



Research article

organo acid-activated clays for water treatment as removal agent of Eosin-Y: Properties, regeneration, and single batch design absorber

Abdulaziz M. Alanazi^{a,**}, Ohoud A. Jefri^b, Mohd Gulfam Alam^a, Rawan Al-Faze^c, Fethi Kooli^{a,*}

^a Department of Chemistry, Islamic University of Madinah, Madinah, 42351, Saudi Arabia

^b Department of Biological Science, King Abdulaziz University, Jeddah, 21589, Saudi Arabia

^c Department of Chemistry, Taibah University, Al-Madinah Al-Munawarah, 30002, Saudi Arabia

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ABSTRACT

Organoclays have been proposed as efficient removal agents for colored wastewater treatment. In this study, organo-acid-activated clays were investigated for their ability to remove eosin Y dye molecules. Firstly, the clay was acid activated using sulfuric solution at 90 °C for overnight. Secondly, the resulting materials were treated by hexadecyltetramethylammonium bromide solutions to obtain organo-acid-activated clays. Several techniques were used, such as X-ray diffraction, carbon hydrogen nitrogen analysis, silicon-29 and carbon-13 solid-state nuclear magnetic resonance, and nitrogen adsorption isotherms. The cation exchange capacity values were reduced and the specific surface area values increased from 80.1 m²/g to 183.2 m²/g during the acid activation process. The resulting organo-acid-activated clays had a similar expansion of interlayer spacing of 3.90 nm with less intercalated hexadecyltetramethylammonium surfactants, ranging from 0.80 mmol/g to 1.22 mmol/g; 13C solid NMR indicated that the intercalated surfactants exhibited different degree of conformation. Many factors, including the solid dose, solution pH, amount of intercalated surfactants, and starting eosin-Y concentrations, were studied in relation to the removal capabilities of organo acid-activated clays. Based on the Langmuir model, the removal capacity of the organo acid-activated clays ranged from a minimum of 43.5 mg/g to a maximum of 79.3 mg/g, dependent on the surfactant quantities and acid activation degree. , and the pH. The removal percentage of eosin-Y was increased from 50.5 % to 80.8 % by treating the organo acid-activated clay with HCl solution before the removal procedure. Regeneration and reuse of two selected organo acid-activated clays were carried out for seven successive cycles, and a reduction in the initial efficiency was in the range of 26.4 %–30.1 %. However, for organoclay (without acid activation), approximately 52.1 % efficiency was maintained. Using the Langmuir model and mass balance equations, a single-stage adsorber design was suggested for different dye volumes at a constant starting concentration.

* Corresponding author.

** Corresponding author.

E-mail addresses: a-aziz@iu.edu.sa (A.M. Alanazi), fkooli@iu.edu.sa (F. Kooli).

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1. Introduction

Clay minerals exhibit interesting properties in catalytic and environmental applications [1]. The modification of clay dependent on its application has been proposed. For example, catalytic applications require a stable material with porosity and acidity similar to those of zeolites [2]. Clay minerals are readily available in nature, they are suggested as a promising candidate for remediation of contaminated water owing to their low cost or the removal of acidic dyes (negatively charged species), many reports have mentioned that clay minerals are not efficient adsorbents owing to their negatively charged surface [3]. To get over this problem, the alteration of the raw clay minerals surface from hydrophilic to organophilic was proposed using quaternary ammonium cations with long aliphatic chains of carbon atoms [4–7]. Table 1 shows the application of organoclay-based adsorbents to treat the spoiled water by a selected eosin Y (EY) dye. As shown in Table 1, most of the reported efforts are mainly concerned with organoclays per treatment set.

The interest in the acid activated clays (AACs) remains widespread with several applications [13]. The AACs were obtained after the treatment of clay minerals by HCl or H₂SO₄ acid solutions [13], resulting a decrease in the cation exchange capacity (CEC) and enhancement of the specific surface area (SSA) and acidity [13]. Combination of AACs and organic molecules was described, short tetraalkylammonium molecules such tetramethylammonium, tetrapropylammonium cations were used [14]. These derivatives were explored in a catalytic reaction to convert of α -pinene to camphene [15]. The OAACs modified with cetyltrimethylammonium (C16TMA) was proposed for the synthesis of porous AAC- heterostructures, and for the preparation of polyvinylpyrrolidone-OAAC composites [16,17]. The amount of the C16TMA cations was tuned and controlled by many factors. For an extent acid activation process, OAACs with lower contents of C16TMA⁺ cations were prepared using C16TMABr solution [18]. However, in case of C16TMAOH solution, the contents of C16TMA cations were higher starting from a certain acid to clays ratios [19]. The surfactants amount was also influenced by the temperature of acid activation process [20]. As expected, the starting C16TMA concentrations have influenced the uptake amounts of the OAACs and thus the thermal properties [18,20].

As mentioned above, the use of organoclays for the adsorption of dyes is still gaining a considerable attention, and many studies were reported in the literature [21,22]. However, only one study was reported using an OAAC prepared from a natural acid clay and decylamine [23] as a modifier agent. The application of OAACs prepared from AACs acid/clay levels was not reported in the removal of acidic dyes. The eosin Y (EY) dye was selected in this study, owing to its diverse usages. It is used as an ingredient in food coloring agent in food, cosmetics, pharmaceuticals, textiles, and as biological tissues' counterstain. It is employed as photoredox catalyst in organic synthesis and in production of dye-sensitized solar cells and [24–29]. The eosin Y is soluble in different solvents, such as alcohols with different carbon numbers, dimethyl formamide, dimethyl sulphoxide, and glycerol. Wastewater containing this dye causes serious environmental problems due to its stability and dark color [27], and its removal by different adsorbents is usually affected by a series of variables, involving the starting concentration, adsorbent dose, and pH.

During the adsorption phenomena, the dyes are transferred from the aqueous phase to the adsorbent's surface. Depending on the adsorbate, the spent adsorbent may become a pollutant and cannot be disposed of in landfills [30,31]. Therefore, it is essential to regenerate and reuse the adsorbent. Conventional regeneration methods fall into three categories: physical, chemical, and biological [32,33]. In case of spent organoclays different eluents including ethanol, sodium hydroxide, sodium bicarbonate, sodium acetate and hydrochloric acid were used as desorbing agent to remove adsorbed dyes from OCs [34,35]. In another case, the thermal desorption method was proposed, the fresh organoclays after adsorption were treated at temperature of 110 °C to 150 °C at different times (10, 30, 50 and 60 min). Further increase of temperature resulted to the decomposition of the intercalated surfactants in OCs [32,33]. The recycled adsorbent proved to be effective for adsorbing color dyes for a minimum

three to five consecutive cycles. In the present work, the removal properties of eosin Y were explored using OAACs. AACs were prepared from a selected clay mineral acid-activated at various sulfuric acid/clay ratios at 90 °C for overnight. The OAACs derivatives were obtained after an exchange reaction with cetyltrimethylammonium bromide (C16TMABr) solution at room temperature. The derived OAACs were characterized using different techniques. Effective parameters of dye removal, including dye concentration, solid dosage, surfactants, and pH were optimized. Generally, EY pH solution is altered by HCl or NaOH solution before the removal process. An alternative method was proposed consisting of treating a selected OAAC with an HCl or NaOH solution prior adding to EY solution at natural pH. For the regeneration of selected OAACs, oxone and cobalt nitrate solution were used to decompose the adsorbed EY dyes on the organoclays [9]. This process is friendly operated and resulted to good performance [12]. Finally, the design for a single-stage adsorber was suggested using the Langmuir fitting and the mass balance equations.

