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Effect of a new regeneration process by adsorption-coagulation and flocculation on the physicochemical properties and the detergent efficiency of regenerated cleaning solutions

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ABSTRACT

Reprocessing soiled cleaning-in-place (CIP) solutions has large economic and environmental costs, and it would be cheaper and greener to recycle them. In food industries, recycling of CIP solutions requires a suitable green process engineered to take into account the extreme physicochemical conditions of cleaning while not altering the process efficiency. To this end, an innovative treatment process combining adsorption-coagulation with flocculation was tested on multiple recycling of acid and basic cleaning solutions. In-depth analysis of time-course evolutions was carried out in the physicochemical properties (concentration, surface tension, viscosity, COD, total nitrogen) of these solutions over the course of successive regenerations. Cleaning and disinfection efficiencies were assessed based on both microbiological analyses and organic matter detachment and solubilization from fouled stainless steel surfaces. Microbiological analyses using a resistant bacterial strain (*Bacillus subtilis* spores) highlighted that solutions regenerated up to 20 times maintained the same bactericidal efficiency as *de novo* NaOH solutions. The cleanability of stainless steel surfaces showed that regenerated solutions allow better surface wettability, which goes to explain the improved detachment and solubilization found on different types of organic and inorganic fouling.

1. Introduction

Cleaning-in-place (CIP) procedures are commonplace in matter-transforming processes across the pharmaceutical, cosmetic, textile and food industries as they both protect equipment and increase production yields (Pan et al., 2006; Guglielmotti et al., 2011). CIP procedures are generally carried out with various empirical sequences performed with appropriately complex cleaning solutions (Dif, 2012). The most common industry-scale chemical cleaning detergent used is mainly composed of two agents: an alkaline (typically sodium hydroxide (NaOH) as surfactant at pH 11.5–13.5) to remove organic matter, and an acid (generally nitric acid at pH 1.6 down to below 1) to remove mineral (limescale) fouling (Paugam et al., 2013). The major problem with these operations is that they use a lot of water and chemical reactants, which has significant economic and environmental impacts. Indeed, in most cases, CIP unit effluent gets discharged to sewage treatment plants after one or few cleaning cycles. The volume of these effluents varies with type of production process and nature of products treated. For example, dairy industries processing 10^6 L of milk per day generate up to 5 L of effluent per 1 L of processed milk, and 54%–98% of this volume comes straight from CIP units (Dif, 2012). To overcome this problem, a number of recycling processes have been developed to save on the water, chemical reactants and energy used (Fernández et al., 2010; Suarez et al., 2012) while maintaining process efficiency and reducing variations in pH and volume of effluent to be treated. The development effort started with sedimentation and centrifugation processes studied by Dresch (1998) as a way to regenerate cleaning solutions and thus ensure lower global cleaning costs, and then continued with membrane filtration methods like microfiltration (Tragardh and Johansson, 1998), ultrafiltration (Dresch et al., 2001) and nanofiltration (Räsänen et al., 2002). However, these methods are either inefficient at removing the bulk of pollution in the cleaning solutions

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(sedimentation and centrifugation processes) or expensive in terms of investment and implementation (membrane filtration). The application of a physicochemical coagulation-flocculation process becomes possible once the reagents used are efficient under the routine environmental conditions encountered in CIP procedures. The coagulation-flocculation process is widely used in wastewater treatment as it is more affordable, less energy-intensive, and cheaper to maintain than the other available CIP solution regeneration techniques (Dif, 2012). In wastewater reprocessing, the physicochemical process is generally performed by adding chemical reagents such as electrolytes and polymers to modify the behaviour of the dispersion components (Judd and Hillis, 2001). These reagents operate either by reducing the electrostatic forces between particles, thus promoting attractive van der Waals forces, or by adsorbing and trapping dispersed particles (Mo and Huanga, 2003). However, the coagulant/flocculant reagents used in wastewater reprocessing plants (WWTP) are ill-suited to this application due to the high temperatures (80–90 °C) and extreme pH values (pH 1 and 14) of the cleaning solution (Dif et al., 2013). Indeed, all the salts used in WWTPs as coagulant/flocculant reagents have restricted activity at the vicinity of their isoelectric points, which are generally reached in near-neutral-pH solutions. However, the pH and temperature conditions typically encountered in CIP solutions will modify these salts (Condat-Ouillon, 1995) and render them inactive for the removal of the pollutant load in these solutions.

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 Na-bentonite 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 Na-bentonite 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 Na-bentonite adsorbent still has a coagulative effect that contributes to global process efficiency by adsorption and carryover of the organic matter. Na-bentonite 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. However, the issue of microbiological safety in regeneration-based cleaning solutions has been disregarded, as regeneration processes are just emerging technologies. Here, a series of experiments were run to track cleaning and disinfection efficiencies over several cleaning cycles.

The aims of this work are multiple. First, the principle of a recycling process combining adsorption/coagulation and flocculation mechanisms was 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. Reactants used in the physicochemical regeneration

2.1.1. The adsorbent/coagulant

Experiments were performed using crude Na-bentonite (US BENTONITE, Wyoming, USA). The product was sieved to select particle sizes between 40 and 80 μm in order to homogenize the clay suspensions used for subsequent adsorption tests. The mineralogical composition of the Na-bentonite was identified using the X-ray diffraction (XRD) method. Analyses showed that the clay sample contains mainly (27.6%) montmorillonites (Smectite) and minor amounts of quartz and feldspath.

Elementary analyses have confirmed the sodic nature of the clay used in this study, which has a sodium/calcium ratio of 1.75. This composition has an effect on clay swelling and hydration in an aqueous medium, and therefore its ability to increase the interlayer space, given that the smectite swelling is promoted by the presence of small and weakly charged cations (Salle et al., 2013).

2.1.2. The flocculant

The separation of colloidal residues previously destabilized by using the adsorbent/coagulant (Na-bentonite) requires the use of synthetic flocculants compatible with the physicochemical properties (pH, temperature and chemical potential) of CIP solutions. Thus, in the case of caustic soda recycling, the flocculation step was performed using a high-molecular-weight cationic polymer ($\approx$5–6 10^6 Da) provided by FLOPAM EM 949 CT (SNF Floerger, FRANCE). For the acid solution, a high-molecular-weight anionic polyacrylamide ($\approx$9–11 10^6 Da) in hydrosoluble powder form provided by FLOPAM AN 997 SH (SNF Floerger, FRANCE) was used.

2.2. Identification of optimal reagent concentrations

In order to determine optimal reagent (sodium hydroxide and acid nitric) concentrations for use in CIP solution regeneration cycles, several trials were led at various concentrations of Na-bentonite (1–4 g L^{-1}) and flocculants (1–30 mg L^{-1}). Soiling was done with 1% (v/v) whole milk, which induces a COD equivalent to that currently encountered in industrial CIP solutions (Gésan-Guiziou et al., 2007). Regeneration experiments were carried out