COAGULATION-ADSORPTION-FLOCCULATION PROCESS TO REGENERATE CIP SOLUTIONS. EFFECT ON THE PHYSICOCHEMICAL AND CLEANING PROPERTIES OF REGENERATED SOLUTIONS

Mehdi DIF [(a)], Olivier BARRAULT [(a)]

[(a),]Elodys International, Allé du lac Bleu, Avrillé, France

md@elodys.eu,

ABSTRACT
The regeneration of Cleaning In Place (CIP) solutions presents an increasing interest for chemical industries (food, cosmetic and textile sectors) and sewage treatment plants.
For the industrial sector, the regeneration of cleaning solutions allows to perform economies of water and chemical reactants. It is also involved indirectly in the improvement of the industrial productivity by reducing the downtime of the production equipment destined to the CIP operation.
On the other hand, the operation of regeneration allows to reduce global costs, in sewage treatment plants, of used solutions rejected by CIP units. Indeed, for the dairy industry, this volume can be up to 95% of the rejected volume to treatment plants. The present study exposes a new regeneration method of CIP solutions using sequences of adsorption-coagualtion-flocculation processes, coupled with a physical separation by decantation, flotation or membrane filtration

Keywords: Adsorption, Caustic soda, Cleaning-in-place Green chemistry, Regeneration

1. INTRODUCTION

Cleaning In Place (CIP) procedures are widely used, especially in the pharmaceutical and food industries, in order to ensure food hygiene and product safety as a whole (Gillham et al., 1999). The use of water and chemical reagents required for these cleaning operations have significant economical and environmental impacts. For the industrial sector, the regeneration of cleaning solutions allows to perform economies of water and chemical reactants by changing the cleaning sequences while maintaining constant the process efficiency. The improvement of the industrial productivity by reducing the downtime of the production equipment allowed to the CIP operation is also of concern. Besides, the operation of regeneration allows to reduce the process global costs, in sewage treatment plants, of used solutions rejected by CIP units. The volume of these effluents varies with the type of the process production and the nature of the treated products. Indeed, for dairy industries, processing 10^6 L of milk per day, up to 5 L of effluent per 1 L of processed milk are generated and 54 to 98 % of this volume comes straight from CIP units. In most cases the replacement of the CIP solutions is based on subjective criteria, such as color or odor and can be related to the characteristics of the equipment to be cleaned (Alvarez et al., 2007; Gésan-Guiziou et al., 2007). Different works have been carried out in order to investigate techniques used in the regeneration of cleaning solutions. Dresch (1998) studied sedimentation and centrifugation processes. Membrane filtration, such as microfiltration (Tragardh andJohansson, 1998), ultrafiltration (Dresch et al., 1999) and nanofiltration (Räsänen et al., 2002), have been tested. The present study highlights a new regeneration method of CIP solutions using sequences of adsorption-coagulation-flocculation processes and coupled with a physical separation by decantation. The chemical nature of effluents (strongly acidic or alkaline pH) and the extreme temperatures (70 °C to 75 °C) do not allow the application of reactants commonly used in water purification by physicochemical treatment, such as aluminium sulphate ($Al_2(SO_4)_3$), ferric chloride ($FeCl_3$) or ferrous sulfate ($FeSO_4$ $7H_2O$). Indeed, the coagulation of suspended solids in an aqueous solution is only possible within a defined pH range for each type of coagulant (pH values above 4 for ferric chloride and between 6 and 7 for aluminium sulphate). Studies led by Dif et al. (2013) based on a patent filed by Tastayre (2010) have made it possible to remedy this problem by using crude clay minerals as adsorbent/coagulant reagent. It has been demonstrated that clays such as montmorillonite, kaolinite and bentonite operate either by reducing electrostatic repulsion forces between the particles and thereby increasing the contribution of attractive van der Waals forces in the coagulation of suspended particles, or by adsorption and sequestration of suspended particles (Lagaly and Ziesmer, 2003). Assaad et al. (2007) showed the capacity of Smectite to coagulate at low concentrations in the solution. This effect is also advantageous in the recycling of CIP solutions due to the entrainment of pollutant particles by clay aggregates. Indeed,
Dif et al. (2013) demonstrated that the treatment effect of Smectite can operate over the whole pH range. It was shown that acidic pH causes destabilization and agglomeration of the adsorbent, which in turn induces the precipitation of the adsorbate and increases the

amount of organic matter removed from the CIP solution by carryover mechanisms in addition to the adsorption mechanism. At alkaline pH, the Smectite adsorbent still has a coagulative effect that contributes to global process efficiency by adsorption and carryover of the organic matter. Smectite thus emerges as a compound of choice for processing alkaline CIP solutions (Dif et al., 2013). Moreover, Delgado et al. (1986) and Kalra et al. (2003) have shown that characteristics (pH and ionic strength) inherent to polluted solutions significantly modify the physicochemical properties (average diameter and zeta potential) of complexes of clay-organic/inorganic pollutants and the electrostatic interactions governing adsorption at the clay surface. It would be productive to explore these parameters in order to increase treatment process efficiency.

To save on the water and chemical reagents needed to clean CIP solutions, the recycling operation should be performed several times to increase the profitability of the process. This requires that any residual organic and inorganic matters in the regenerated CIP solution do not contribute to equipment contamination. Indeed, cleaning efficiency is dependent on various parameters such as surface roughness, physicochemistry (Jullien et al., 2008) of the equipment, cleaning procedures and operating conditions. However, the physicochemical properties of the cleaning solution remain the most determinant parameter (Eide et al., 2003). Likewise, the disinfectant properties of CIP solutions remain crucial for qualifying cleaning procedures as hygienic. The aims of this work are multiple. First, the principle of a recycling process combining adsorption/coagulation and flocculation mechanismswas tested over several cycles on caustic soda and nitric acid CIP solutions soiled by whole milk. Physicochemical characteristics of regenerated solutions, such as total chemical oxygen demand (COD_T), total nitrogen content, surface tension and the loss of active material (acid or base) were tracked over time.