Table 1
Eosin Y removal efficiency of various organoclays and organosilicates

Samples	q _{max} (mg/g)	References
Organocloisites	39.2–51.5	[8]
Organo-polymer grade montmorillonites	75.1–94.2	[9]
Organo-local clays	48.6	[10]
Organo-magadiites	69.1	[11]
Organo-kenyates	48.1	[12]

2. Experiments and characterization

2.1. Materials

STx-1 (Ca^{2+} -montmorillonite, Ca-Mt) with a CEC of 92 meq/100 g) was supplied by the Source Clays repository, Purdue University (USA). Sulfuric acid and cetyltrimethylammonium bromide (C16TMABr) salt were supplied by Aldrich. Eosin Y, oxone, and cobalt nitrate reagents were provided by Across. All reagents were utilized as obtained. The structures of the C16TMA surfactant and the eosin Y dye are presented in Fig. 1A and B, respectively.

2.2. Acid activation

Ca-Mt was mixed with sulfuric acid solution (at a fixed volume of acid/clay mass ratio of 20 mL g^{-1}) at 90 °C overnight. This acid/clay fraction (in weight) was altered in the range of 0.1–0.5 and was calculated based on dried mass of Ca-Mt and H_2SO_4 (98 %). The obtained AAC samples were frequently rinsed using distilled water until neutral pH and free SO_4^{2-} ions were obtained, as tested by BaCl_2 solution, followed by drying at ambient temperature. The solid is identified as AAC-0.1, where 0.1 indicates the acid/clay ratio used.

2.3. Organo acid-activated clays

Typical preparation consisted of dispersing 1 g of AAC-0.1 to 25 mL of C16TMABr solution hours n containing 1.2 g of C16TMABr salt. The suspension was mixed for 18 h at ambient temperature using a magnetic stirrer. The solid was separated by filtration and washed with distilled water until liberated of Br^- ions (AgNO_3 solution test) and dried at ambient temperature. The as prepared solid was identified as OAAC-X (where X indicates the acid/clay ratio used).

In some cases, various OAAC-0.3 were prepared using different amounts of the C16TMA cations and following the same procedure described above.

2.4. Chemical stability

One gram of selected OAAC-0.3 sample was suspended in 25 mL of different concentrations of HCl or NaOH solutions varying from 0.1 M to 3 M for 18 h. The solid was rinsed rigorously by distilled water and left at ambient temperature.

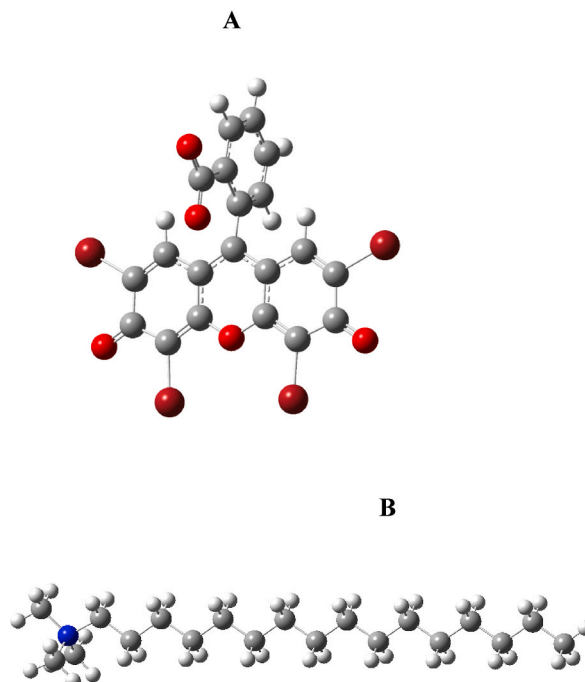


Fig. 1. The molecular structures of (A) eosin Y dye (A) and (B) C16TMA surfactant optimized at B3lyp/6-31G (d).

2.5. Removal of eosin-Y

The procedure was followed as reported in a recent work [8]. A stock solution of EY dye (1000 mg/L) was prepared and used for further preparation of other diluted solutions. Normally, starting concentrations of 25–900 mg/L were used for removal trials.

The removal tests were achieved by a standard batch procedure. Fixed amounts of C16-AAC-X (0.1 g) were suspended in a volume of 10 mL of different concentration of EY dye in closed tubes.

These tubes were shaken in a water bath shaker with a shaking speed of 120 rpm at temperature (25 ± 0.5 °C), and the removal equilibrium was reached after a period of 18 h. The residual concentration of EY was collected by centrifugation and estimated by spectrophotometry.

2.6. Regeneration process

Regeneration studies were undertaken following the procedure described previously [9]. The procedure consisted of using fresh material treated with EY solution ($C_i = 200$ mg/L) for 6 h. The spent material was treated with 12 ml of solution containing 12 mg of oxone and cobalt nitrate for 30 min. The resulted sample was separated and suspended again in 50 mL of fresh EY solution at 25 °C, separated, rinsed with distilled water and then subjected to the same procedure for seven cycles.

2.7. Characterization

CEC of received clay mineral was estimated by the micro-Kjeldahl method [36]. EURO EA elemental analyzer was used to determine the carbon, nitrogen, and hydrogen (CHN) in the modified OAAC-Xs. Advance 8 X-ray diffractometer from Bruker equipped with Ni-filtered and Cu-K α radiation was used to collect the powder x-ray patterns at scanning angle of 2θ was from 2 to 50°. Solid-state nuclear magnetic resonance (NMR) experiments were achieved on a Bruker 400 spectrometer. More details on these procedures were reported in previous work [18]. Quantachrome Autosorb 6 instrument was employed to estimate the SSA, P.V. (pore volume) and A.P. D. (average pore diameter) of AACs and derived OAACs. SSA values were calculated using the BET equation. While P.V. values were estimated at nitrogen relative pressure P/P_0 of 0.95. The absorbance of the equilibrium EY concentrations was determined using a Cary 100 Conc. VARIAN spectrophotometer at a maximum absorption wavelength (λ_{max}) of 516 nm.

2.8. Computational calculation

The theoretical computations have been performed using Gaussian09 suit of program at the B3lyp/6-31G(d) level at temperature of 25 °C and a pressure of 1 atm. Water was selected as a solvent. The geometries optimization of the molecules was adjusted by a frequency calculation to check that every structure didn't correspond to any negative value. More details are discussed in Ref. [29].

3. Results and discussion

3.1. CHN analysis

The CHN contents of the various OAAC-Xs is presented in Table 2. The starting clay mineral exhibited the highest percentages of C and N elements. These percentages decreased following the increase in the acid/clay ratios from 0.1 to 0.5 (Table 2).

Equation (1) was used to estimate the intercalated C16TMA cations in mmol/g.

$$\text{Intercalated amount} = C(\%)/[12 \times (\text{number of carbon atoms in } C_{16})] \times 1000 \quad (1)$$

The maximum intercalated C16TMA cations (1.22 mmol/g) were obtained for the starting clay mineral (AAC-0.0); as the acid activation progressed, this value kept decreasing, with the lowest value of 0.80 mmol/g for ACC-0.5, which could be related to the reduction in the CEC values, as reported in Table 2.

The estimated molar ratios C/N in OAAC-Xs were in the range of 17.51–18.89, and the computed value for the pure C16TMABr salt

Table 2
Elemental (CHN) analysis of different organo acid-activated clays.

