Purification of real car wash wastewater with complex coagulation/flocculation methods using polyaluminum chloride, polyelectrolyte, clay mineral and cationic surfactant

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ABSTRACT

In the present study, real car wash wastewater was purified by different coagulation/flocculation methods. As coagulant, polyaluminum chloride ('BOPAC'), conventional iron(III) chloride, iron(III) sulfate, and aluminum(III) chloride were used, while as flocculant non-ionic and anionic polyelectrolytes were investigated. The effects of added clay mineral (Na-bentonite) and cationic surfactant (hexadecyltrimethyl ammonium bromide – 'HTABr') were also investigated. The use of BOPAC was significantly more effective than conventional coagulants. Extra addition of clay mineral was also beneficial in relation to both the sediment volume and sedimentation speed, while polyelectrolyte addition enhanced further the sedimentation. Moreover, the simultaneous addition of HTABr significantly enhanced the color removal efficiency due to the successful *in-situ* generation of organophilic bentonite. In summary, the application of 100 mg L^{-1} Na-bentonite with 20 mg L^{-1} Al^{3+} (from BOPAC) and 0.5 mg L^{-1} anionic polyelectrolyte resulted in the efficient reduction of the turbidity (4–6 NTU), the COD (158 mg L^{-1}) and the extractable oil content (4 mg L^{-1}) with efficiencies of 98%, 59%, and 85%, respectively. By applying organophilic bentonite in high concentration (500 mg L^{-1}) with identical concentrations of BOPAC and anionic polyelectrolyte, significant color removal (5 times lower absorbance at $\lambda = 400$ nm) and 27% lower sediment volume were achieved.

Key words | bentonite, BOPAC, car wash wastewater, coagulation, flocculation

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INTRODUCTION

Finding solutions to the global 'water problems' is one of the biggest challenges of the 21st century (Smalley 2005), which requires actions such as promoting the more rigorous protection of water sources, the development of low-water technologies and novel water treatment methods and the maximization of used water reclamation. For the treatment of industrial wastewaters, special purification methods are required, since they usually contain different toxic and/or non-biodegradable contaminants like hydrocarbons, dyes, pesticides, etc. (Iqbal 2016; Abbas *et al.* 2018; Iqbal *et al.* 2019). Oily contaminants can be harmful to microorganisms, plants and animals; moreover, they can accumulate in the food chain and inflict various genotoxic, carcinogenic or mutagenic damage (Abdel-Shafy & Mansour 2016; Iqbal 2016; Ukpaka & Wami 2017; Abbas *et al.* 2018; Tasker *et al.* 2018). Oil contaminations can increase the number of degenerative diseases and decrease the life expectancy (Morounke *et al.* 2017; Johnston *et al.* 2019).

Car wash stations produce large and increasing volumes of wastewater, since the number of registered vehicles exceeded 1.2 billion in 2014 (worldwide), and it is estimated to be 2.0 billion until 2035 (Zhao *et al.* 2017; Currie 2018). Car wash wastewaters contain several pollutants such as hydrocarbons, oily pollutants, brake dust, detergents, surfactants, heavy metals, etc. (Jönsson & Jönsson 1995; Kiran *et al.* 2015). Efficient purification and reclamation of these waters are required both from environmental and economic reasons (Al-Odwani *et al.* 2007; Panizza & Cerisola 2010; Kiran *et al.* 2015). Moreover, the useable freshwater per vehicle is already limited in some countries, such as in the

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Netherlands, Scandinavian countries or in Australia (60–100 L/car), which makes the reclamation of used waters imperative (Kiran *et al.* 2015; Pinto *et al.* 2017).