Based on these analyses, the efficiency of the recycling treatment process and its impact on CIP solutions was assessed. Second, the impact of multiple regenerations of caustic soda solutions on cleaning quality was investigated. Microbiological analyses were performed on stainless steel surfaces contaminated with bacteria and spores recognized as highly CIP-resistant. Finally, the solubilizing power of the regenerated CIP solutions on organic matter was tested by running the cleaning operation on soiled stainless steel surfaces fouled with sour cream.

2. MATERIALS AND METHODS

2.1. The adsorbate

The coagulation/adsorption tests were carried out, firstly on pure compounds of casein, lactose and triglycerides (vegetable fat). This product is often found, in significant amounts, in the dairy CIP solutions after cleaning process (Condat-ouillon; 1995). On the second time, analyzes were performed on whole milk in order to put forward potential cross-effects between the different compounds mentioned above on the treatment process.

2.2. The adsorbent

Analyses were performed with the Smectite (Elofloc 2-1, Elodys International, France) at the crude state. The sieving technique was carried out in order to select particle sizes between 40 and 80 μm, and thus to homogenize the clay suspensions used for adsorption tests. The flocculation step was performed using a cationic polymer with high molecular weight (D9645A, DESHENG, CHINA).

2.3. Regenerations of cleaning solutions

2.3.1. Treatment application on pure compounds

Regeneration cycles performed according to the reprocessing mechanism described by Dif et al. (2013) were investigated on a model of caustic soda (99% purity, VWR) and nitric acid (68% AnalaR NORMAPUR, VWR) CIP solutions presenting similar physicochemical properties to soiled those found in industry at the CIP unit outlet. In order to mimic cleaning conditions in the dairy industry, average concentrations of soda caustic and nitric acid solutions (i.e. 2% w/w or 0.53 M and 0.45 M M concentration, respectively) were used as reported by Räsänen et al. (2002) and Alvarez (2003).

Fig. 1 presents the setup for regeneration of CIP solutions. The reprocessing procedure consists in heating the acid or basic solutions to typical CIP station temperatures, i.e. 80 °C for sodium hydroxide solution and 60 °C for nitric acid solution (Ricketts, 2008).

Smectite and flocculant were used in optimal amounts as determined earlier. Regeneration experiments were carried out at 50 °C and the Smectite and flocculant were added after a 3 min time step. After the treatment steps, the suspended particles are separated from the liquid phase by sedimentation for 30 min.

Each regeneration cycle lasts 1 h 30 min, which corresponds to combined duration of heating, cooling and decantation. Added to this time is the 20 min duration of the centrifugation step used to process by-products. After each regeneration, the by-products recovered at the bottom of the decanter are centrifuged for 20 min at 15,000 g (10,000 rpm). This procedure recovers the supernatant, to be reintroduced into the initial solution, and the compact sludge, at 21% dry matter. Volume of treated solution is measured after each recycling cycle. This procedure tracks solution loss during processing and separation. Solution loss is estimated at 5% of the initial volume at each regeneration cycle, so this amount is added before each new recycling cycle in order to keep constant the treatment conditions. Reprocessing efficiency was monitored on regenerated solutions by measuring the

turbidity, COD_T (soluble and insoluble) and total nitrogen (TN) content of the treated solutions.
Photometric test kit method was applied for COD_T and TN measurements.

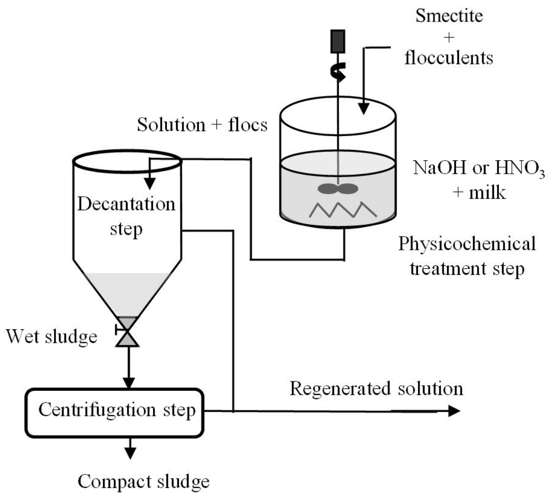


Figure 1 : Regeneration setup

2.3.2. Analysis of the cleaning capacity of the regenerated solutions

Analyses were led in order to study the cleaning and disinfection performance of regenerated solutions (R5, R10, R15, and R20). For each test, the solutions were compared against freshly prepared solutions (R0). First, efficiency of the regenerated solutions was checked by studying the cleaning kinetics of stainless steel tubes fouled with dairy cream. This was achieved by monitoring solution turbidity during the cleaning cycles to identify both rate of soiling detachment and ability of the solution to solubilize the fouling matter. Figure 2 depicts the setup used in this part.