Samples	CEC meq/100 g	C%	H%	N%	C/N ^a	Intercalated (mmol/g)
C16TMABr	N.A	62.62	3.87	11.67	19.29	N.A.
OAAC-0.0	92	28.14	5.40	1.87		1.22
OAAC-0.1	89	24.84	4.84	1.64		1.08
OAAC-0.2	81	21.40	4.33	0.88		0.93
OAAC-0.3	75	20.52	4.03	0.78		0.90
OAAC-0.4	69	19.61	3.88	0.71		0.85
OAAC-0.5	64	18.26	3.55	0.68		0.80

N.A. not applicable.

^a C/N molar ratio.

was 19.26, which is comparable to the theoretical value of 19. However, a molar C/N ratio of 16.29 was also reported [37]. These results indicated that the alteration of ACC-X by C16TMA⁺ cations was successfully achieved.

In addition, the uptake of C16TMA⁺ cations by AAC-Xs were greater than the CEC values.

It was possible to tune the amount of intercalated C16TMA⁺ cations in a selected OAAC-0.3 by adjusting the initial loading concentrations of surfactants. Indeed, the intercalated amounts were varied from 0.22 mmol/g to 0.37 mmol/g, and a maximum of 0.90 mmol/g was obtained.

These data suggested that the insertion of C16TMA⁺ cations took place first through the cation exchange reaction for intercalated values less than or equal to CEC. At values exceeding the CEC, ion-pairs and chain-chain interactions were also proposed by different authors [37,38]. These interactions affected the arrangement and orientation of the intercalated surfactants.

The difference between intercalated amounts and CEC values was used to calculate a net charge of the resulting OAACs. The OAACs exhibited a net positive charge varying from 0.3 to 0.16, and indicated that the surface of the organoclay was indeed transformed to positively charged, that made possible the removal of the acidic dyes.

3.2. X-ray diffraction

The PXRD patterns of the Ca-Mt and AAC-X materials are presented in Fig. 2A. The pristine clay displayed an interplanar d_{001} of 1.54 nm corresponding to a montmorillonite clay mineral phase containing mainly Ca²⁺ cations in the interlayer space with two layers of water [39]. A progressive loss in intensity of the diffraction peak (001) and the widening of the peak occurred as the extent of acid activation raised. During acid activation, the Ca²⁺ cations were exchanged with protons, and a reduction of d_{001} from 1.54 nm to 1.27 nm occurred [13]. However, in the present case, there was no change in the position of the reflection at 1.54 nm. In previous reports, this value was assigned to the proton phase with two layers of water in the interlayer spacing [40], or to the auto-transformation of AACXs that occurred during the aging at longer periods of time [13]. In addition to the protons exchange process, the acid activation induced the liberation of the structural cations in the clay layers (so called leaching) and their relocation to the interlayer spacing, and Al-, Fe-, or Mg- forms of AACXs might occur [41]. In the present case, the prepared AACs were not aged for a longer period of time, after washing, they were dried for overnight. In meantime, the formation of the silica amorphous phase was associated to the improvement of reflection's intensity at 0.41 nm [18].

Shift of diffraction peak (001) occurred to lower angles after treatment of AACX-s with C16TMABr solution, a corresponding to a d_{001} basal spacing of 3.80 nm. The existence of higher orders of diffraction peaks, such as d_{002} and d_{003} , in the PXRD patterns of OAACXs for X ratios below 0.3 (Fig. 2A') revealed a regular prearrangement of alkyl chains of C16TMA in the interlayer space of host clays. However, the degree of crystallinity decreased for OAAC-X for X values higher than 0.3, and the PXRD patterns mainly exhibited a 002 diffraction peak equivalent to a d_{002} value of 1.80 nm, with a broad 001 reflection corresponding to a d_{001} of 3.80 nm [18]; this was related to the gradual loss of crystallinity of the starting AACs.

Fig. 3 depicts the PXRD patterns of AAC-0.3 reacted with different concentrations of C16TMABr solutions. A regular expansion in

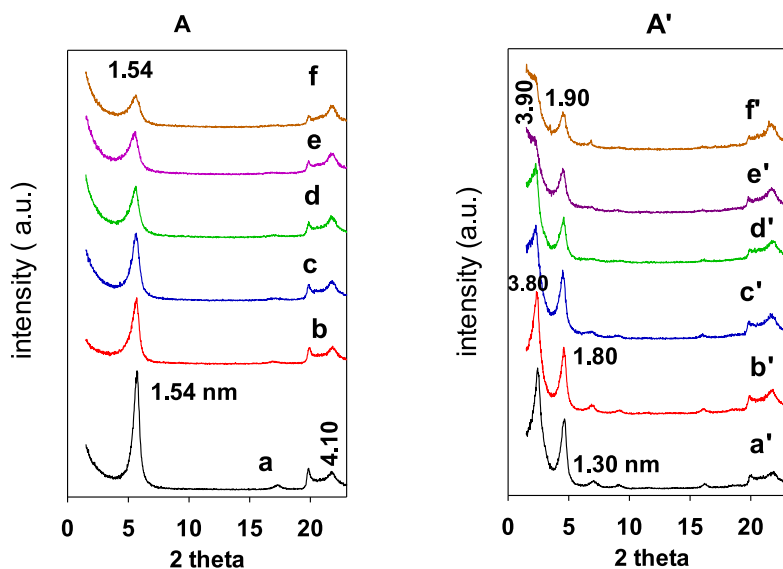


Fig. 2. APowder XRD patterns of Ca-montmorillonite (a) acid activated at different acid/clay ratios, (b) 0.1, (c) 0.2. (d) 0.3. (e) 0.4, and (f) 0.5. Fig. 2A' corresponds to powder XRD patterns of organo acid activated clays after reaction with C16TMABr solution. Ca-montmorillonite (a'), (b') 0.1, (c') 0.2. (d') 0.3. (e') 0.4, and (f') 0.5.

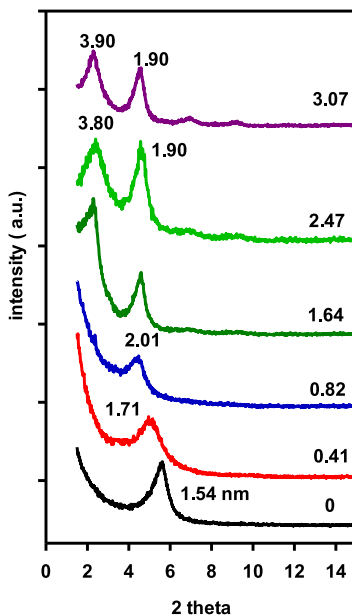


Fig. 3. Powder XRD patterns of AAC-0.3 reacted with C16TMABr solution at different concentrations.

the interlayer distance occurred from 1.54 nm to 1.71 nm–2.01 nm, and sudden increase to 3.80 nm happened when 1.64 mmol of C16TMABr was used. The expansion value of 3.80 nm was maintained for concentrations higher than 1.64 mmol. However, when using a clay mineral from a different source, an expansion of 1.90 nm was achieved regardless of the C16TMABr concentrations being higher than the CEC values [8]. It is mentioned that the alkyl chain length and the layer charge of the clay mineral affected the prearrangement of inserted surfactants [42,43]. Indeed, the number of interlayer charges affected the expansion of the layers. When the charge per cell is low (<0.5), C16TMA⁺ cations displayed a monolayer parallel to the host montmorillonite, and double-layers of C16TMA⁺ cations for the charge between 0.5 and 1.0. However, C16TMA⁺ cations exhibit an oblique orientation within the

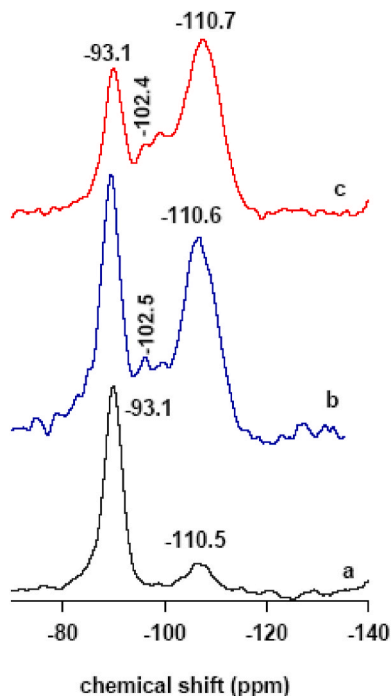


Fig. 4. Magic-angle spinning (MAS) ²⁹Si NMR spectra of Ca-montmorillonite (a) acid activated at selected acid/clay ratios, (b) 0.3, (c) 0.5.

montmorillonite space for charge values higher than 1.0 [44].

