New Physico-Chemical Regeneration Process of CIP Solutions

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The regeneration of Cleaning In Place (CIP) solutions presents an increasing interest for chemical industries (food, cosmetic and textile sectors) and sewage treatment plants.

This study was designed to present a new regeneration method of CIP solutions combining sequences of adsorption-coagulation-flocculation processes, coupled with a physical separation by decantation. The chemical nature of effluents (strongly acidic or alkaline pHs) and the extreme temperatures (70 °C to 75 °C) do not allow the application of reactants commonly used in water purification by physicochemical treatment. The application of clays in the treatment and the purification of effluents from the CIP process present an innovative alternative to reduce energy costs and environmental impact of this operation due to the regeneration and the recycling of these effluents during the cleaning process.

Several treatment conditions were tested on soiled CIP solutions, such as the temperature, the ionic strength, the reactants concentration and the pH of the medium. The physicochemical characteristics of solutions resulting from several regeneration cycles were determined in order to assess the efficiency of the treatment process and to identify its impact on the CIP solutions.

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 and

Johansson, 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 physico-chemical 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).

The large capacity of Na-bentonite, to adsorb organic and inorganic matters allows the application of this compound in various treatment and water purification involved in food and cosmetic industries. In comparison with other regeneration processes, the use of Na-bentonite as an adsorption-coagulation reagent constitutes a new alternative to reduce the energy costs and the environmental impact of this operation. The regeneration process could be carried out several times which allows the reuse of the regenerated CIP solutions in many cleaning cycles.

The aim of this study is to investigate the regeneration treatment using the physico-chemical process on different CIP solutions and under different operating conditions of temperature, pH and ionic strength. Firstly, analyzes were performed using synthetic cleaning solutions which contain separate compounds such as casein, lactose and fat as a source of organic matter. These compounds were chosen for their high concentration in the cleaning solutions recovered at the outlet of the CIP stations of dairy industries. The second part of this work consists of checking the regeneration process combining the mechanisms of adsorption / coagulation and flocculation on a caustic CIP solution soiled by whole milk in order to put forward the treatment efficiency on soluble and insoluble pollutions. In this part, physico-chemical characteristics of regenerated solutions, such as the chemical oxygen demand (COD), the total nitrogen content, the surface tension and the loss of active material (acid or base), were followed for several regeneration cycles. These analyses allow to put forward the efficiency of the regeneration treatment process and to identify its impact on the CIP solutions.

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 Na-bentonite (US BENTONITE, Wyoming, USA) at the crude state or after modifications using acid and quaternary ammonium activations. 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 Adsorption analysis:
2.3.1 Treatment application on pure compounds
The protein adsorption on Na-bentonite was made under varying pH conditions (1-13), temperature (20 °C and 50 °C), ionic strength (10^{-3} M, 10^{-2} M and 10^{-1} M) and concentration of the adsorbate in solution (between 0.1 and 1 g/L). The residual concentration of casein remaining after adsorption was measured using a calibration curve: soluble casein concentration at the tested conditions versus absorbance at 280 nm. To explore the Na-bentonite effect on lactose and triglycerides, the same experimental conditions are used and the quantification of the residual polution after the adsorption treatment is carried out by measuring the total carbon.

2.3.2 Applying the treatment process to the CIP solutions:

Treatment mechanisms using the natural Na-bentonite were investigated on a model of caustic CIP solutions presenting similar physicochemical properties than the soiled industrial ones collected at the outlet of CIP units. The soiling was made with 1 % (v/v) of whole milk. This volume of milk was chosen because it induces an equivalent COD that ones encountered currently in industrial CIP solutions. The mixture between whole milk and the NaOH solution (2% w/w, pH≈13.7) was made at the industrial cleaning temperature of 80 °C during 20 min. In this part, different concentrations of Na-bentonite (from 1 to 3 g/L) were used in order to determine the optimum amount for the treatment. The flocculation step was carried out using a cationic polymer at the concentration of 10 mg/L.

Regeneration experiments were carried out at 50 °C using a jar test capable of simultaneously stirring six beakers at 150 rpm for the step of the adsorption – coagulation and at 100 rpm for the second step of flocculation. The addition of the Na-bentonite and the flocculent occurs at a 3 min interval.