2.3.3. Analysis of the effect of regeneration on fouled tube cleaning kinetics

The cleaning efficiency of regenerated solutions on organic and inorganic fouled matter was assessed using kinetics analysis on pipe walls (316 L stainless steel, polished inside to an average surface roughness Ra of ≤ 0.8 µm) cleaning. Turbidity measurements were used as parameter characterizing fouled dairy cream detachment and solubilization from the stainless steel surfaces, which was made possible due to the good solubility of fat matter in alkaline solutions. Triplicate experiments were performed on three separate tubes (L = 140 mm, inner Ø 23 mm) presenting very similar characteristics to tubes used in the food industry.
The fouling procedure consists of placing steel tubes, containing 13 g of dairy cream spread perfectly evenly throughout, in an oven at 130°C for 1 h 30. Each tube was turned every 15 min to evenly distribute the cream. The tubes were then reintroduced into a second oven at 100°C for 20 min. The fouled tubes were then fitted into the CIP installation at the test section designed as illustrated in Figure 2. This setup creates a modular system able to operate reduced volumes of cleaning solutions (10 L) using tank 3 (Figure 2). Experiments consisted in starting the cleaning step with tank 1 (30 L) and quickly switching the rig to tank 3 in order to concentrate the detached matter and thus assay solution turbidity during CIP cycles. Trials were performed with regenerated CIP solutions (R5, R10, R15 and R20) at 50-55°C for 30 min at 1500 $L.h^{-1}$. This time interval was set to be consistent with the fouled pipe preparation conditions and CIP procedure that enable good cleanability of pipe walls. Indeed, preliminary tests carried out with various solutions showed that surfaces are well cleaned after 10 min. Comparisons were made against freshly prepared solutions (R0) under the same conditions. Turbidity was measured at the outlet of tank 3 using a Hach 2100 turbidimeter (Hach Company, USA).

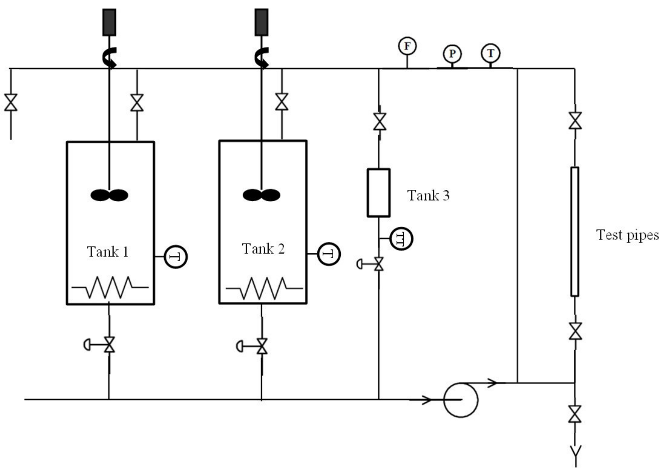


Figure 2: Diagram of the experimental setup

3. RESULTS AND DISCUSSIONS

3.1. Identification of optimal treatment reactant concentrations

Development of physicochemical regeneration of CIP solutions requires the identification of optimal treatment concentrations of Smectite and flocculant. Thus, the turbidity of regenerated solutions is chosen as a criterion of comparison between tests. This characterization method is considered as a reliable and easily implementable for reproducible process scale-up.
Figure 3 plots turbidity as a function of both Smectite (1.5 to 3 $g.L^{-1}$) and flocculant (1 to 25 $mg.L^{-1}$) concentrations applied to 2% (w/w) NaOH solutions soiled with 1% (v/v) whole milk.
Turbidity measurements on the supernatant, for each sample, were used to identify optimal cross-concentrations of Smectite and flocculant. At low flocculant concentration, turbidity decreased rapidly at

clay concentrations from 1.5 to 4 g.L^{-1} then increased or stabilized as higher concentrations (Fig. 3).

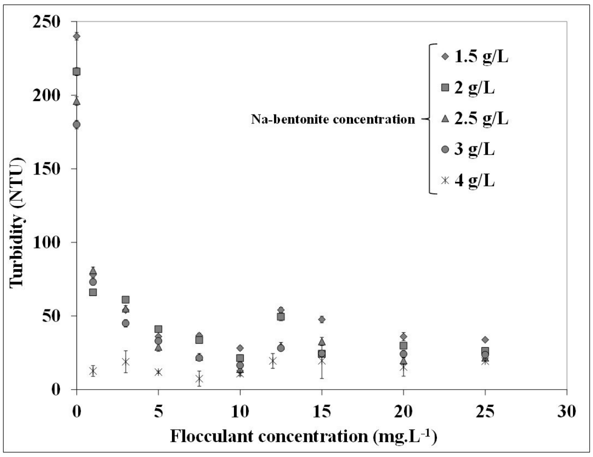


Figure 3: Effect of reactant concentrations on turbidity in NaOH regenerated solutions

The slight increase beyond the concentration of 10 g.L^{-1} is likely driven by the reactants and not contamination in the solution, as the water treatment literature reports that an overestimation of the flocculant and coagulant amount used in the physicochemical depollution induces an increase in turbidity of the medium caused by excess reactants remaining in suspension in the medium (Assaad et al., 2007). A clay concentration of 3 g.L^{-1} is considered sufficient to adsorb or carryover the pollution contained in the solution according to the mechanisms described by Dif et al. (2013). Beyond this concentration, small particles of clay that have not interacted with the pollutant matter remain in suspension in the solution. Thus, a Smectite concentration of 4 g.L^{-1} yields low turbidity values but increases experimental variability (see the larger standard deviations in Fig. 3) due to an excess of clay relative to the actual pollution content. The overestimation of the amount of flocculant able to facilitate and speed up the decantation of formed aggregates also induces an increase in turbidity of the NaOH solutions, highlighted by the significant standard deviation values observed at the flocculant concentration of 15 mg.L^{-1}. Thus, successive regenerations of NaOH solutions will be conducted using concentrations of 3 g.L^{-1} Smectite and 10 mg.L^{-1} flocculant (D9645C, DESHENG, CHINA).