There are several methods which can be used for the reclamation of car wash wastewaters, such as sand filtration (Al-Odwani *et al.* 2007; Zaneti *et al.* 2011), oil skimming (Al-Odwani *et al.* 2007), flotation (Zaneti *et al.* 2011), adsorption (Hamada & Miyazaki 2004), coagulation/flocculation (Zaneti *et al.* 2011; Etchepare *et al.* 2014; Mohamed *et al.* 2014; Rodriguez Boluarte *et al.* 2016), ozonation (Rodriguez Boluarte *et al.* 2016), electrochemical oxidation (Panizza & Cerisola 2010), biological treatments (Suzuki *et al.* 2000; Rodriguez Boluarte *et al.* 2016), electrocoagulation (Mohammadi *et al.* 2017) and membrane separation (Hamada & Miyazaki 2004; Li *et al.* 2007; Boussu *et al.* 2008; Lau *et al.* 2013; Kiran *et al.* 2015; Pinto *et al.* 2017). Due to the complexity of car wash wastewaters, single methods usually are not efficient enough and/or the achievement of satisfactory purification efficiency often proves to be too expensive (Brown 2000; Rodriguez Boluarte *et al.* 2016). Membrane separation is one of the most promising techniques, which can result in excellent purification efficiency (Lau *et al.* 2013; Pinto *et al.* 2017). The main advantages of membrane filtration are its low cost, easy scalability and low energy consumption (Chelme-Ayala *et al.* 2009). However, a general drawback of membrane filtration is the inevitable fouling mechanism, which leads to flux reduction and membrane amortization, hence reduced lifetime and high replacement costs (Li *et al.* 2007; Boussu *et al.* 2008; Panizza & Cerisola 2010). Therefore, efficient pre-treatment of car wash wastewaters is necessary to protect the membrane and to slow down the fouling, thus achieving lower cost and higher flux. Among the contaminants of car wash wastewaters, finely dispersed floating materials and even more the emulsified oil droplets are responsible for the membrane fouling and flux reduction, since these droplets form blocks in the pores and hydrophobic cake layer on the surface (Veréb *et al.* 2017a). Conventional oil skimming and flotation can eliminate free and dispersed oil ($d_{\mathrm{oil\ droplets}} > 20\ \mu\mathrm{m}$), but oil-in-water emulsions require more effective elimination methods (Gryta *et al.* 2001; Chakrabarty *et al.* 2008; Souza *et al.* 2016; Veréb *et al.* 2017a).

Although common coagulants such as iron and aluminum chlorides/sulfates are not efficient enough for the elimination of emulsified oil, but in our previous study (Veréb *et al.* 2017b) it was proved that the combination of specific coagulant and flocculant like polyaluminum chloride and anionic polyelectrolyte can be efficient for the destabilization of micro- and nanosized oil droplets. Therefore, the mentioned coagulant/flocculant combination might be useful for the purification of car wash wastewaters before membrane filtration, resulting in significant fouling reduction and longer lifetime of the membranes. In this study, purification of real car wash wastewater was investigated by the application of different coagulants/flocculants, including polyaluminum chloride, polyelectrolytes, and clay mineral. This latter material can intensify the sedimentation of the flocks, and its adsorption capacity also can be favorable to reach higher elimination efficiency of dissolved organic compounds (Zhu & Ma 2008; Szabo *et al.* 2011; Djehaf *et al.* 2017). Additionally, the effect of organophilic clay mineral – generated *in situ* by the addition of hexadecyltrimethyl ammonium bromide cationic surfactant – was also investigated. Since HTABr as an organic cation carrier can exchange the Na^+ ions of clay minerals, thus it can make them suitable for the adsorption of different organic contaminants such as anionic (Shen *et al.* 2009) or cationic (Tonlé *et al.* 2008) dyes and different non-polar contaminants such as hydrocarbons (Wiles *et al.* 2005; Chikwe *et al.* 2018; Jennifer & Ifedi 2019), phenols (Senturk *et al.* 2009; Jennifer & Ifedi 2019) and naphthalene (Zhu *et al.* 2008). The main aim of the present study was to investigate the possibly beneficial combination of polyaluminum chloride, bentonite, a suitable polyelectrolyte and a cationic surfactant to achieve outstanding purification efficiency by a relatively simple coagulation/adsorption/sedimentation method in the case of real car wash wastewaters.

MATERIALS AND METHODS

Coagulation/flocculation experiments

The purification of real car wash wastewater was investigated in a F4P Jar Test flocculator (VELP Scientifica). As coagulants polyaluminum chloride (‘BOPAC; Unichem Kft., technical grade), iron(III) chloride (‘UNIFLOC-C’, Unichem Kft., technical grade), iron(III) sulfate (‘UNIFLOC’, Unichem Kft., technical grade) or aluminum(III) chloride (‘UNIPAC’, Unichem Kft., technical grade) were used. As flocculants, non-ionic or anionic polyelectrolytes (‘UNIFLOC-M20’ and ‘UNIFLOC-LT27’, respectively; Unichem Kft., technical grades) were applied. Addition of clay mineral (Na-bentonite; Unikén Kft., technical grade) and a cationic surfactant – hexadecyltrimethyl ammonium bromide (‘HTABr’; Sigma-Aldrich, analytical grade) – was also investigated since organophilic clay minerals can adsorb different dyes and non-polar contaminants.