The dehydrated clay mineral exhibits a thickness of 0.96 nm, and from the basal spacing value of 3.90, an interlayer spacing of 2.94 nm was estimated, and it was longer than the estimated length of C16TMA⁺ cations of 2.20 nm–2.5 nm [18,45]. Thus, a bilayer paraffin-arrangement of C16TMA⁺ cations was predicted with an inclination angle of 37° to the clay layers [9]. The bilayer and pseudotrimolecular layer arrangements were associated to basal distances of 1.70 nm and 2.10 nm, respectively [46].

The chemical stability of OAAC-0.3 was tested in HCl and NaOH solutions, as reported in Section 2.4. When OAAC-0.3 was suspended into HCl solution (2 M and above) a reduction of the basal spacing from 3.90 nm to 1.20 nm occurred. This fact was associated to the exchange of inserted surfactant cations by protons. However, these intercalated surfactants were difficult to exchange using a mild HCl or NaOH solutions (concentrations less than 2 M). Other organo-silicate materials exhibited the same results [11,12,47,48]. This finding is useful for studying the removal of acidic dyes at different pH values (see below).

3.3. Solid NMR studies

The changes in the silicon environment during the acid activation progress and the configuration of the C16TMA⁺ cations in the OAAC materials were investigated by solid NMR probe. The ²⁹Si MAS NMR spectra changes are depicted in Fig. 4. The starting AAC-0 material exhibited mainly one peak about at −93.1 ppm, associated with Q³-type Si species, with a shoulder at −110.6 ppm originating from amorphous silica impurities and assigned to Q⁴-type Si species (Fig. 4a) [49]. As the acid/clay ratios increased, the band at −93.1 ppm decreased in intensity; however, the band around −110.6 ppm increased in intensity. These changes were related to the degradation of the layers and the production of amorphous silica in the products (Fig. 4b and c) [48,49]. These observations were consistent with the PXRD data. The amorphous silica exhibited three-dimensional cross-linked framework, and Si species showed weak resonances from −100 to −105 ppm, in our case, only one peak at −102.5 ppm was detected [49].

In the case of the OAACs, no major changes occurred after the reaction with C16TMABr solution, as deduced from ²⁹Si MAS NMR data (spectra not shown). Thus, the C16TMA intercalation did not alter the structure of the layers. The mild pH of the C16TMABr solution did not effectively alter the host layers of AACs structure, as reported for other OCs from different sources [8].

The mobility and the conformation of intercalated surfactant molecules are assessed by ¹³C CP/MAS solid NMR analysis [50]. It was reported that the ¹³C chemical shift is sensitive to the packing orientation and conformation order of the surfactants [51]. For instance, in the solid-like crystalline structure, the chains exhibited a resonance peak at 33–34 ppm, while in the disordered phase, a mean shift to 29–30 ppm was detected. The spectrum of solid C16TMABr salt is presented in Fig. 5, and indicated that the inner methylene (C₃–C₁₄) units of C16TMA species exhibited a *trans*-conformation as an ordered crystalline structure associated to an intense peak at 32.4 ppm. The *gauche* conformation with less extent was detected at a broad resonance with low intensity at 30.0 ppm. It was reported that the *gauche* conformations provided an idea regarding the chain mobility [52]. In the case of the OAAC-0.0 material, the main resonance band at 33.6 ppm was attributed to the all-*trans* conformation of C16TMA cations, and additional bands at 54.3, 25.3, and 16.1 ppm were also reported and assigned to C1, C16 and C17 carbons in the surfactant chain, respectively [8,50]. For OAAC-0.3, the *gauche* conformations at a resonance band of 31.6 ppm were clearly enhanced, in addition to the other resonance bands, as reported in

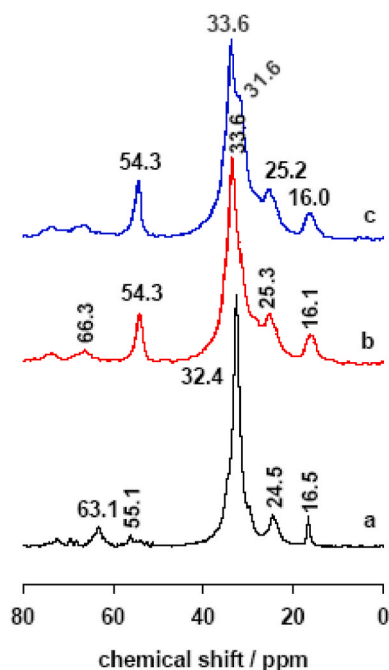


Fig. 5. ¹³C CP/NMR spectra of different organo acid activated clays (b) OAAC-0.3 and (c) OAAC-0.5. (a) corresponds to C16TMABr solid.

Fig. 5. All the OAAC-X displayed the same basal spacing of 3.90 nm; however, the conformation heterogeneity was different and indicates that the local environment between AAC layers may be different than that of non treated clay minerals. These results were in accordance with previously published work [18].

3.4. Surface properties

The surface properties AACs and OAACs materials are presented in Table 3.

The SSA values were enhanced with acid treatment's levels (means acid to clay ratios) and varied from 80.1 m²/g to 183.2 m²/g. The increase in SSA was more than two fold for AAC-0.5 owing to the production of an amorphous silica phase that contributed to an increase of the SSA, or to acid leaching that caused large empty spaces in the layers, in addition to the formation of mesopores [13,53]. After reaction with C16TMABr solution, the SSA values of OAACs decreased three-to five-fold, associated to a decrease in the total pore volume (P.V.) values. The presence of C16TMA⁺ cations in the interlayer spacing blocked the mesopores in the samples, and thus leading to a drop of SSA values. The relatively high SSA indicated that the contribution of the amorphous phase was still significant. Similar data were reported for other organoclays without acid activation because the surfactant occupied the available adsorption sites for nitrogen molecules, and only the external surface was available for nitrogen adsorption [18].

The average pore diameters were in the range of the mesopore values, and it was difficult to conclude the mesoporous character of the examined samples due to the low SSA values.

3.5. Water treatment and EY removal data

In this study, many parameters were studied independently to estimate the optimum conditions for an efficient removal process for water treatment using organo acid-activated clays.

3.5.1. Effect of initial concentration

The effect of EY C_i values on the removal properties of a selected organoclay (OAAC-0.3), different concentrations between 25 and 900 mg/L were used. The other parameters were unchanged. The trend revealed that EY removed was enhanced with the increase of C_i values (Fig. 6). It was observed that the lowest removed amount occurred in the 25 mg/L solution, while the highest uptake occurred at 800 mg/L. While, EY removal percentage decreased from 100 % to 76 % by increasing the EY C_i values. The removal amount increased as more free removal sites were accessible. This behavior was described for other acidic dyes and using different organoclays [54–57].