The same approach was used to determine optimum concentrations for nitric acid reprocessing (results not shown in this work). The lowest turbidity was obtained for concentrations of 2.5 g.L^{-1} Smectite and 30 mg.L^{-1} flocculant (F9907A, DESHENG, CHINA). These concentrations will be used in further successive regenerations of nitric acid CIP solutions. The use of flocculant at high concentration, in comparison to the treatment of NaOH solutions, can be explained by the pH effect on the soluble fraction of the pollution. As described by Dif et al. (2013), the acidic pH induces soluble matter precipitation, in addition to the dispersion of particles present in the solution. Thus, the decantation of these particles needs the utilization of high flucculant concentration compared to the basic pH.

3.2. Successive regenerations of cleaning solutions

Successive recycling tests were performed using the same 2% (w/w) NaOH or nitric acid solutions several times in ageing and recycling cycles. The purpose of these trials was to systematically investigate the effect of the regeneration process on the composition and characteristics of cleaning solutions over successive ageing and recycling cycles. Since turbidity measurements alone are not sufficient to analyse the process efficiency, residual COD_T and TN measurements were applied on both acid and alkaline solutions.

3.2.1. Successive regenerations of soiled NaOH solutions

The COD_T present in NaOH solutions was monitored along the successive regeneration cycles before and after reprocessing to determine the COD_T reduction rate after each cycle and COD accumulation in successively regenerated solutions. Figure 4 shows initial and residual COD_T and total nitrogen (TN) at each regeneration cycle, where initial COD_T or TN corresponds to calculated values of pollution induced by the addition of 1% (v/v) whole milk.

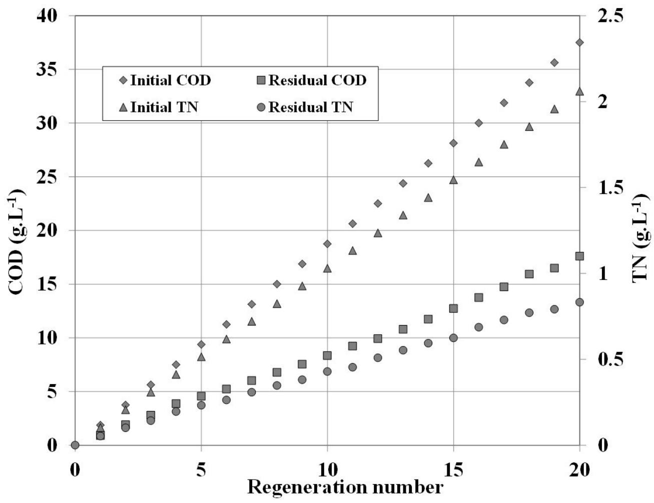


Figure 4: Initial and residual COD and TN of NaOH solutions over successive regeneration cycles.

Repeat addition of milk induces an increase in COD_T of 1.9 g.L^{-1} at each cycle. COD_T reduction rate, i.e. the ratio of removed COD_T to accumulated COD_T, was calculated after each regeneration cycle. The obtained values reveal that about half of the COD_T is removed at each cycle. The physicochemical regeneration reprocessing substantially eliminates all suspended and colloidal solids. Reduction in solution turbidity after recycling is better than 95% of the initial value. End-of-treatment turbidity values were between 5 and 20 NTU (Fig. 5). This result shows that the increase in COD_T values is due to the accumulation of a fraction of the soluble organic matters partially removed by the treatment process, and confirms the results obtained by Dif et al. (2013) on the adsorption of soluble casein molecules by the Smectite particles. Adsorption experiments performed by Dif et al. (2012) showed the physicochemical reprocessing with Smectite which removes the milk triglycerides and proteins fraction but not the lactose fraction. Indeed, the values of total carbon before and after treatment remain unaltered, which indicates that most of the COD_T accumulated in the regenerated solutions originates in lactose addition besides residual fat and proteins. This is supported by a study performed by Dresch (1998) on the regeneration of CIP solutions rejected by the dairy industry, which highlighted the contribution of fat matter to the increase in COD_T values in NaOH solutions since the skimmed milk/COD_T ratio was 1.8.

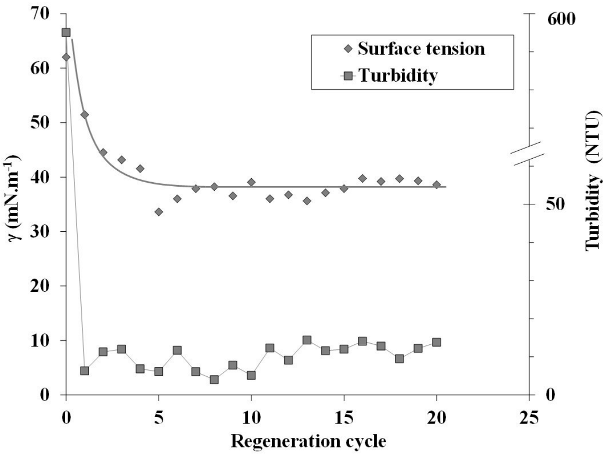


Figure 5: Surface tension (mN m^{-1}) and turbidity (NTU) of NaOH solutions (NTU) over successive regeneration cycles

The amount of nitrogenous matter contained in regenerated solutions is also evaluated using the photometric test kit method.