Coagulants/flocculants and other supporting materials were added in calculated amounts during the intense stirring (200 rpm) of 0.5 L car wash wastewater, and 30 seconds after the last material was added, 2 min slow stirring (20 rpm) was applied, then the formed flakes were allowed to sediment for 30 min. In the case of Na-bentonite addition, it was always added firstly in suspension form (before the experiments the bentonite was allowed to swell in stirred water for 48 h at minimum, $c_{suspension} = 10$ g/L). The HTABr – whose amounts were calculated according to the total cation exchange capacity – was added directly after the clay mineral and the suspension was left to be stirred vigorously for 20 min (200 rpm) to enable the complete exchange of Na^+ ions of the clay mineral with the cationic surfactant. After 20 min of stirring, the coagulant and flocculant were also added to the beakers, then 2 min of gentle stirring (20 rpm) was applied. The volumes of the produced sediments were determined by Imhoff cone sedimentation experiments.

Determination of purification efficiencies

Purification efficiencies were determined by measuring the turbidity of the supernatants after 30 min of sedimentation with a Hach 2100N nephelometric turbidity meter. Additionally, chemical oxygen demand (COD) and extractable oil content were also measured in some cases. COD was measured by the standard potassium dichromate oxidation method using standard test vials (Hanna Instruments) applying 120-min-long digestions at 150 °C in a Lovibond ET 108 digester, then the measurements were carried out via a Lovibond COD Vario photometer. Extractable oil content was measured by a Wilks InfraCal TOG/TPH analyzer, using hexane (VWR International Ltd, analytical grade) as extracting solvent.

Characterization of the investigated car wash wastewater

The car wash wastewater was collected from a South Hungarian car wash station and the results of its characterization were the following: COD was 357 ± 8 mg L^{-1}, conductivity was 1.43 ± 0.1 mS cm^{-1}, turbidity was 333 ± 10 NTU, extractable oil content was 26 ± 2 mg L^{-1}, and the pH was 7.30 ± 0.2.

RESULTS AND DISCUSSION

Effects of polyaluminum chloride

In the first series of experiments, different amounts of BOPAC coagulant were added to the wastewater and the achievable purification efficiencies were determined by turbidity measurements. The sediment volumes were also measured (Figure 1).

The turbidity values of the supernatants decreased intensely in accordance with the increasing concentration of Al^{3+} (from 2 to 20 mg L^{-1}), resulting in 35 ± 4 NTU and 89 ± 1% purification efficiency, but higher concentrations resulted in only slightly lower turbidity values. At the same time, the volume of the produced sediment showed a nearly linear increase with the increasing Al^{3+} content. Considering the purification efficiencies, the quantity of the used chemicals and the produced sediment volumes, the 20 mg L^{-1} Al^{3+} concentration could be recommended. 50 mg L^{-1} aluminum content resulted in just a slightly higher purification efficiency (93 ± 1%), but twice higher sediment volume compared to the observed values in the case of 20 mg L^{-1} added aluminum content.

Effects of clay mineral

In the next experimental series, different amounts of Na-bentonite (0, 100, 250, 500 mg L^{-1}) were added before the BOPAC addition (20 mg L^{-1} Al^{3+} content was applied). The purification efficiencies (calculated from turbidity) and the sediment volumes are summarized in Figure 2(a).

100 mg L^{-1} Na-bentonite addition significantly increased the purification efficiency (98 ± 1%) and the sediment volume decreased slightly. Following the application of higher bentonite amounts, almost the same purification efficiencies were measured and the sediment volume decreased only slightly. Therefore, higher than 100 mg L^{-1} Na-bentonite concentration cannot be recommended, even though the sedimentation was slightly faster at higher

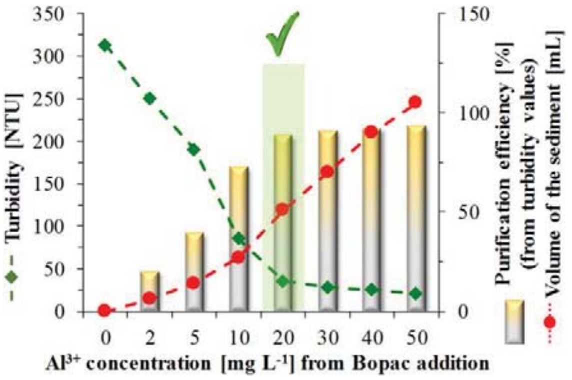

Figure 1 | Effects of Al^{3+} concentration (originating from BOPAC addition) on the coagulation: turbidity values after sedimentation, calculated purification efficiencies, and sediment volumes.