Since the quantity of OAAC-0.3 was unchanged, so was the number of binding sites. The lack of binding sites required for the EY molecules at higher C_i values was the cause of the drop in removal percentage. However, a higher amount of dye was removed at low C_i values because there were more bonding sites available for fewer EY species on the OAAC-X s surface [56,57].

3.5.2. Effect of dose

For a volume of 10 mL of dye solution (C_i = 200 mg/L), different masses of OACC-0.3 were added to each tube. The EY removed has enhanced from 60 % to 93 % when 0.025 g–0.1 g of additional masses were used. The percentage enhanced steadily till it reached 100 % when 0.8 g of OACC-0.3 was utilized. At the same time the removed amount (qe) decreased (see Fig. 7) [8]. The number of EY molecules remained constant for a fixed volume; however, as the dose of OACC-0.3 was upraised, more removal sites became available and were completely occupied by the EY molecules, leading to an increase of the removal percentage. Conversely, with a lower OACC-0.3 dose, there were fewer binding sites that were adequate to remove every dye molecule present, resulting in a lower percentage. Furthermore, the maximum removal capacity was achieved with the smaller mass of OACC-0.3 because the mass of the adsorbent is inversely proportional to the removal amount (qe).

3.5.3. Effect of surfactant content

Because of the repulsive forces between the negative charge of EY and the clay's surface for AAC-0.0, a low removal ability of EY was anticipated due to the layers of clay minerals' negative charge [8,56]. Other studies have reported that the presence of protons marginally increased the acidic dye elimination after acid activation [58,59]. As previously stated, surfactants were required to modify the surface of the clay mineral in order to change the charge character from negative to positive.

The impact of the C16TMA cations content in the OACC-X materials is shown in Fig. 8A. The raw clay mineral, OAAC-0.0, showed

Table 3
Surface characteristics of organo-acid activated clays.

sample	SSA (m ² /g)	P.V. (cc/g)	A.P.D. (nm)
OAAC-0.0	25.2 (80.1) ^a	0.080 (0.13)	12.81 (6.50)
OAAC-0.1	22.0 (98.3)	0.084 (0.16)	15.23 (6.52)
OAAC-0.2	27.1 (150.8)	0.091 (0.26)	13.8 (6.93)
OAAC-0.3	29.7 (164.8)	0.081 (0.30)	11.15 (7.36)
OAAC-0.4	38.8 (176.3)	0.096 (0.32)	10.17 (7.22)
OAAC-0.5	49.3 (182.2)	0.090 (0.31)	7.37 (6.75)

^a correspond to the starting AAC-X materials.

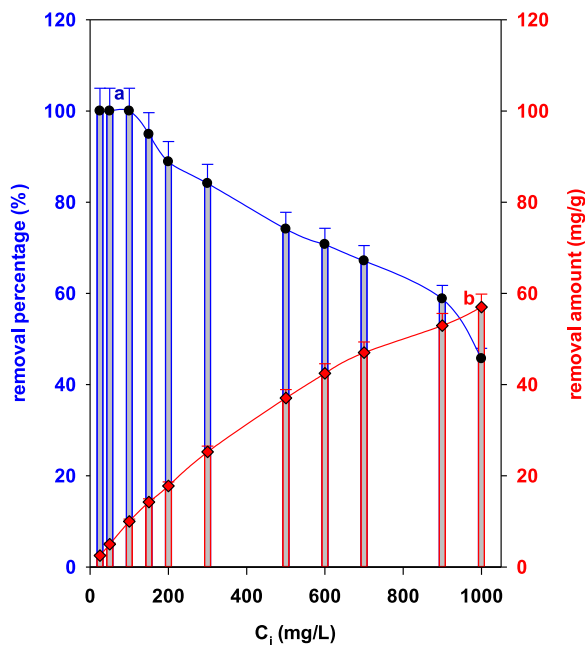


Fig. 6. Effect of EY initial concentrations (C_i) on (a) the removal percentage (% , blue color) and (b) removed amount (mg/g, red color) using an organo acid activated clay (OAC-0.3).

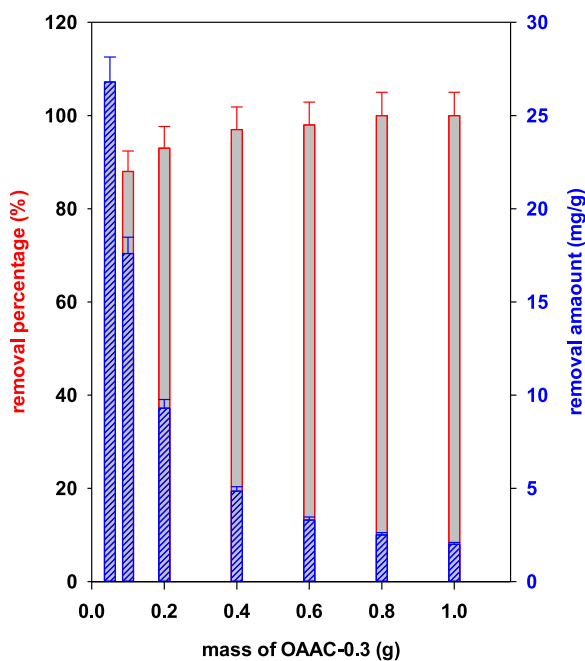


Fig. 7. Effect of the added mass of OAC-0.3 on the removal percentage(%, red color) and removed amount (mg/g, blue color) of EY dye.

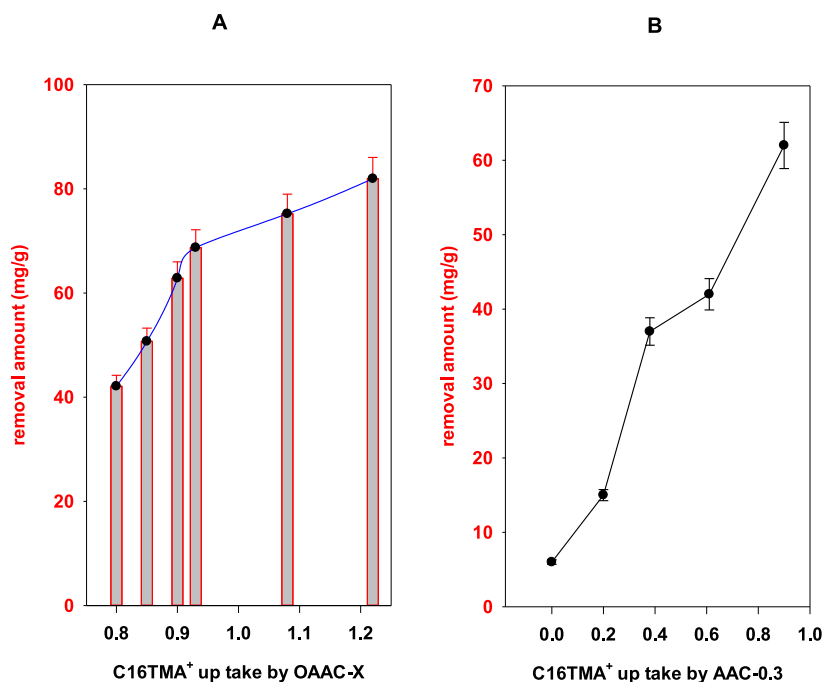


Fig. 8. AEffect of the C16TMA⁺ cations contents on the removed amount of EY by different organo acid activated clays, at initial concentration of 800 mg/L. Fig. 8B represents the variation of removed amount of EY (mg/g) by AAC-0,3 with different content of C16TMA⁺ cations.

an 81.95 mg/g elimination capability at a Ci of 800 mg/L. For OAAC-0.1, this value was lowered to 75.34 mg/g and to 62.86 mg/g for OAAC-0.3.