Preliminary tests of freshly prepared NaOH solutions (without milk), in which Na-bentonite and flocculant are added at the optimum concentrations, showed the absence of nitrogenous matter in the medium. Thus, the residual TN contained in regenerated solutions is due to the remaining proteinaceous matter after treatment and not to the excess of flocculant. Figure 4 shows the evolution of initial and residual total nitrogen contents for different regeneration cycles. These test results suggest that an accumulation of proteinaceous matter occurs through regeneration cycles even though about 60% of total nitrogenous matter is removed at each cycle (Figure 4). Dif et al. (2013) showed that Na-bentonite treatment of caustic soda solutions containing casein is incomplete, as 50% of soluble proteins initially introduced remains in the solutions subsequent to each regeneration cycle, which closely matches the results here observed. The reduction rate stabilizes at the 6^{th} regeneration. Under the imposed process conditions, this plateau (60%) is likely due to solution saturation with surfactants due to saponification of the fat matter and degradation of the protein matter. Figure 4 also shows that the amounts of COD_T and total nitrogen in regenerated solutions similarly evolve. However, Dif et al. (2012) found that the effectiveness of the physicochemical treatment is not the same for casein, lactose or triglyceride molecules. As molecules of lactose have a low molecular weight compared to proteins and TG, lactose molecules are less efficiently discarded by adsorption and coagulation processes. Accordingly, along successive regenerations a higher increase in COD_T content relative to TN is expected. This result shows that during treatment, aggregations of various compounds found in the solution may occur due to the action of the Na-bentonite and that matter removal is achieved by decantation and carryover regardless the nature of compound (Dif et al., 2013). This hypothesis is supported by Condat-Ouillon (1995) who showed that a fraction of proteins aggregates into larger particles, being associated to fat, will eventually sedimentate.

Modifications of the composition and physicochemical properties of regenerated solutions were observed by monitoring wetting properties based on surface tension measurements. Fig. 5 shows that surface tension decreases monotonously during the five first cycles of regeneration and then stabilizes at around 35 – 40 mN.m^{-1}. The initial value features the surface tension of freshly-prepared 2% (w/w) NaOH solution. The decrease of this value is due to the accumulation of surfactants formed by amino acid degradation products resulting from the saponification of lipids and other molecules that, under these pH and temperature conditions, are hydrolysed and form surfactant molecules (Condat-Ouillon, 1995).

These results confirm findings by Alvarez et al. (2007) showing a decrease in surface tension throughout regenerations of CIP solutions by membranes processes. The slow saponification of fat matters in alkaline medium allows the formation of glycerol and fatty acid salts (soap) which further contribute to this phenomenon.

According to Condat-Ouillon (1995), only 34% of fat matter is saponified after 8 h of reaction between fat matter (0.5 g L_1) and caustic soda (2% w/w) at 80 _C. The stabilization of surface tension at the 5th regeneration could be related to the critical micelle concentration (CMC) reached in the solution due to the accumulation of surfactants. Indeed, surfactant molecules have the ability to self-associate above a critical concentration called critical micelle concentration (Akisada et al., 2005) and thus form macromolecular aggregates of a few nanometers in diameter, called micelles.

Beyond this CMC, the chemical potential of the surfactant remains almost constant. Thus, any surfactant added beyond the CMC is associated to micelles. The surface tension at the CMC is therefore the lowest surface tension attainable.

To sum up, tests performed on soiled NaOH solutions showed that using Na-bentonite as a reagent in alkaline detergent treatments makes it possible to adsorb and trap substantially all of the particulate pollution and a large fraction of the soluble pollution (more than 60% of COD_T at each cycle). The active matter is preserved up to 97.5%. Surface tension measurements on regenerated caustic soda solutions showed stabilization at around 35 $mN.m^{-1}$ from the 5th regeneration, corresponding to the CMC. The effect of decreasing surface tension on the cleaning properties of regenerated solutions was tested on stainless steel surfaces.

3.2.2. Successive regenerations of soiled HNO_3 solutions

The recycling protocol for nitric acid is substantially the same as that used to treat NaOH solutions, the only difference being the flocculation operation which uses a high-molecular-weight anionic polyacrylamide.

Measurements of HNO_3 concentration in regenerated acid solutions show a slight decrease in the molarity of nitric acid during the first two regenerations. For subsequent regenerations, the molarity loss can be considered as negligible due to the volume correction. Indeed, concentrations measured from the second regeneration were at 0.43 $mol.L^{-1}$ as compared to an initial concentration of 0.45 $mol.L^{-1}$. The turbidity measurements showed near-zero values from the first regenerated solution, which reflects the total elimination of suspended solids.

Efficiency of the treatment process through regenerations was also studied by monitoring COD and TN evolutions. Figure 6 shows a reduction of total COD down to 80% for the last regenerations (13 to 20). TN elimination rate was also good, at 58% of initial accumulated amount (Figure 6).

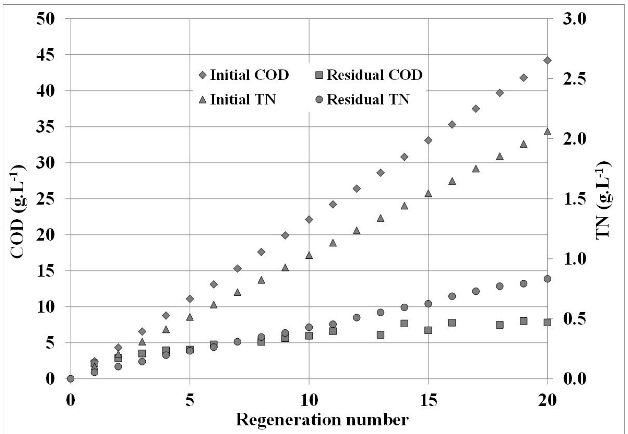


Figure 6: Initial and residual COD and TN of nitric acid solutions over successive regeneration cycles.

Compared to NaOH, nitric acid demonstrates a higher total COD reduction rate. This result can be explained by the elimination of most of the compounds present in the solution as a result of the acidic effect on matter precipitation. Dif et al. (2013) also found that during adsorption experiments on molecules of casein in acid medium, neutralization of the total protein charge at this pH directly impacts the solubility of the molecule, causing precipitation. This phenomenon is enhanced by the presence of clay particles.