The treatment efficiency was followed by measuring the turbidity, the total COD (soluble and insoluble) and the total nitrogen content of the treated solutions

3. Results and Discussions:

3.1 Adsorption of casein:

Figure 1 presents the amount of casein adsorbed on the Na-bentonite Qe (g/g) plotted as a function of the equilibrium concentration of the casein solution Ce (g/L) at different pH values. The curve shapes are similar to the Brunauer type 1 model (Donohue and Aranovichv, 1998), which is an isotherm generally obtained in the case of a progressive saturation of adsorption sites, and to the L2 type according to the classification of Giles for the adsorption of the solute from a dilute solution (Giles et al., 1960). According to Quiquampoix (1992) and Causserand (2001), the adsorption of casein on the clay is considered as optimal at pH values close to neutrality.
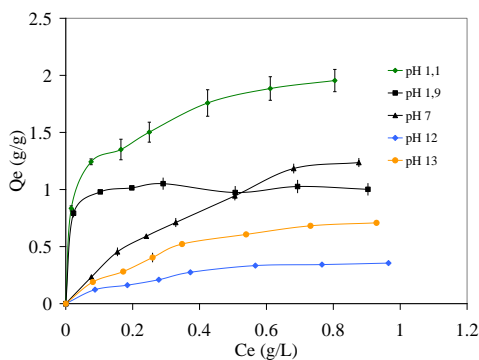

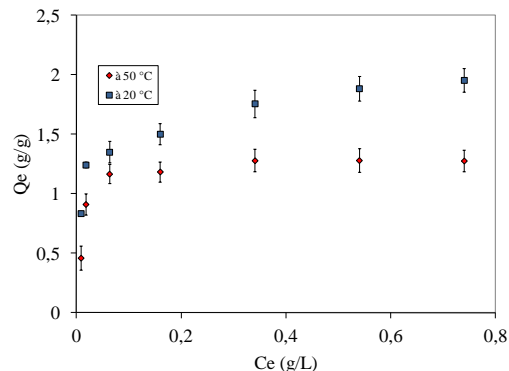*Figure 1: Evolution of the adsorbed casein amount on the bentonite (g/g) at different pH*

Figure 2: Amount of adsorbed casein on Na-bentonite depending on the temperature at pH 1.1

The Qe value decreases at moderate alkaline and acidic pH (respectively for pH 12 and 1.9), which means that, when one moves away from the neutral pH, the adsorption decreases. This can be explained by increased macromolecules structural rearrangements that are adsorbed at the surface of the particles. Since the fraction of the surface area occupied by each protein would then be greater, the amount to be adsorbed would decrease.

This result can be explained by the improvement of the casein adsorption (Qe) due to the increase of the electrostatic forces at extreme pH, as shown in Figure 1. Experiments show that the amount of eliminated casein (Qe) by the Na-bentonite at pH 1.1 is larger (Figure 1). These results point out that adsorption is not the only mechanism involved in the elimination of casein at pH close to those of the CIP solutions (1.1, 1.9, 12 and 13). The hypothesis of the casein elimination by carry-over due to Na-bentonite coagulation appears to be the most appropriate.

3.2 Temperature effect

Analyses were carried out at different temperatures in order to investigate the effect of this parameter on the structure and the adsorption capacity of Na-bentonite. The goal was to simulate real environmental conditions of CIP solutions which prevail in the industry. Figure 2 shows that the amount of adsorbed casein on the clay at equilibrium is less important at 50 °C than at 20 °C. This result emphasizes the fact that the adsorption of casein on bentonite is an exothermic phenomenon. Indeed, the amount of adsorbed casein on the clay at equilibrium decreases from 1.95 g/g to 1.28 g/g when the temperature increases from 20 °C to 50 °C. This may be explained, firstly, by the desorption mechanism, which is favored by the temperature increase, and second, by the modification of the adsorbate structure due to both effects of temperature and pH, resulting in the agglomeration of molecules and the increase in size (Renner, 1989).