For OAAC-0.5, a noteworthy decrease to 42.21 mg/g was attained due to less amounts of C16TMA⁺ cations [8,21] in the organo acid-activated clays, It was reported that the surface area values were correlated with the removal of dye molecules. In this instance OAAC-0.5 had the lowest removal effectiveness while having the largest surface area values (see Table 3).

AAC-0.3 was chosen in order to examine the impact of C16TMA⁺ cations without altering the properties of the host material. By altering the loading of C16TMA⁺ cations in the initial C16TMABr solution, the effect of C16TMA⁺ content was accomplished. Repulsion between the anionic dye and the residual negative charge of the ACC-0.3 material resulted in a decrease of the removal capacity of 15.21 mg/g for C16TMA⁺ adsorption of 0.20 mmol/g for OAAC-0.3 (Fig. 8B). The rise in EY removal from 15.21 mg/g to 37.37 mg/g for C16TMA⁺ cations to 0.38 mmol/g. The entire conversion of ACC-0.3 from hydrophilic to organophilic at a content value of 0.90 mmol of C16TMA/g was responsible for the maximum removed amount of EY of 66.31 mg/

3.5.4. Effect of pH

3.5.4.1. pH effect of EY solution. Generally, the pH of the dye solution was adjusted at various pH values from 2 to 12 by adding diluted HCl and NaOH solutions prior to adding the solid material. In this case, 0.10 g of organoclay (OAAC-0.3) was treated separately with 10 mL of EY solution (200 mg/L) at various pH values. The initial pH of the used EY solution was 4.1. The removal of EY was pH dependent. Fig. 9A depicts the variation in the removal percentage of OAAC-0.3 with the initial pH of EY solution. Because EY was precipitated under acidic conditions at pH values lower than 2 [8], This investigation was done at pH values higher than 3. Generally speaking, an increase in pH near to 7 had an impact on the removal percentage of EY to 95.03 %; at pH values greater than 8, it dropped to 60.51 %.

3.5.4.2. pH effect of OAAC-0.3. Another alternate strategy was suggested in this work, which involved treating a certain mass of OAAC-0.3 with basic or acidic solutions before adding it to the EY solution without adjusting the pH level (Ci of 200 mg/L). Previous investigations have shown that the organoclay was stable in basic solution, which is not the case in HCl acidic solution. Additionally, employing strong HCl solution (3 M and above), the basal spacing of 3.90 nm collapsed to 1.27 nm as a result of C16TMA⁺ cations exchanging with protons. In this instance, when treating with an acidic solution, some safety measures need to be considered.

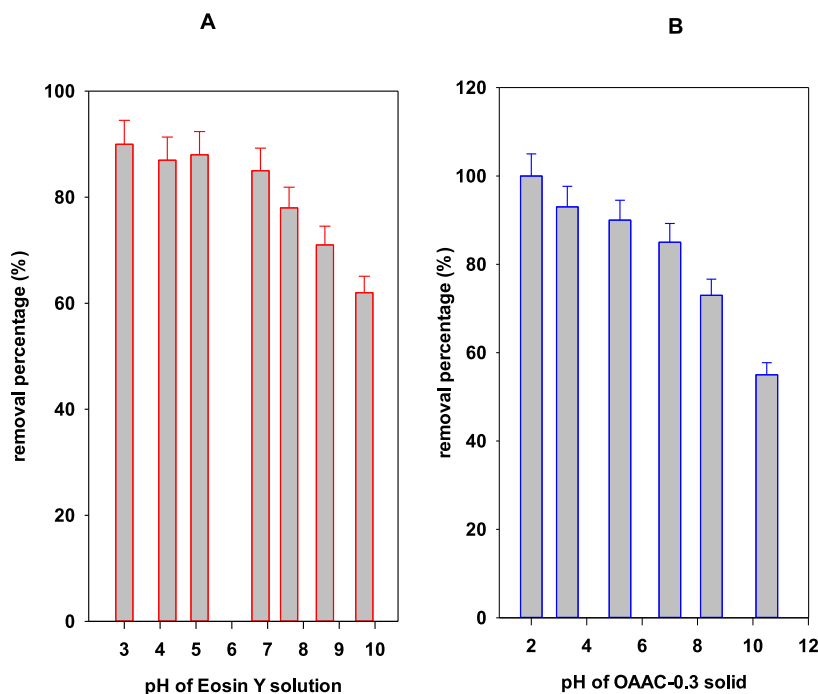


Fig. 9. AEffect of pH solution of eosin Y on the removal efficiency (%) using OAAC-0.3. **Fig. 9B** represents the effect of solid OAAC-0.3 pH of EY removal efficiency (%).

Fig. 9B illustrates when OAAC-0.3 underwent basic treatment, it removed roughly 50.21 % of EY, whereas OAAC-0.3 underwent acid treatment, it removed roughly 80.29 % of EY using a moderate HCl solution (0.1–1 M). When OAAC-0.3 was treated with a strong HCl solution (2 M or above), the removal percentage of EY was 100 %. The unexpected improvement indicated the low pH of the resultant solid that had an impact on the pH solution of EY.

The hydrogen atoms of the carboxylic and hydroxyl groups of EY dissolve in solution since it is an acidic dye; it has been observed that the hydroxyl group dissociates more readily than the carboxylic acid group, generating a monoanion or dianion [60]. The hydroxyl group ($pK_a = 7.7$) in ethanol releases its proton far more readily than the carboxylic group ($pK_a = 9.8$), according to the pK_a constants for proton dissociation [61]. On the other hand, EY's ionisation constants (pK_{a1} and pK_{a2}) in an aqueous solution were reported to be 2.9 and roughly 5 [60]. More than 80 % of EY anions exist as dianion species.

Furthermore, the pH of the solution has an impact on the charge of the solid surface [62]. The ACC-Xs' pH point of zero charge (pHpzc) values are claimed to be between 4 and 3. The pHpzc values increased from 5 to 6 following reaction with the C16TMABr solution. Therefore, in systems with pH values lower than the pHpzc the surface has positive charge, and in systems with pH values greater than the pHpzc, the surface of OAACs is negative. The positively charged surface of OAAC-0.3 and the EY dye electrostatically attracted one another at lower pH values, improving the amount of removed EY in the pH range below 7. The EY dye maintained its negative charge at higher pH levels, and electrical repulsion happened on the negatively charged surface of OAAC-0.3, which led to a reduction in the amount of EY removed. All subsequent studies used an unmodified pH value for the dye in order to avoid doing an additional step to adjust the pH.

Table 4

presents the estimated Langmuir parameters for the eosin Y removal by various OAACXs materials.

Sample	q_{max} (mg/g)	K_L (L/mg)	R^2
OAAC-0.0	86.8	0.105	0.9835
OAAC-0.1	79.3	0.096	0.9823
OAAC-0.2	70.4	0.072	0.9808
OAAC-0.3	69.0	0.074	0.9923
OAAC-0.4	52.1	0.0615	0.9850
OAAC-0.5	43.5	0.0353	0.9914

3.5.5. Maximum removal amount of EY

The often used model to calculate the maximum quantity that a surface solid can remove is the Langmuir equation [63]. This model is based on the uniformity of the adsorption sites and the development of an entire monolayer of adsorbate molecules on the surface of the adsorbent. Equation (2) presents the linear form:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} \cdot K_L} + \frac{C_e}{q_{\max}} \quad (2)$$

where q_e represents the removed amount at equilibrium (mg/g) and C_e represents the concentration at equilibrium (mg/g), respectively. K_L is the Langmuir constant (L/mg), and q_{\max} is the maximum removal capacity (mg/g). The intercept and slope of the linear plot of the experimental data of C_e/q_e vs C_e were used to estimate these constants. The parameters of the Langmuir model are shown in Table 4.