3.3. Effect of successive regenerations on the cleaning and disinfection efficiencies of NaOH solutions

The recycling process combining adsorption-coagulation with flocculation allows cleaning solutions to acquire new physicochemical properties throughout the ageing process with an increase in total COD, by accumulation of the residual COD after treatment, and a decrease in surface tension. Here, is also investigated the effect of multiple regenerations on the detergent efficiency of NaOH solutions. Microbiological analyses were carried out on stainless steel pipes contaminated with bacteria and spores frequently isolated from dairy products and equipment surfaces.

3.3.1. Cleanability study on stainless steel pipes contaminated by *B. subtilis* spores under dynamic flow conditions

Trials under dynamic flow conditions were carried out on a CIP setup containing a hydraulic rig formed by 3 pipes previously contaminated with spores of *B. subtilis*. The cleaning step was operated using NaOH solutions freshly prepared or regenerated several times over.

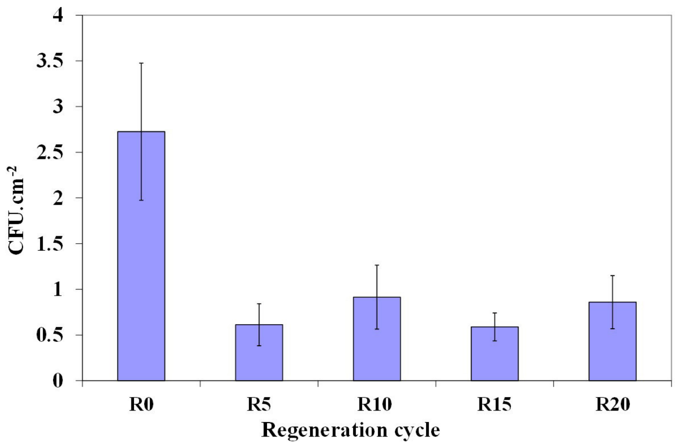


Figure 7: Residual contamination of stainless steel pipes after cleaning in dynamic flow conditions with freshly-prepared and regenerated NaOH solutions

This part of the study worked with moderate cleaning temperatures and flow rates in order to keep enough residual contamination after cleaning allowing comparison between disinfection properties of tested solutions. The aim was to quantify residual contamination after cleaning with fresh and regenerated NaOH solutions (Figure 7) and to compare the cleaning efficiencies of the solutions. Cleaning efficiency was evaluated by the ratio of residual contamination after cleaning to initial maximum contamination, which was fixed at 50 CFU.cm^{-2}. Results showed a high (> 95%) percentage of spores eliminated for all tested solutions, and that regenerated NaOH solutions maintained their efficiency against the sporulated form of *B. subtilis* as their bactericidal action was preserved through regenerations. Comparisons based on percentage of eliminated spores showed that regenerated solutions were actually more efficient than freshly-prepared solutions. Indeed, regenerated solutions posted cleaning efficiencies of between 97% and 99% whereas a freshly prepared NaOH posted spore removal rates of between 94% and 95%. This added efficiency could be due to regenerated solutions acquiring new physicochemical properties. Throughout the regenerations, residual organic matters remaining after regeneration induce a decrease in surface tension that allows better surface wettability and consequently faster cleaning than with fresh NaOH solutions. Finally, comparison between regenerations R5, R10, R15 and R20 does not allow us to draw firm conclusions on an increase in bactericidal effect of solutions with increasing in number of regenerations and, thereafter, accumulation of soluble matters. Analysis of the microbiological quality of regenerated solutions used in cleaning trials or inoculated with 10^5 CFU.mL^{-1} of *B. subtilis* spores showed that this strain can survive but in very low amounts compared to the amount initially introduced.

3.4. Study on fouled pipe CIP kinetics using freshly prepared and regenerated NaOH solutions

The detachment kinetics of matter (dairy cream) adhering to stainless steel pipe walls were investigated in response to regenerated solutions R5, R10, R15 and R20 and freshly-prepared solutions. Cleaning was performed using a reduced volume in order to concentrate the detached matter. Turbidity measurement was considered a good characterization parameter for both detachment and solubilization effects. Each regenerated solution was tested against a fresh solution in order to compare the results obtained under the same operating conditions.

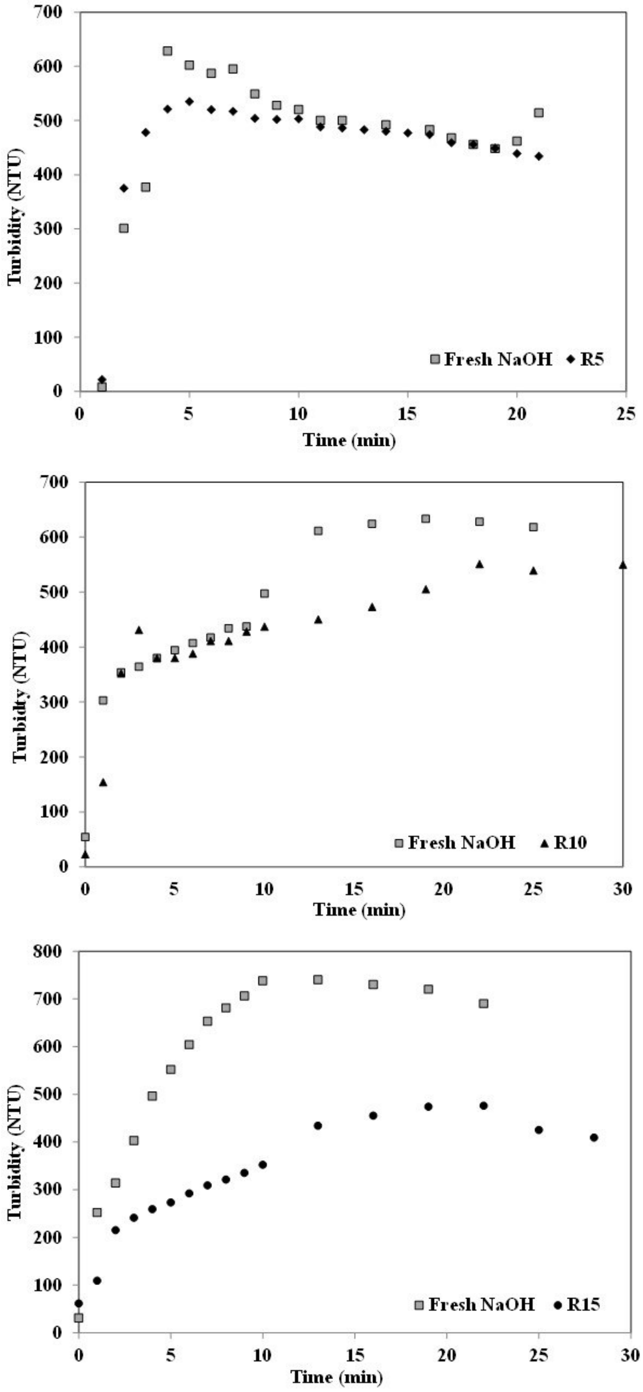
The different curves plotted (Figure 8) distinguish three phases in the cleaning kinetics:

- The first phase involves the detachment of weakly-adhered matter. During this phase (2 to 3 min), flow rate tends to stabilize, which explains the between-trial variation in turbidity,

- The second phase involves an increase in the turbidity in the different test solutions. This phase (lasting roughly 10 min) allows the detachment of all matters fouling the pipe walls,

- The third phase involves the solubilization of matters detached into the cleaning solutions. This solubilization occurs under the combined action of the agitation caused by solution circulating through the rig and the effect of thermal action of cleaning.

Figure 8 also shows that turbidity remains low in regenerated solutions compared to freshly-prepared solutions. Knowing that after 10 min of cleaning, all the matter adhering to the surface has detached, this result may be due to a larger solubilizing effect of regenerated solutions than freshly-prepared solutions.



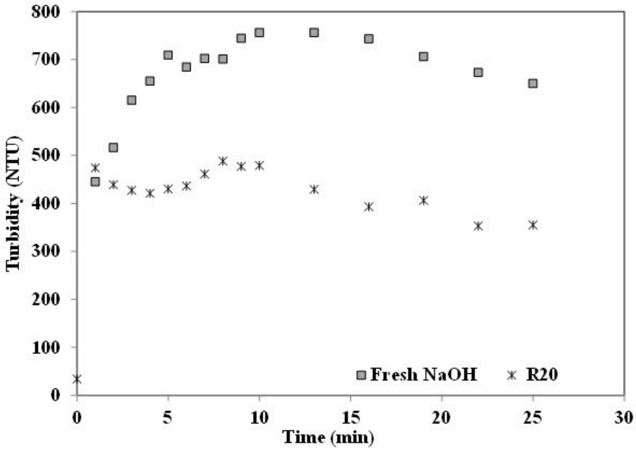


Figure 8: Study of fouled pipe cleaning kinetics using turbidity measurement. Fresh NaOH solutions compared against regenerated solutions (R5, R10, R15 and R20)

4. CONCLUSION

For food and cosmetic industries using CIP stations, excessive utilization of commercial detergents containing sequestering, surfactant, foaming and stabilizer agents creates heavy economic and environmental costs. A physicochemical recycling process combining adsorption–coagulation–flocculation operations enables CIP solutions to self-activate by producing surfactants from the organic matter removed from equipment surfaces. Here, different experiments demonstrated Na-bentonite to be an efficient CIP solution treatment reagent by adsorbing and sweeping of a portion of the contaminant load at the CIP station outlet. The purifying effect comes from its physicochemical properties and its ability to coagulate at extreme pHs, leading to the following efficiencies:

- NaOH solution regeneration with up to 97.5% of active matter, on top of eliminating over 60% total COD in each cycle,
- HNO_3 solution regeneration with over 95% of active matter, on top of eliminating over 80% of total COD in each cycle,
- Physicochemical reprocessing under extreme conditions of temperature (from 15 to 70°C) and pH (from 0 to 14).

Regenerated cleaning solutions can be directly reused for other cleaning cycles. During cleaning trials testing bactericidal effects found that, regenerated solutions outperformed fresh-prepared solutions and maintain their bactericidal activity for at least 20 regenerations. Analysis of cleanability kinetics on fouled pipes found that regeneration solutions have lower turbidity than freshly-prepared solutions, especially at the end of the cleaning cycle. This is due to an accumulation of soluble organic matter that, transformed over the regeneration process into surfactant compounds, leads to a decrease in surface tension and a subsequently solubilization of matter detached from pipe walls. The improved bactericidal and detergent properties of regenerated solutions can be exploited for cleaning equipment that conventional solutions struggle to clean. Thus, regenerated solutions could also be used as an additive to freshly-prepared solutions to improve their cleaning efficiency.

ACKNOWLEDGMENTS

The authors are greatly indebted to the Région Bretagne for its financial support to the present study and University of Bretagne Sud our partner in our research works.

REFERENCES

Akisada H., Kuwahara J., Noyori K., Kuba R., Shimooka T., Yamada A., 2005. Critical micelle concentrations and interaction parameters of aqueous binary surfactant: ionic surfactant mixtures. J. Colloid Interface Sci. 288, 238–246.

Alvarez N., 2003. Rationalisation du nettoyage en place en industrie laitière: durée, pertes de matière, effluents. PhD Thesis, Ecole Nationale Supérieure d’Agronomie de Rennes. France.

Alvarez N., Gésan-Guiziou G., Daufin G., 2007. The role of surface tension of re-used caustic soda on the cleaning efficiency in dairy plants. Int. Dairy J. 17, 403–411.