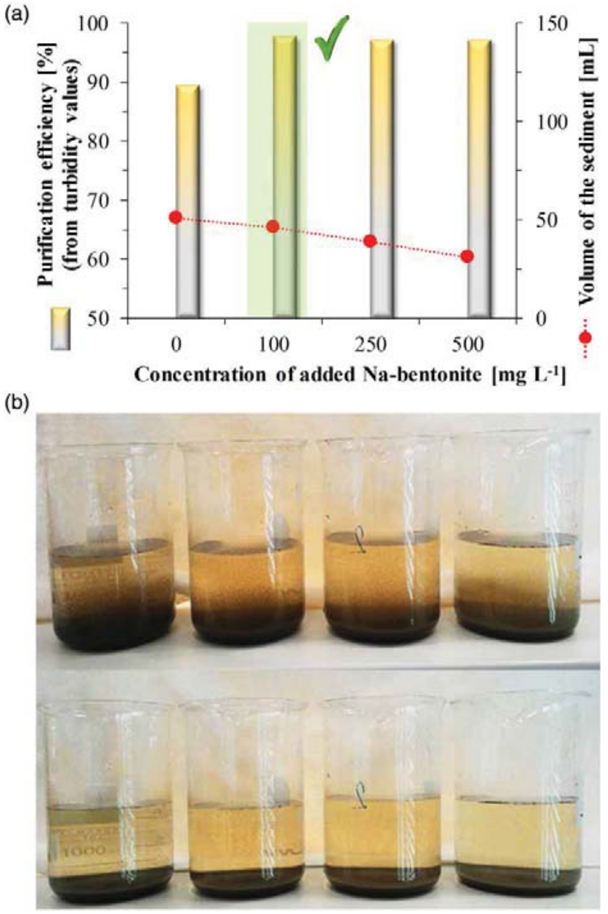

Figure 2 | (a) Effects of Na-bentonite addition (applied before the BOPAC addition) on the purification efficiency and sediment volume; (b) photographs after 30 and 60 s of sedimentations in the cases of 0, 100, 250 and 500 mg L^{-1} Na-bentonite additions, respectively.

bentonite concentrations as it can be seen in Figure 2(b). The effects of the sole addition of Na-bentonite was also investigated as reference experiments, and the measured turbidity values (333, 210, 285, 355 and 580 NTU in the cases of 0, 100, 250, 500 and 1,000 mg L^{-1} bentonite additions, respectively) proved the necessity of the coagulant addition.

Effects of non-ionic and anionic polyelectrolytes

Table 1 | Achievable purification efficiencies (calculated from turbidity values) and the resulted sediment volumes after polyelectrolyte addition (in 0.5 mg L^{-1} concentration)

Added materials	Turbidity (NTU)	Purification efficiency (%)	Sediment volume (mL)
–	333	–	–
UNIFLOC-M20 (0.5 mg L^{-1})	100	70	Not measured
UNIFLOC-LT27 (0.5 mg L^{-1})	65	80	Not measured
Na-bentonite (100 mg L^{-1}) + BOPAC (20 mg L^{-1} Al^{3+}) + UNIFLOC-M20 (0.5 mg L^{-1})	4	98.5	30
Na-bentonite (100 mg L^{-1}) + BOPAC (20 mg L^{-1} Al^{3+}) + UNIFLOC-LT27 (0.5 mg L^{-1})	4	98.5	15

The extra addition of two different types of polyelectrolytes – after the Na-bentonite (100 mg L^{-1}) and BOPAC (20 mg L^{-1} Al^{3+}) additions – was investigated in two beakers, while in another two beakers reference experiments were carried out by using the polyelectrolytes alone. The non-ionic (UNIFLOC-M20) and anionic (UNIFLOC-LT27) polyelectrolytes were applied in a low concentration (0.5 mg L^{-1}). The results (Table 1) confirmed that the extra addition of both polyelectrolytes increased the purification efficiency, but concerning the sediment volume the anionic UNIFLOC-LT27 was more beneficial, as the measured sediment volume (V = 15 mL) was only half the value compared to the one measured after the addition of non-ionic polyelectrolyte (V = 30 mL).

