Treatment of cosmetic wastewater using physicochemical and chemical methods

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The current state of knowledge about treatment of wastewater from the cosmetics industry is poor, which is evidenced by the number of publications treating on the subject. The reason for this may be the false assumption that components of cosmetic wastewater, because of the application of the product, are not toxic and readily undergo biodegradation.

Substances found in cosmetic wastewater belong to the group of the so-called PPCPs (pharmaceuticals and personal care products), which includes drug and cosmetic ingredients, dietary supplements and products of their metabolism [10]. These substances may, to a large degree, be toxic to humans and the environment [10, 17], and may accumulate in many components of the ecosystem [18].

The main source of PPCPs emission into the environment are sewages [13]. PPCPs concentrations discharged into receiving waters depend on many factors, such as: wastewater treatment process, physicochemical properties of the substances (including biodegradability) and climate conditions [13]. The amount of PPCPs released also depends on the affluence of the society. The wealthier is the society, the higher is the consumption of drugs and cosmetics.

Cosmetic wastewater contains various compounds, both organic and inorganic. Among organic compounds the following ones may be distinguished in the first place: hydrocarbons, proteins, ethers, esters, aldehydes and ketones, alcohols, carboxylic acids, and also more complex derivatives thereof and products of various biochemical transformations. Inorganic include: acids, hydroxides, salts, oxides and heavy metal compounds.

These substances perform various roles in cosmetics: they may form the base (carrier) of the cosmetic formulation, or be active ingredients. The active substances include moisturizers, fragrances, surfactants, antiseptics, colours, vitamins, UV filters and other.

Cosmetic wastewater may have very high COD (>100000 mg/l), BOD_5 and TOC levels, high concentrations of petroleum ether extract, organic nitrogen and organic phosphorus.

Most of the contaminants found in cosmetic wastewater are scarcely biodegradable. This applies not only to surfactants and organic dyes, the properties of which have been known for a long time now, but also to fragrances and sunscreen UV filters. These substances are non-polar and hardly biodegradable. Chen *et al.* [7] have found that the concentrations of individual substances did not exceed 0.1 mg/l. In a biological wastewater treatment plant they are removed primarily by adsorption on activated sludge [10, 12, 18]. During sludge fermentation they undergo extensive decomposition. The studies of Zeng *et al.* [22] have shown that in a sewage treatment plant in Guandong, the removal rate of cashmeran (DPMI) was 61÷75%, that of galaxolid (HHCB) was 86÷97%, and that of tonalid (AHTN) was 87÷96%. The remainder (at concentrations of 0.1, 2.05 and 0.14 *µ*g/L, respectively) was discharged to surface waters. Similar results were obtained by Rosal *et al.* [19], Reiff *et al.* [18] and Carballa *et al.* [6]. Similar values were also reported for substances used as sun filters [15, 19]. As demonstrated by the results of other studies [9, 16], the concentrations of these substances in surface waters and treated effluents have not exceeded the level of a few *µ*g/l [7, 10, 11, 13, 17, 18]. Among them, the highest concentrations were reported for HHCB and AHTN.

The least expensive and most widely used method of cosmetic wastewater processing is biological treatment. The effect obtained, however, is not always satisfactory, particularly in the case of high oil and grease concentration [8]. The reason of low efficiency of biological treatment is the high variability in time of contaminant composition and the resulting differences in compound properties (described by the values of K_{ow}, pKa, D_{ow}) [10, 12, 18, 20]. As many substances in cosmetic wastewater are scarcely susceptible to biodegradation, it is advisable to pretreat the wastewater prior to biological treatment. Cosmetic wastewater pretreatment may comprise physicochemical methods, such as: coagulation, flotation and electrocoagulation, chemical oxidation and membrane processes [7, 10, 12]. In some cases good results are obtained by applying advanced oxidation processes (AOPs). Oxidation may be applied either instead of or, as a second step of pre-treatment, after performing physicochemical processes.

Not much research has been done on the application of these methods to cosmetic wastewater treatment, and the results of such research have only been published in recent years. The most investigated process was coagulation. Results of studies were published in 3 papers [1, 5, 8]. The following coagulants were used in the process: $Al_2(SO_4)_3$, polymeric aluminium chloride, $FeSO_4$ and $FeCl_3$. All these coagulants provided similar results, and their performance ranking changed depending on the wastewater treated. COD was reduced by 48÷77%. Slightly better results were achieved with electrocoagulation, which was carried out simultaneously, and an iron anode proved to be better than aluminium one [1]. Application of pressure flotation after coagulation had not improved the treatment effect; it did, however, reduced the sludge volume.