3.3 Effect of the ionic strength

According to Figure 3A, zeta potential measurements at pH 12 present negative values for the casein and the Na-bentonite. As a result, electrostatic repulsions appear, inducing the decrease in adsorption capacity (Figure 1).
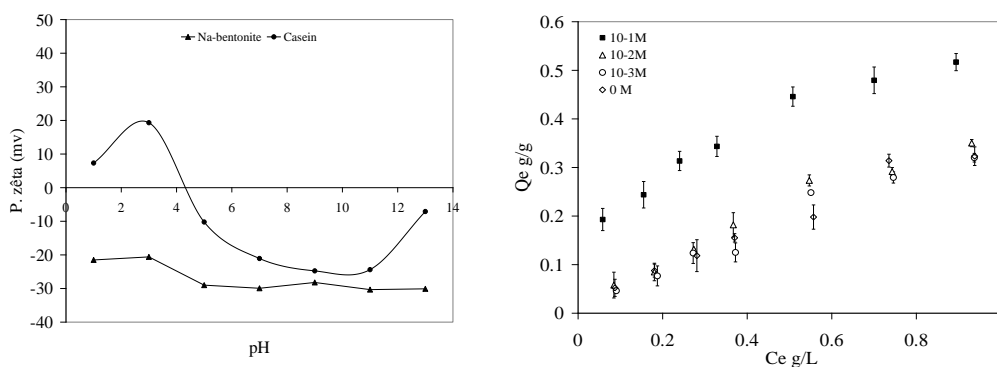

Figure 3A: Effect of pH on the Zeta potential of Na-bentonite and casein

Figure 3B: Adsorption isotherm of casein on the Na-bentonite at various NaCl concentrations at 20° C and pH 12

In the case of acid solutions, the electrostatic attractions between the Na-bentonite and the casein appear due to their opposite global charge. This promotes adsorption and increases the amount of removed casein. This result is further confirmed on figure 3B, which shows, at pH 12, an increase in the adsorption of casein on the bentonite with NaCl addition. This result was verified at NaCl concentration of 10^{-1} M. The other concentrations show no significant differences compared to the adsorption without salt. Figure 3B also shows a constant increase in the adsorbed amounts of casein (≈ 54 %) between solutions with (10^{-1} M) and without salt addition. Measurements of the zeta potential (Figure 3A) showed that at alkaline pH solution, casein and Na-bentonite particles have the same surface charges. For these two compounds, the increase of the ionic strength allows the surface charges screening and thereafter, the reduction of repulsive electrostatic forces. This phenomenon is observed between the casein molecules and also between casein and bentonite particles. The Debye-Hückel length, which repersents the electrical double layer width at the particles surface (Walstra, 2003), is reduced at high ionic strength (10^{-1} M) allowing particles (Na-bentonite and casein) to be closer. Thus, other interactions could be established such as Van der Waals bonds and allow to explain the increase of the adsorption phenomenon at high ionic strengths (Figure 3B).

3.4 Application of the treatment process on CIP solutions containing soluble lactose

The treatment of cleaning solutions soiled with soluble lactose was carried out under distinct temperatures (20 and 50 °C) and pHs (1.9, 12 and 13). Various Na-bentonite concentrations were tested. The obtained results show no purification effect of the Na-bentonite on lactose, since the values of total carbon before and after treatment showed no significant change. Indeed, measurements of total

carbon carried out on untreated and treated solutions with 1 g/L of Na-bentonite (treatment at 50 °C and pH 13) present, respectively, very close values of 329.18 ± 20.73 mg/L and 323.97 ± 11.61 mg/L. On the other hand, the alteration of pH lacks to induce any effect on the lactose adsorption. Thus, analyzes carried out at 50 ° C and pH 1.9 have given 372.22 ± 13.54 mg/L for the untreated solution and 369.5 ± 10.22 mg /L for the treated one. These results can be explained by the fact that lactose dissolved in an aqueous solution forms a true solution, the solute particles are of molecular dimensions rarely exceeding one nanometer. Thus, molecules of solute are statistically distributed in the solvent due to the similarity of size between the two compounds. Therefore, the repulsion forces between the solute and solvent are considered as null which excludes the electrostatic interaction with Na-bentonite particles which are considered as critical for the adsorption phenomenon.

3.5 Application of the treatment process on CIP solutions containing triglycerides

The effect of the Na-bentonite on the adsorption of triglycerides was tested using a suspension of vegetable oil in alkaline solution at pH 13.6.