Comparison of conventional coagulants and BOPAC polyaluminum chloride

Polyaluminum chloride (BOPAC) was compared with different conventional coagulants (iron(III) chloride, iron(III) sulfate and aluminum(III) chloride) to determine the achievable turbidities. Coagulants alone (used in 20 mg L^{-1} metal ion concentrations), and together with the anionic polyelectrolyte (0.5 mg L^{-1}) and/or Na-bentonite (100 mg L^{-1}) were also investigated (Table 2).

The results confirmed the outstanding efficiency of polyaluminum chloride in the case of the real car wash wastewater, as the measured turbidity values were 4–35 NTU, while in the case of conventional iron or aluminum coagulants 88–190 NTU and 22–82 NTU values were measured, respectively. The outstanding purification efficiency of the BOPAC can be explained by its prehydrolyzed form and Keggin structure, which enable its advanced adsorption ability. In the series where BOPAC was added to the system, the COD values and extractable oil contents of the supernatants were also measured, and

Table 2 | Achievable turbidity values of the supernatants in the case of different coagulants

Added materials	Turbidity values of the supernatants			
	Polyaluminum chloride (BOPAC)	Iron(III) chloride	Iron(III) sulfate	Aluminum(III) chloride
20 mg L^{-1} M	35	160	175	75
100 mg L^{-1} Bent. +20 mg L^{-1} M	7	173	190	82
20 mg L^{-1} M +0.5 mg L^{-1} PE	5	91	96	22
100 mg L^{-1} Bent. +20 mg L^{-1} M +0.5 mg L^{-1} PE	4	88	110	44

M: given coagulant metal ion; Bent.: Na-bentonite; PE: UNIFLOC-LT27 anionic polyelectrolyte.

57 ± 1% and 83 ± 3% purification efficiencies were determined, respectively.

Effects of *in situ* generation of organophilic clay minerals by HTABr addition

The effect of *in situ* addition of HTABr was also investigated, since it can exchange the Na^+ ions of bentonites to organic cations, hence it can modify the surface to be organophilic, making them suitable for the adsorption of different types of organics such as dyes and different non-polar contaminants. Different amounts of Na-bentonite (0, 100, 500 and 2,000 mg L^{-1}) and HTABr (in calculated concentrations, according to the bentonite's cationic exchange capacity) were added before the BOPAC (20 mg L^{-1} Al^{3+}) and UNIFLOC-LT27 (0.5 mg L^{-1}) addition. Turbidity, COD and extractable oil content of the supernatants and the sediment volumes were measured (Table 3).

The reduction of turbidity, COD and extractable oil content values were very similar in all cases, but enhanced color removal of the supernatants were observed visually when the organophilic bentonite was used. Absorbance measurements confirmed the increasing color removals from sample 1 to sample 4, as the absorbance values significantly decreased at $\lambda = 400$ nm (Figure 3(a)).

Considering the turbidity values, the color removal, and the reduced sediment volumes (Table 3), the usage of 500 mg L^{-1} organophilic bentonite can be considered advantageous. The beneficial effect of HTABr addition via the formation of more compact flocks (which resulted in reduced sediment volumes) can be seen in Figure 3(b), where the treated waters were stirred slowly (20 rpm).

DISCUSSION

Similarly to the research of Rodriguez Boluarte *et al.* (Rodriguez Boluarte *et al.* 2016) the present study also proved that the usage of polyaluminum chloride is more effective than conventional coagulants like aluminum

Table 3 | Turbidity, COD and extractable oil contents of the supernatants and the sediment volumes

No.	Added materials	Turbidity (NTU)	COD (mg L^{-1})	Extractable oil content (mg L^{-1})	Sediment volume (mL)
–	–	333	357	26	–
1	100 mg L^{-1} Bent. + 20 mg L^{-1} Al^{3+} + 0,5 mg L^{-1} PE	6	158	4	15
2	100 mg L^{-1} Bent. + HTABr + 20 mg L^{-1} Al^{3+} + 0,5 mg L^{-1} PE	6	156	5	13
3	500 mg L^{-1} Bent. + HTABr + 20 mg L^{-1} Al^{3+} + 0,5 mg L^{-1} PE	3	156	4	11
4	2,000 mg L^{-1} Bent. + HTABr + 20 mg L^{-1} Al^{3+} + 0,5 mg L^{-1} PE	4	154	4	20