Pressure flotation of raw wastewater, performed in parallel with coagulation, provided much worse results [8]. The concentrations of AHTN and HHCB were reduced by ca. 40% (70% after coagulation). Flotation effect improved with the increase of oil and grease content in wastewater.

Cosmetic wastewater was also treated using advanced oxidation processes. The best results were obtained with the Electro-Fenton process [1]. COD (11423 mg/l) was reduced by ca. 80%, while the concentration of surfactants (3148 mg/l) decreased by 98%. The treatment effect was much better than that in the coagulation process, with the results obtained as follows: ca. 50% and ca. 60%. The Fenton process was also applied to wastewater pre-treated by coagulation [2]. The optimum pH value was 3. TOC value was reduced (from 785 and 1215 mg/l) by 45%. The decrease of COD (not determined) was presumably much higher. Another wastewater sample, with COD of 1753 mg/l, was subjected to electrocoagulation, followed by photocatalytic oxidation on TiO_2 [4]. COD values obtained after each of these processes were as follows: 160 and 50 mg/l, respectively. Bautista *et al.* [3] have also applied catalytic oxidation using H_2O_2 and $Fe/\gamma Al_2O_3$ catalyst at the temperature of 79÷85°C. After 4h of treatment, COD (initial value 4730 and 2300 mg/l) decreased by nearly 80%. This process resulted also in improvement of further biological treatment of wastewater, which was evidenced by the increase of the BOD_5/COD ratio from 0.22 to 0.53.

Substances such as: grease and mineral oils, organic dyes and surfactants, present in all cosmetic wastewaters, are also common in other industrial wastewaters. Their susceptibility to removal from wastewater by physicochemical methods and oxidation has been thoroughly discussed in numerous publications. Greases and oils can effectively be removed by coagulation and flotation. AOP methods are also effective, to a lower degree though. Surfactants and dyes can be oxidized by means of AOP [21], and the oxidation products formed are more readily biodegradable. Coagulation thereof is also effective, to a lower degree though [1]. No research has been reported on the effectiveness of advanced oxidation processes in the removal of fragrances and sun filters from cosmetic wastewater. One publication dealt with the applicability of ozonation [20]. The effectiveness of the process, however, proved to be poor when applied to fragrances (AHTN removal rate ca. 38%), and even more so when applied to sun filters (ca. 20%).

Authors' own research

Wastewater was treated by means of coagulation using $Al_2(SO_4)_3$ at pH 7 and $FeCl_3$ at pH 6 and 9, Flopam flocculant at pH 3 and the following H_2O_2/Fe^{2+} doses: 1000/125, 1500/250, 1000/250 mg/dm^3 [14]. The results of these studies are summarized in Figure 1. They indicate that in the case of coagulation COD reduction varied within the range of 56.4 to 63.9%, depending on coagulant type and dose. The best effects were observed for $FeCl_3$ at pH 6 with Flopam flocculant used. In the case of the Fenton process, COD removal varied between 31.1 and 54.9%. The best effects were observed for a 1000/125 mg/l reagents dose.

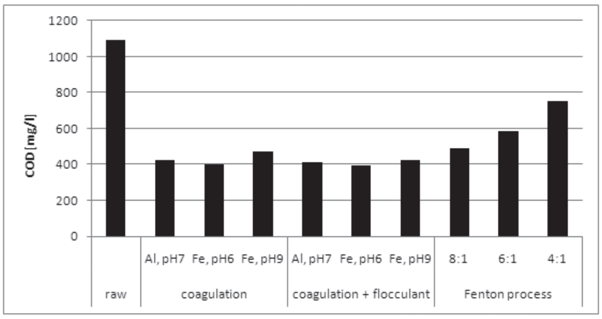

Fig. 1. The effectiveness of cosmetic wastewater treatment using coagulation, coagulation with flocculant and Fenton process [14]

Summary and Conclusions

The results obtained by the various researchers are difficult to compare because of the diversity of wastewater compositions and, consequently, wastewater parameters. The selection of treatment method must always be preceded by appropriate process research. According to the published research results, the best effect was achieved with catalytic oxidation: COD reduction close to 80%.

The best effect in our own tests was attained when coagulation was applied using $FeCl_3$ at pH 6 and Flopam flocculant: COD reduction by 63.9%.

A pre-treatment may be applied to improve biological treatability of wastewater.

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