The removal EY dye was first improved by the raw surface clay through acid activation and then surfactant modification. Second, the q_{\max} values are correlated to the amount of C16TMA + cations inserted in OAAC-X samples; as a result, the sample OAAC-0.0 has reached the maximum value of 86.8 mg/g. The OAACs with lower C16TMA + cations exhibited intermediate values less than 43.5 mg/g. As it was already established, in addition to the electrostatic force between the anionic EY dye and the positive surface of the OAACs, the amount of intercalated surfactants above the CEC values may also play a role in the partitioning phase [64].

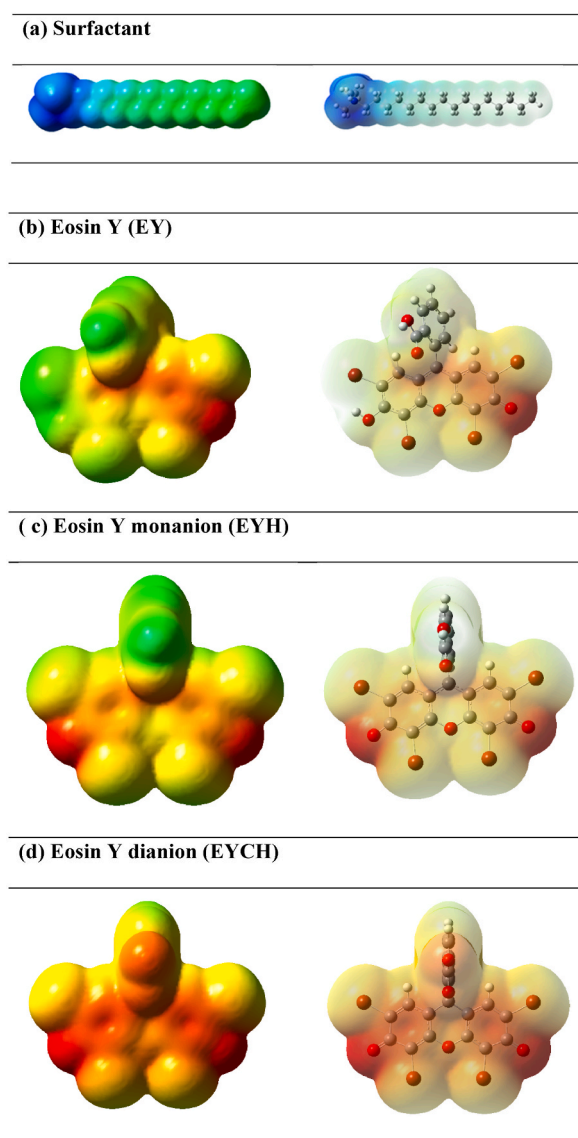


Fig. 10. The molecular electrostatic potential of (a) C16TMA surfactant and the three studied EY derivatives (b) EY, (c), Eosin Y monanion and (d) Eosin Y dianion (isovalue of 0.0004 a.u.).

The Langmuir constant (K_L) indicates the extent of contact between the adsorbate and the surface. The intercalation of C16TMA cations resulted in a progressive drop in K_L values in the current study. Anionic dyes are preferred by OAAC-Xs. The exchangeable interlayer cations (Ca^{2+}) of the ACC minerals were replaced with the positively charged head of the C16TMA⁺ cations, and the hydrophobic head of the cationic surfactants was oriented outward. The intercalated C16TMA⁺ cations formed an organophilic phase partition in the interlayer space to increase the quantity of removed EY, in addition to dye-cationic C16TMA⁺ cations' interaction. Given their remarkable removal efficiency, the OAACs prepared in this work could be seen as a potential candidate for cleaning water contaminated with EY dye.

3.6. Theoretical calculations

For electrostatic surface potential (ESP), the bluish end means that the atoms in this area tend to be very electropositive and the ESP value will be positive and the reddish end means that the atoms here tend to be very electronegative and then the ESP value is negative. The areas in green mean neutral regions.

The molecular electrostatic potential of the surfactant molecule (Fig. 10) indicated that the electrophilic region was localized in the nitrogen atom surrounded by its three directly bonded methyl substituents; the fourth region is the first ethyl group belonging to the rest of the linear carbon chain, and the fourteen carbons left in the chain represent the neutral part of this molecule [65].

The molecular electrostatic potential of the EY molecule (Fig. 10) indicated that the nucleophilic zone covers mainly the oxygen atom and its phenyl group. The rest of the molecule is neutral, and no part is bluish, indicated that there is no electrophilic region. In the eosin Y monoanion (EYH), the nucleophilic area, after being deprotonated, is extended to the oxygen atom of the phenyl group on the right, touching even the area of the heterocyclic center. Finally, in eosin Y dianion (EYCH), the nucleophilic zone touches not only the center of the molecule composed of the phenyl groups and in the peripheral areas but the carboxylic group as well, creating a larger nucleophilic area. A potential interaction with the electrophilic surfactant molecule is thus envisaged because of the neutral/nucleophilic nature of the peripheral phenyl groups, particularly the oxygen atoms, and the lack of any electrophilic area in the three EY systems under examination [66].

3.7. Regeneration studies

As mentioned in paragraph 2.6, a simple process was used in this case to regenerate the spent OAAC-Xs without compromising their surfaces. An appropriate substance is suitable as a removal agent will also depend on its stable efficiency after regeneration.

Fig. 11 displays the results of the study conducted on two OAAC-0.3 and OAAC-0.5 samples as well as the organoclay (OAAC-0.0

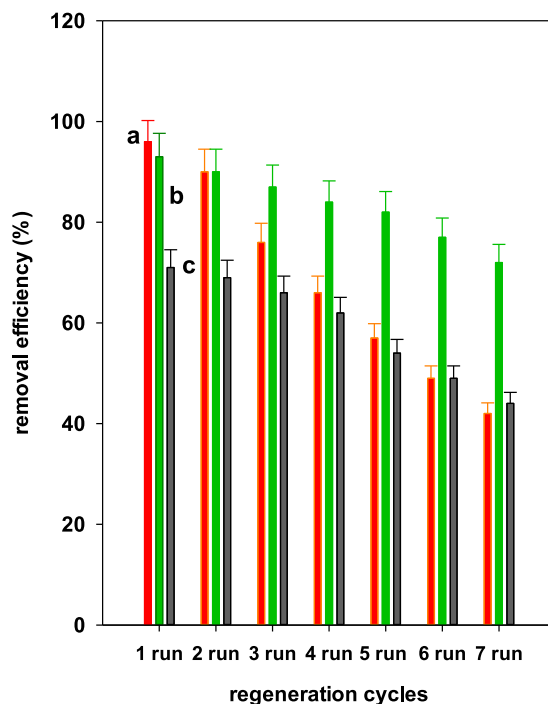


Fig. 11. Regeneration tests for of three different organo acid activated clays(a) OAAC-0.0; (b) OAAC-0.3 and (c) OAAC-0.5.

derived from the pristine clay without acid activation). The removal effectiveness of 93.1 % was retained in the OAAC-0.3 sample, but it decreased from 93.5 % to 82.1 % for six cycles. After the seventh cycle, the removal efficiency dropped to 72.2 % (Fig. 11b). In contrast, OAAC-0.5 showed a 71.2 % initial removal efficiency that held after four regeneration cycles, albeit at a lower level of 62.8 %. After seven rounds, the removal efficiency fell to 44.8 % (Fig. 11c). The initial removal efficiency of 96.1 % for the organoclay containing a larger amount of C16TMA + cations (OAAC-0.0 sample) dropped to 76.4 % after just three reuse cycles, and it further declined to 42.3 % after seven cycles (Fig. 11a).