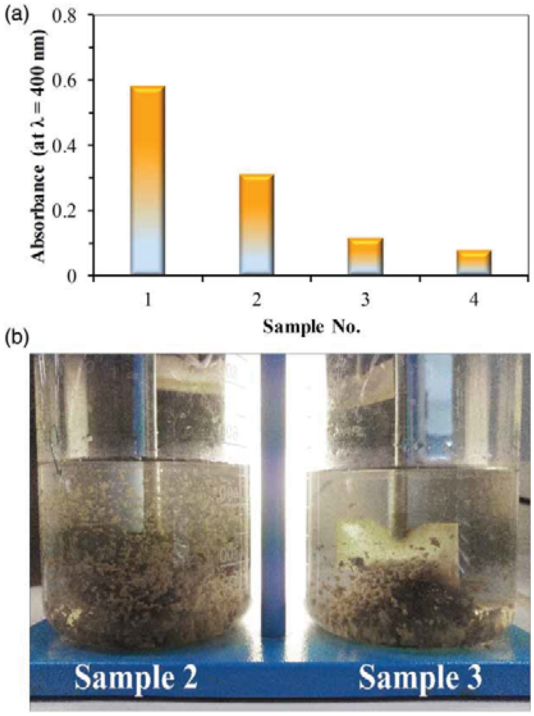

Figure 3 | (a) Absorbance values of the supernatants ($\lambda = 400$ nm), (b) photographs of samples 2 and 3.

chloride, or iron-salts in the case of the chemical destabilization of real car wash wastewaters. The mentioned authors did reduce the turbidity to a very similar value (~4 NTU), but polyaluminum chloride was used in a significantly higher concentration (500 mg/L) without any polyelectrolyte, bentonite, or cationic surfactant addition. Therefore, the treated wastewater was still colorful which was then treated by an additional ozonation step, but it was not able to further reduce the turbidity or COD of the wastewater. In the present study, turbidity, COD and color were also significantly reduced by a simple and cost-effective method. The achieved turbidity (4 NTU) was significantly lower compared to other studies: 12.5 NTU (Zaneti *et al.* 2011), 13–28 NTU (Etchepare *et al.* 2014) and 22 NTU (Mohamed *et al.* 2014). Simultaneously, the total cost of the presented purification method was calculated to be only 0.092 \$ m^{-3} in the case of BOPAC (20 mg L^{-1} Al^{3+}), anionic polyelectrolyte (0.5 mg L^{-1}) and bentonite (100 mg L^{-1}) addition, and it was 0.372 \$ m^{-3} when HTABr addition was also applied with 500 mg L^{-1} bentonite in the case of the same BOPAC and polyelectrolyte addition. These costs are significantly lower compared to the calculated costs of other publications, which were e.g. 0.85–1.12 \$ m^{-3} (Etchepare *et al.* 2014) and 0.812 \$ m^{-3} (Mohammadi *et al.* 2017).

CONCLUSIONS

In the present study, it was demonstrated that the usage of BOPAC by itself (without Na-bentonite or polyelectrolyte addition) was not effective enough for the purification of real car wash wastewaters. The extra addition of anionic polyelectrolyte was crucial to significantly increase the size of the produced clusters, intensify the sedimentation and decrease the sediment volume. BOPAC proved to be significantly more effective than conventional coagulants due to its pre-hydrolyzed form and Keggin structure. Taking the efficacy and economical aspects into account the usage of 100 mg L^{-1} Na-bentonite with 20 mg L^{-1} Al^{3+} and 0.5 mg L^{-1} anionic polyelectrolyte were the most effective to decrease the turbidity, COD and the extractable oil content of real car wash wastewaters with efficiencies of 98%, 59%, and 85%, respectively. These results reinforced that, by the combination of these materials, high purification efficiency can be achieved via a very simple method, without high investment cost. Simultaneous addition of the cationic surfactant (HTABr) resulted in the successful *in-situ* generation of organophilic clay minerals which resulted in significant color removal, slightly lower turbidity value (99% efficiency) and significantly lower sediment volume. The application of both these last two combinations can be recommended as easily feasible, but efficient pretreatments of car wash wastewaters before the final membrane filtration step for the efficient removal of floating particles, emulsified oil, and hydrocarbons.

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