophilic colloids as the physical forces of attraction or the Vander Waal forces may not be effective in coagulating such impurities. It was observed that at low TOC input, DOC removal was better, resulting in lower DOC residual and lower negative zeta potential . The presence of Al b species may be responsible for complexing and neutralizing hydrophilic impurities and then causing them to co-precipitate (Figure 7). This precipitate can form a bridge with the other, which can be explained by the electrostatic coagulation model in which the positive part of coagulant adsorbed on one particle can interact with the exposed negative surface of the other particle.

Figure 7 – Complexation interactions between impurities (a) and neutralization of Al charges with impurities (SAXENA; BRIGHU; CHOUDHARY, 2019).



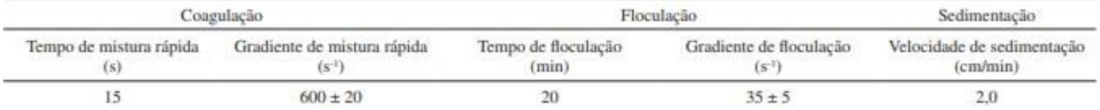
(a)(b)

In summary, the removal mechanisms in a sludge blanket clarifier could be essentially tangle of impurities in the dense sludge blanket with higher prevalence of the NCP model. For CC, the adsorption of Al(OH)3 amorphous precipitate and gradual growth precipitate, i.e., initial PNC and then NCP, to favor the entanglement of impurities could be the removal mechanism.

REMOVAL OF MICROCONTAMINANTS – DICLOFENAC – MECHANISMS

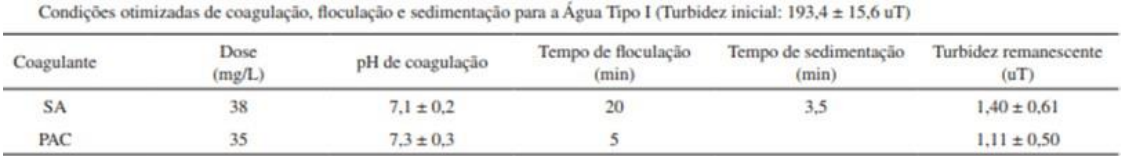
Lima et al., (2014) evaluated the removal of some drugs, including diclofenac, by the clarification process (coagulation, flocculation and sedimentation). The process was carried out on a bench scale using a jar test with characteristics presented in Figure 8. The presence in two types of waters, with higher and lower turbidity, and two different coagulants, polyaluminum chloride ((Aln(OH)mCl3 - PAC) and aluminum sulfate (SA) (Figures 9 and 10) were also evaluated. The results showed low diclofenac removals, with an average of 9% and 7% for PAC and SA, respectively.

Figure 8 - Conditions of the clarification used.



Coagulação		Floculação		Sedimentação
Tempo de mistura rápida (s)	Gradiente de mistura rápida (s^{-1})	Tempo de floculação (min)	Gradiente de floculação (s^{-1})	Velocidade de sedimentação (cm/min)
15	600 ± 20	20	35 ± 5	2,0

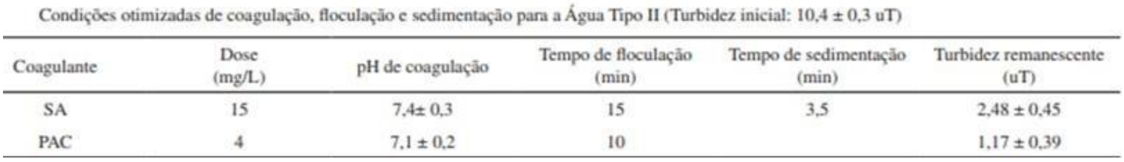
Figure 9 - Optimal clarification conditions for Type I water



Condições otimizadas de coagulação, floculação e sedimentação para a Água Tipo I (Turbidez inicial: 193,4 ± 15,6 uT)

Coagulante	Dose (mg/L)	pH de coagulação	Tempo de floculação (min)	Tempo de sedimentação (min)	Turbidez remanescente (uT)
SA	38	7,1 ± 0,2	20	3,5	1,40 ± 0,61
PAC	35	7,3 ± 0,3	5		1,11 ± 0,50

Figure 10 - Optimal clarification conditions for Type II water



Condições otimizadas de coagulação, floculação e sedimentação para a Água Tipo II (Turbidez inicial: 10,4 ± 0,3 uT)

Coagulante	Dose (mg/L)	pH de coagulação	Tempo de floculação (min)	Tempo de sedimentação (min)	Turbidez remanescente (uT)
SA	15	7,4± 0,3	15	3,5	2,48 ± 0,45
PAC	4	7,1 ± 0,2	10		1,17 ± 0,39