Assaad E., Azzouz A., Nistor D., Ursu A.V., Sajin T., Miron D.N., Monette F., Niquette P., Hausler R., 2007. Metal removal through synergic coagulation-flocculation using an optimized chitosan-montmorillonite system. Appl. Clay Sci. 37, 258–274.

Condat-Ouillon C., 1995. “Etude du comportement des constituants laitiers en milieu fortement sodique et de leurs interactions en filtration sur membrane: application à la régénération par filtration tangentielle des solutions alcalines de NEP de l’industrie laitière”. PhD. Thesis, INP Toulouse, France.

Delgado A., Gonzalez-Caballero F., Bruque J., 1986. On the zeta potential and surface charge density of montmorillonite in aqueous electrolyte solutions. J. Colloid Interface Sci. 113, 203–211.

Dresch M., Daufin G., Chaufer B., 2001. Integrated membrane regeneration process for dairy cleaning-in-place. Sep. Purif. Technol. 22-23, 181–191.

Dif M., Blel W., Tastayre G., Lendormi T., Sire O., 2013. Identification of transfer mechanisms involved in soiled CIP solutions regeneration at extreme pH and high temperature. J. Food Eng. 114, 477–485.

Dif M., 2013. Application d'un procédé d'adsorption-coagulation-floculation à la régénération de solutions acide et basique de Nettoyage En Place. Effet bénéfique du traitement sur les propriétés physicochimiques et nettoyantes des solutions régénérées. PhD thesis, University of Nantes, France.

Dif M., Blel W., Sire O., 2012. New physico-chemical regeneration process of CIP solutions. Chem. Eng. Trans. 29, 829–834.

Dresch M., 1998. Procèdes à membrane de régénération des solutions de nettoyage de l'industrie laitière PhD. Thesis, Ecole Nationale Supérieure d'Agronomie de Rennes. France.

Eide M.H., Homleid J.P., Mattsson B., 2003. Life cycle assessment (LCA) of cleaning-in-place processes in dairies. Lebensm. Wiss. Technol. 36, 303–314.

Faille C., Fontaine F., Bénézech T., 2001. Potential occurrence of adhering living Bacillus spores in milk product processing lines. J. Appl. Microbiol. 90, 892–900.

Fernández P., Riera F.A., Álvarez R., Álvarez S., 2010. Nanofiltration regeneration of contaminated single-phase detergents used in the dairy industry. J. Food Eng. 97, 319–328.

Gésan-Guiziou G., Alvarez N., Jacob D., Daufin G., 2007. Cleaning-in-place coupled with membrane regeneration for re-using caustic soda solutions. Sep. Purif. Technol. 54, 329–339.

Guglielmotti D.M., Mercanti D.J., Reinheimer J.A., Quiberoni A. del L., 2011. Efficiency of physical and chemical treatments on the inactivation of dairy bacteriophages. Front. Microbiol. 2, 1–11.

Husmark U, Benezech T., Faille C., Ronner U., 1999. Bacillus spores and moulding with TTC AGAR: a useful method for the assessment of food processing equipment cleanability. Biofouling 14, 15–24.

Judd S.J., Hillis P., 2001. Optimisation of combined coagulation and microfiltration for water treatment. Water Res. 35, 2895–2904.

Jullien C., Bénézech T., Le Gentil C., Boulangé-Petermann L., Dubois P., Tissier J., Traisnel M., Faille C., 2008. Physico-chemical and hygienic properties modifications of stainless steel surfaces induced by conditioning with food and detergent. Biofouling 24, 163–172.

Kalra S., Pant C.K., Pathak H.D., Mehata M.S., 2003. Studies on the adsorption of peptides of glycine/alanine on montmorillonite clay with or without co-ordinated divalent cations. Colloids Surf. A. Physicochem. Eng. Asp. 212, 43–50.

Lagaly G., Ziesmer S., 2003. Colloid chemistry of clay minerals: the coagulation of montmorillonite dispersions. Adv. Colloid Interface Sci. 100-102, 105–128.

Mo L., Huanga X., 2003. Fouling characteristics and cleaning strategies in a coagulation-microfiltration combination process for water purification. Desalination 159, 1–9.

Pan Y., Breidt Jr., F., Kathariou S., 2006. Resistance of Listeria monocytogenes biofilms to sanitizing agents in a simulated food processing environment. Appl. Environ. Microbiol. 72, 7711–7717.

Paugam L., Delaunay D., Diagne N.W., Rabiller-Baudry M., 2013. Cleaning of skim milk PES ultrafiltration membrane: On the real effect of nitric acid step. J. Memb. Sci. 428, 275–280.

Räsänen E., Nyström M., Sahlstein J., Tossavainen O., 2002. Purification and regeneration of diluted caustic and acidic washing solutions by membrane filtration. Desalination 149, 185–190.

Ricketts N., 2008. Cleaning-in-Place: Dairy, Food and Beverage Operations. A.Y. Tamime (Ed). Int. J. Dairy Technol. 61, 412–413.

Salle F., Douillard J.M., Bildstein O., Gaudin C., Prelot B., Zajac J., Van Damme H., 2013. Driving force for the hydration of the swelling clays: case of montmorillonites saturated with alkaline-earth cations. J. Colloid Interface Sci. 395, 269–76.

Suarez L., Diez M.A., Garcia R., Riera F.A., 2012. Membrane technology for the recovery of detergent compounds. J. Ind. Eng. Chem. 18, 1859–1873.

Tastayre G., 2010. "Method and device for the regeneration of polluted scrubbing solutions" WO2010063906. WIPO, France.

Tragardh G., Johansson D., 1998. Purification of alkaline cleaning solutions from the dairy industry using membrane separation technology. Desalination 119, 21–29.