This solution was prepared by mixing, at high temperature, the vegetable oil in the NaOH solution, at the concentration of 2 g/ L, until obtaining a single and stable phase. The same experimental conditions, as the lactose analysis, were used and the residual amount of fats after treatment was estimated by measuring the total carbon. Figure 4 features the amount of total carbon measured before and after treatment as a function of the bentonite concentration.
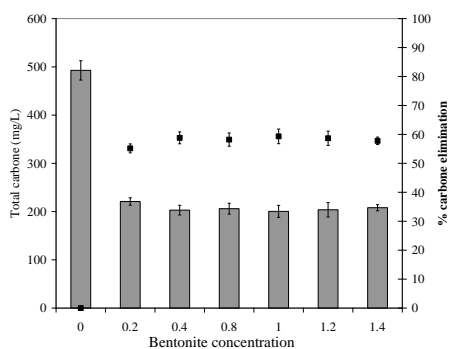

Figure 4: Measurement of total carbon of a solution of triglyceride treated and the percentage of carbon abated with different concentration of bentonite at pH 13.6
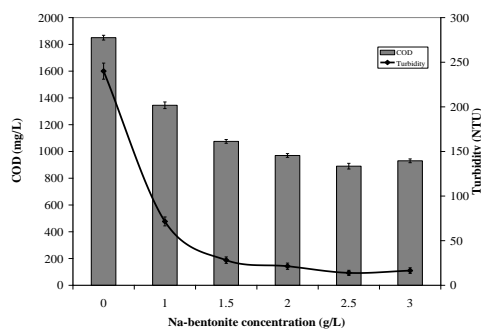
Figure 5: Efficiency evaluation of the regeneration process in the case of models cleaning solutions. Evolution of the turbidity and the total COD

Figure 4 shows that more than 59 % of triglycerides are removed whatever the Na-bentonite concentration in comparison to the untreated solution. In addition, no significant differences are observed in the total carbon amounts between the tested Na-bentonite concentrations. Indeed, between the tow Na-bentonite concentrations of 0.2 and 1.4 g/L, reducing total carbon does not exceed 4 %. This result showed that the action of the Na-bentonite is not related to its concentration and could be explained by the fact that the fatty matter presents an hydrophobic character, allowing its attachment to Na-bentonite particles and thereafter the decantation of aggregates under the flocculation effect.

3.6 Applying the regeneration process to model CIP solutions

In order to validate the regeneration process on CIP solutions which mimic the characteristics encounterd in industry, analyses were performed at distinct Na-bentonite concentrations. The treatment efficiency was followed by measuring the total COD and the turbidity of treated solutions.

The figure 5 illustrates the evolution of these two parameters for untreated and NaOH treated solutions at various Na-bentonite concentrations Analyses showed that the increase in the Na-bentonite concentration from 1 g/L to 2.5 g/L allows for the reduction of both turbidity and COD. At the Na-bentonite concentration equal to 2.5 g/L, the COD decreases down to 890 mg/L, which corresponds to

a treatment yield of 51 % in comparison with the soiled solution. A significant reduction of the turbidity was also observed at this concentration of Na-bentonite (13 NTU versus 240 NTU). Beyond the Na-bentonite concentration of 2.5 g/L, a slight increase of the two parameters of characterisation was obtained. This result underlines that this concentration corresponds to a threshold value for which the adsorption process reaches a maximum value that depends on the saturation of available sites at the Na-bentonite surface for trapping organic molecules contained in the solution.

The disproportion between the coagulant and flocculant concentrations explains this increase in the pollution amount that remains in the solution. Indeed, the used concentration of flocculent may be low enough to precipitate the excess of bentonite which contains organic matter beyond the concentration of 2.5 g/L. Thus, this complex remains suspended in the treated solution and warrants for the COD increase.

3.7 Conclusion

A new regeneration method of soiled CIP solutions combining sequences of adsorption-coagulation-flocculation processes, coupled with a physical separation by decantation was tested. Analyzes carried out on cleaning solutions at extremely acidic or alkaline pH and high temperatures (70 °C to 75 °C) allowed to assess the process efficiency in the treatment of soluble and insoluble organic matters. These results allow confirming the process efficiency for both soluble and insoluble matters contained in the whole milk. Analyzes showed also that the treatment performance could be increased by tuning the environmental parameters such as the temperature, the ionic strength, the reactants concentration and the pH of the medium. Treatment efficiency on soluble organic matter is linked to the size of molecules present in the medium and subsequently to the electrostatic interctions established with Na-bentonite particles.

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