The higher percentage of removal with the use of PAC can be explained by the mechanism of floc formation. The formations of positive species are responsible for promoting the destabilization of the particles, ensuring the formation of flocs and, in the case of the use of SA, in general, they form Al(OH)2 +; Al(OH)2+; Al2(OH)2 4+; Al3(OH)2 5+ and Al13O4(OH)24 7+ (or "Al13")

However, these authors state that polyaluminum chloride already contains highly charged positive species, such as "Al13", in high concentration in the form of salt. Thus, its dependence on hydrolysis reactions is not characterized, its dissociation in water is sufficient. They also state that in the presence of CAP, the velocity and size of the flakes are greater than those observed when using SA.

According to Lima et al, (2014), the processes of removal of microcontaminants may be linked to the adsorption mechanism in the formed flakes. If the predominant removal mechanism is adsorption, it is possible that it is due to chemical interactions for most of the microcontaminants studied. The basis of this hypothesis can be supported by analyzing the zero load point (PCZ) values of the sludge generated by both coagulants. The PCZ values of the generated sludge (PCZ = 7.90 for PAC and PCZ = 7.75 for SA) were higher than the coagulation pH, indicating that the surface loads of the sludge flakes under the working conditions were slightly positive.

As the pka 4,15, DCF is lower than the coagulation pH, indicating that it has an acidic character and is in the deprotonated form, that is, they have a negative charge in solution. Such behavior strengthens the hypothesis of electrostatic interactions between the sludge generated in the clarification stage. However, DCF has only one acidic hydrogen, with pKa1 = 4.15, which gives it only a negative charge on the coagulation pH, which disfavors effective removal.

In another research conducted by Huang et al., (2019), the clarification step was also evaluated on a bench scale in the removal of diclofenac in water with pH 7.4. The amount of coagulant alum and reduction of turbidity were evaluated. The maximum total removal of residual turbidity occurred at an alum dosage of 60 mg/L, when the removal efficiency of the DCF compounds was 18.5%, in contrast to a 27% reduction in UV 254 and a 17% reduction in DOC.

The mechanism of removal of target compounds by coagulation has been mainly attributed to co-precipitation and adsorption. Co-precipitation allows the incorporation of soluble target compounds, especially anionic species, into an increasing phase of aluminum hydroxide by inclusion or occlusion.

Therefore, Al hydroxide flakes should be positively charged under moderately acidic to neutral conditions. How DCF exists as anions in the neutral solution. Electrostatic attraction plays an important role in the interaction between positively charged Al hydroxide flakes and anionic DCF. In addition, a certain fraction of DCF was transferred from the aqueous phase to the solid phase through co-precipitation. It was also observed that the efficiency of removing DCF in solution increased with the increase in coagulant dosage.

The interaction between NOM and the target compounds may affect the adsorption of the contaminantates on Al hydroxide flakes. The different removal rate of residual turbidity and target compounds suggests that the target compounds were not removed with suspended solids during the coagulation-flocculation-sedimentation process by alum at the dosage of 0 to 100 mg/L. Coagulation of suspended solids results mainly from physical collisions and aggregation. However, the removal of soluble organic contaminants through coagulation depends mainly on their adsorption on Al hydroxide flakes (HUANG et al., 2019).

CONCLUSION

The solids contact unit as a sludge blanket clarifier offers a combination of processes such as mixing, flocculation, and clarification in a zone with high surface overflow rate, thereby reducing reactor size, mechanical impeller requirement, and area. The use of CMLs may be advantageous for waters with high DOC., however, for waters with low DOC and TOC and especially inorganic turbidity, conventional clarifiers may be a better choice.

Some differences were pointed out in the mechanism. CC showed a prevalence of load neutralization or complexation of Al13 species and subsequent chemical and physical adsorption in monolayer and multilayer for higher turbidity. In the CML mechanism, physical adsorption in multilayer prevailed and due to the sludge blanket, it maintains a high concentration of solid, favoring contact, providing a surface also providing entanglement.

In view of the discussions of diclofenac removal in jar test, the main mechanisms reported were co-precipitation and adsorption in flakes formed, mainly in Al hydroxide.

Thus, analyzing the mechanisms of CC and CML and DCF in jar test, it can be influenced that DCF would also have low removal in these processes responsible mainly for adsorption, due to its negative characteristics in the pH of activity and having only one ionizable site being less favored than the other molecules in the medium, in addition, The formation of precipitates and aggregation of other compounds can compete with the area required for adsorption.

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