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ORIGINAL ARTICLE

# Pollutant removal from industrial discharge water using individual and combined effects of adsorption and ion-exchange processes: Chemical abatement



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**Abstract** In this study, adsorption-oriented processes for pollutant removal from metal polycontaminated surface-finishing discharge water were applied individually as well as in combination with ion-exchange treatment to remove the remaining metal ions and organic load. Several materials were compared using batch experiments, namely an activated carbon, three ion-exchange resins (IRA 402Cl, IR 120H and TP 207), and two non-conventional cross-linked polysaccharide-based biosorbents (starch and cyclodextrin). This article presents the abatements obtained in chemical pollution as monitored by complete chemical analysis. For the same experimental conditions (similar discharge water, pollutant concentrations, stirring rate, contact time, and initial pH), the highest levels of pollutant removal were attained with the combined use of two materials, an activated carbon and a mixture of two ion-exchange resins. This physicochemical treatment effectively lowered the main pollutants present in the discharge water such as Cu, Ni and COD, by more than 96%, 79% and 74% respectively (average values for three samples), while the treatment with carbon alone lowered them by 58%, 9% and 70%, and resins alone by 85%, 61% and 16%. Similar interesting results were obtained with the cyclodextrin-based adsorbent and its use alone was sufficient

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to obtain decreases in Cu, Ni and COD of more than 94%, 77% and 67% respectively. The adsorption-oriented process using cyclodextrin polymer could be an advantageous approach for removing organic and metallic pollutants from metal surface-finishing discharge water due to the non-toxic character of CD to humans and the environment.

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## 1. Introduction

The main approach used by the metal surface-finishing industrial sector to treat its waste water involves physicochemical methods with, after pretreatment steps to deal with cyanides for instance, precipitation of the pollutants by applying an alkaline agent, then separation by physical treatment of the sludge formed (e.g. by decantation) to leave clarified water. The use of physicochemical treatment generally enables the legislation concerning liquid industrial effluent to be respected but this conventional treatment does not completely remove pollution (Chmielewski et al., 1997; Barakat, 2011; Sancey et al., 2011). However, as it has to cope with an increasingly strict framework, the industrial sector continues to look into new treatment methods to decrease the levels of pollution still present in the effluent, the aim being to tend towards zero pollution outflow (Crini and Badot, 2010).

In theory, many methods could be suitable to finish off the work done during the physicochemical treatment. We can mention standard filtration carried out on a filtering medium (sand, carbon, etc.), membrane filtration (microfiltration, reverse osmosis), evaporation, liquid-liquid extraction, oxidation-based processes (conventional i.e. using an oxidizing agent, or advanced e.g. catalytic oxidation), electro-treatments (electrolysis, electrochemical precipitation, membrane electrolysis, electrocoagulation), adsorption, ion-exchange and also biosorption as well as specific biological techniques. Currently, few methods are actually used by small surface finishing plants owing to technical but especially to economic considerations (Chmielewski et al., 1997; Barakat, 2011; Fu and Wang, 2011; Sancey et al., 2011). In addition, two specific points should be borne in mind: firstly there is no single method able to remove the whole range of mineral and organic pollutants present in complex industrial mixtures and secondly it is extremely difficult to remove pollutants present at very low concentrations from effluents that are heterogeneous and variable in nature (Chmielewski et al., 1997).

As the objective is to reach better purification of the discharge water, a sequential approach can be considered: firstly simple filtration to protect the subsequent stages then adsorption onto activated carbons and ion-exchange and/or chelation by means of polymeric organic resins (Alexandratos, 2009; Akpor and Muchie, 2010). This type of decontamination technology links two methods of separation using two distinct commercial materials in order to obtain the required levels of abatement. The role of the activated carbon is to adsorb the residual organic load and in addition to protect the resins from the residual oils and solvents: a non-negligible proportion of the organic load that is not eliminated physicochemically remains in the effluent and can adversely affect the performance of the resins. The resins are then used to exchange or to chelate the dissolved metals remaining in the effluent. When used as a final

treatment, this type of sequence is acknowledged for its efficiency and its economic viability and it can be used on weakly concentrated effluent at the outlet of a standard physicochemical treatment unit. However, this technology does tend to suffer from problems of saturation and disposal after use. Indeed, filters composed of standard adsorbents such as active carbon and organic polymers present the disadvantage of quite rapidly becoming saturated and losing their efficiency. They must be regularly replaced (carbons) or regenerated (resins) entailing added costs. Moreover, the use of these adsorbents also represents a significant environmental cost as their production and regeneration entail high energy consumption. The current goal therefore is to find novel adsorbents that are economically viable, able to eliminate all types of substances present in effluent in one step and that have no impact on the environment (Crini, 2005; Kailash et al., 2010; Fu and Wang, 2011).

Much effort has recently been focused on various materials based on cyclodextrins (CDs) which are molecules derived from starch (Crini, 2005). These substances, and in particular beta-cyclodextrin ( $\beta$ -CD), have the remarkable ability to form inclusion complexes with other molecules through host-guest interactions in solution or in the solid state (Szejtli, 1998, 2004). The specific properties of  $\beta$ -CD combined with its lack of toxicity towards humans have led to its use in numerous applications (pharmacy, medicine, biotechnology, textile industry, toiletries, cosmetics, food additives, etc.). Recently, Morin-Crini and Crini (2013) showed that  $\beta$ -CDs also deserve particular attention in environmental science in terms of removal of pollutants from water and wastewater using oriented-adsorption processes. Numerous recent studies have shown that starch- or CD-based adsorbents can efficiently treat synthetic solutions, but most focused on solutions contaminated with a single type of pollutant. Studies involving treatment of industrial polycontaminated effluent are indeed scarce.

In this article, we compare the performance of several adsorbents – conventional (activated carbon, resins) and non-conventional (starch,  $\beta$ -cyclodextrin) – in the abatement of the metal pollutants and organic load in the discharge water from surface-finishing plants.

## 2. Materials and methods

### 2.1. Industrial discharge waters

Industrial discharge waters were collected from EEA Industry located in Vitreux (Jura, France). Its main activity is plating electrical contacts with copper, nickel, tin, silver and gold. The analytical characteristics of three samples, taken on three consecutive weeks, are shown in Table 1. The effluents are average samples characteristic of that day's activity. The three main issues to be dealt with in the effluent were Cu, Ni, and COD.

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