The decrease in removal efficiency could indicate that some dyes were not destroyed by the utilized oxone. An alternative explanation could be that the dye molecules at greater C16TMA + cations were firmly bonded to the surfactant molecules and got trapped in the partition phase, which constrain their interaction with oxone. Furthermore, the decomposition of adsorbed EY on the surface might depend on the acidity of OAAC-0.3 and OAAC-0.5. When compared to other samples, AAC-0.3 had the highest acidity in terms of protons per gram.

3.8. Design of single-stage batch adsorber

Using equilibrium data, a single stage adsorber design was suggested in order to assess the laboratory scale results from a large-scale perspective. This model is required for possible usage in an industrial wastewater treatment system [67].

The objective of the design is to reduce the starting concentration of C_0 to a concentration of C_1 (mg/L) for a fixed volume of EY solution ($V(L)$) and amount of OAAC-X (M (g)). The amount removed is now q_1 (mg/g) instead of q_0 . When new adsorbent is utilized at time $t = 0$, q_0 equals zero. Equation (3) shows the mass balance over time, and relates the organoclay solid with the EY removed from the liquid [67,68].

$$:V(C_0 - C_1) = M(q_0 - q_1) \quad (3)$$

The Langmuir isotherm equation can be applied to q_1 in the batch adsorber design equation (4), as adsorption isotherm studies demonstrate that the equilibrium data for EY onto OAAC-Xs fit well in the Langmuir isotherm

$$\frac{M}{V} = \frac{C_0 - C_e}{q_e} = \frac{C_0 - C_e}{\frac{q_m K_L C_e}{1 + K_L C_e}} \quad (4)$$

Equation (4) can be rewritten by replacing the $C_0 - C_e$ and C_e expressions with C_0 , and a new format is proposed in Equation (5) [47].

$$\frac{M}{V} = \frac{C_0 - C_e}{q_e} = \frac{RC_0}{q_m \frac{K_L(1-R)C_0}{1 + K_L(1-R)C_0}} \quad (5)$$

The estimated amounts of OAAC-0.3 required to lower different volumes of EY dye solution with a C_i of 200 mg/L to final concentrations of 100, 80, 60, 40, and 20 mg/L are displayed in Fig. 12. Generally speaking, the quantities of materials needed increased together with the treated volume of effluent dye and the desired percentage of reduction.

The mass of OAAC-0.3 required to eliminate EY dye from a solution with a particular volume and concentration was calculated using the plot in Fig. 12. For instance, the masses of OAAC-0.3 needed to lower C_i dye from 200 mg/L to final concentrations of 20, 40, 60, 80, and 100 mg/L are determined to be 21.9, 15.5; 12.5, 10.2, and 8.2 g, respectively, for a fixed volume of dye solution of 5 L. Using OAAC-0.5, the final dye concentrations of 20, 40, 60, 80, and 100 mg/L were obtained by increasing the predicted masses of OAAC-0.5 from 50.2, 31.5, 23.7, 18.7, and 14.8 g, respectively. In case of ACC-0.0 sample, and to reduce 5L of 200 mg/L C_i solution to final concentrations of 20, 40, 60, 80, and 100 mg/L, respectively, they were about 14.8, 11.1, 9.1, 7.5, and 6.1 g.

The variation might be related to higher removal of OAAC-0.0's as opposed to OAAC-0.3 and OAAC-0.5 samples. For other materials, comparable data were reported [47,68,69]. The data that is currently displayed might be expanded to include further dye removal volumes and values up to 100 %. These computations could also be utilized to include any other conditions, such as starting concentrations or process temperatures.

4. Conclusions

The CHN technique revealed that acid-activated had been effectively modified with C16TMA surfactants, with an intake amounts of C16TMA + cations higher than the CEC values. The maximum intake level for the raw clay was around 1.22 mmol/g of clay. A bilayer parafilm containing C16TMA + cations with a basal spacing of 3.90 nm was adopted by OAAC-X. Though, PXRD patterns showed the same basal spacing for the OAAC-Xs, ^{13}C solid NMR revealed that the C16TMA + cations adopted distinct conformations.

As the initial dye concentration and the surfactant content in the OAACX-s increased, the amount of EY dye removal id also improved. The removal effectiveness of OAAC-0.3 was altered by treating it with an acidic or basic solution before adding it to the EY solution. The maximum removal capacity (q_{max}) values were estimated using the Langmuir isotherm model. The determined values ranged between 43.4 and 86.8 mg/g. The regeneration study revealed that, with a certain loss of removal efficacy, the resulting OAAC-X may be reused after seven cycles. Design for a single-stage batch adsorber was suggested for specific OAACs using the mass balance equation and the Langmuir model to determine the masses needed for the appropriate removal percentages of specific volumes of EY dye solution (at a fixed C_i of 200 mg/L). By altering the process temperatures, several new conditions, such as different initial concentrations, might be included in the proposed design.

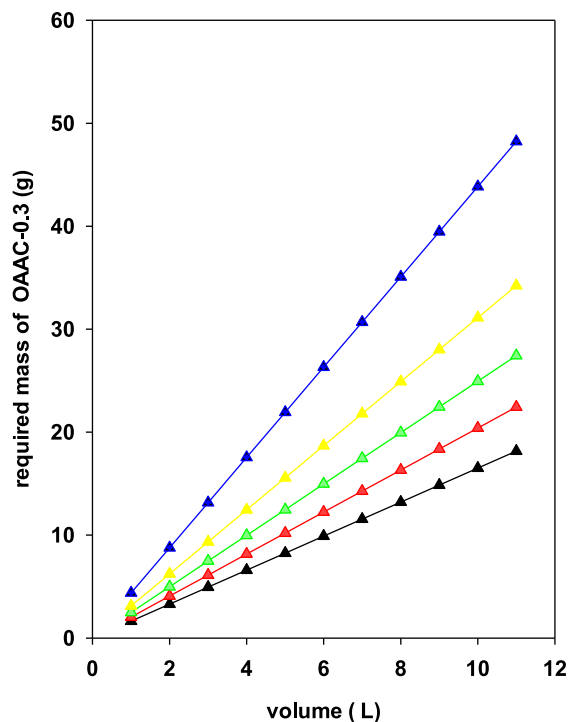


Fig. 12. Required masses of OAAC-0.3 to reduce different volumes (L) of EY solutions ($C_i = 200$ mg/L) to 50 % (black), 60 % (red), 70 % (green), 80 % (yellow), and 90 % (blue). (red), 70 % (green), 80 % (yellow), and 90 % (blue).

Data availability statement

Data will be made available on request.

CRediT authorship contribution statement

Abdulaziz M. Alanazi: Writing – original draft, Supervision, Project administration, Methodology, Investigation, Conceptualization. **Ohoud A. Jefri:** Writing – original draft, Validation, Resources, Investigation, Data curation. **Mohd Gulfam Alam:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Rawan Al-Faze:** Writing – original draft, Methodology, Investigation, Formal analysis. **Fethi Kooli:** Writing – review & editing, Writing – original draft, Supervision, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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