Removal of Hazardous Contaminants from Water by Natural and Zwitterionic Surfactant-modified Clay

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ABSTRACT: In this study, natural clay (NC) was collected from Saudi Arabia and modified by cocamidopropyl betaine (CAPB) at different conditions (CAPB concentration, reaction time, and reaction temperature). NC and modified clay (CAPB-NC) were characterized using X-ray diffraction, thermogravimetric analysis, Fourier transform infrared spectroscopy, field-emission scanning electron microscopy, and N2 adsorption at 77 K. The adsorption efficiency of NC and CAPB-NC toward Pb2+ and reactive yellow 160 dye (RY160) was evaluated. The adsorption process was optimized in terms of solution initial pH and adsorbent dosage. Finally, the adsorption kinetics and isotherms were studied. The results indicated that NC consists of agglomerated nonporous particles composed of quartz and kaolinite. CAPB modification reduced the specific surface area and introduced new functional groups by adsorbing on the NC surface. The concentration of CAPB affects the adsorption of RY160 tremendously; the optimum concentration was 2 times the cation exchange capacity of NC. The equilibrium adsorption capacity of CAPB-NC toward RY160 was about 6 times that of NC and was similar for Pb2+. The adsorption process followed the pseudo-second-order kinetics for both adsorptive. RY160 adsorption on CAPB-NC occurs via multilayer formation while Pb2+ adsorption on NC occurs via monolayer formation.

INTRODUCTION

Water resources are indispensable for life and biodiversity conservation and human development. Regrettably, humans' industrial and agricultural activities have caused a serious degradation in the quality of water resources.1,2 Although a number of effective regulations aim to guarantee safe disposal of industrial effluents, over 80% of global wastewater is still disposed of without appropriate treatment.1 These effluents represent a serious threat to humans and ecosystem because of the presence of hazardous chemicals such as potentially toxic metals and organic dyes.3

Potentially toxic metal contaminants are a widespread and long-lasting environmental problem that has drawn the scientists' attention worldwide because of their persistency, nonbiodegradability, bioaccumulation, and toxicity.2,4,5 Lead (Pb2+) is one of the most prevalent hazardous contaminants in aquatic systems. Pb2+ contamination results from industrial processes (such as painting, electroplating, and battery manufacturing) and corrosion of the old lead-containing plumbing systems.2,6 The high toxicity of Pb2+ makes it one of the most toxic metal contaminants in aquatic environments and can induce considerable permanent damage to humans and the environment. Exposure to Pb2+ at levels >15 μg/L may cause abortion, stillbirths, sterility, neonatal deaths, and intellectual disability.7 Even at low levels, Pb2+ can cause behavior, liver, hearing, learning, and cognition disorders.2,4,5

On the other hand, synthetic dye contaminants are now an emerging area of study owing to their effects on humans, aquatic systems, and biodiversity.7 Synthetic dyes are extensively used in several industries such as textile dyeing, leather tanning, paper printing, color photography, pharmaceutical, food, cosmetics, and plastic.3,8,9 Among the different classes of synthetic dyes, azo dyes are the largest and the most commercially important one. They represent 70% of the worldwide production of synthetic dyes.8,9 Regrettably, they have poor exhaustion properties;9 about 15% are wasted during the industrial processes and contaminate aquatic systems.3,8,9 Introducing azo dyes into the aquatic system degrades its quality via reducing sunlight penetration, dissolved oxygen, and photosynthesis efficiency.3,8,9 The azo group plays a key role in the functions and environmental behavior of azo dyes. First, it, along with the complex aromatic structure, makes azo dye degradation difficult; consequently, azo dyes accumulate in the aquatic systems, and they will persist in the

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environment for long time in the absence of appropriate treatment. 5,9 Second, it renders the azo dyes high toxicity, so even small amounts of dyes are toxic to aquatic organisms. In addition, exposure to azo dyes can lead to allergy, skin and eye irritation, mutation, cancer, and dysfunction of the kidneys, reproductive system, liver, brain, and central nervous system. 1,3,8,9

For these reasons, the removal of Pb2+ and azo dyes from water resources is an urgent need to conserve the human life and biodiversity. Among the several water treatment methods, adsorption has been widely applied to remove potentially toxic metals and azo dyes. 10 The adsorbent is a key factor in the adsorption process; it defines the adsorption capacity, rate, and cost. Reducing the cost and maintaining high adsorption capacity can be realized by using low-cost materials or their modified forms. Several low-cost materials have been used as adsorbents for water/wastewater treatment. 11−17 Natural clays (NCs) have acquired scientists' attention for remediation and containment of pollutants. They are characterized by their abundance, nontoxicity, low cost, porosity, thermal stability, and ion exchange capacity. 18 Several structural and surface modifications of the raw clay can be pursued to enhance its efficiency in the removal of pollutants.

In this context, this study aims to utilize an abundant and inexpensive NC for treating water polluted by potentially toxic metals or azo dyes. Pb2+ and reactive yellow 160 (RY160) were selected as models for potentially toxic metals and azo dyes, respectively. NC was modified by the zwitterionic surfactant cocamidopropyl betaine (CAPB). Although there are a number of studies on the modification of clay with surfactants, 19−25 to the best of our knowledge, the effects of modification reaction time and temperature on the adsorption performance have not been explored yet. This study tackles this gap in the literature by investigating the modification reaction time and temperature along with the concentration of CAPB on the adsorption efficiency. NC and modified clay (CAPB-NC) were characterized using X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FE-SEM), and N2 adsorption at 77 K. The adsorption efficiency of NC and CAPB-NC (at optimum conditions) was compared. The best adsorption conditions (solution initial pH, contact time, and adsorbent dosage) and kinetic and equilibrium studies were also applied.

RESULTS AND DISCUSSION

Characterization. Cation Exchange Capacity (CEC). CEC of a clay plays a vital role in its adsorption capacity. Also, investigating the CEC enables better understanding of the adsorption mechanism. The net amounts of Na+, K+, Ca2+, and Mg2+ released from NC are 0.26, 0.50, 3.21, and 5.49 mequiv/grams of NC and CAPB-NC are shown in Figure 1. NC has CEC in line with those of Ecuadorian kaolinite, 26 Brazilian kaolinite, 25 and Malaysian quartz-rich kaolinite. 27

XRD Crystalline Phase Identification. The XRD diffractograms of NC and CAPB-NC are shown in Figure 1. NC has reflection peaks at 2θ = 20.8° (4.2 Å), 26.6° (3.3 Å), 36.5° (2.4 Å), 39.4° (2.2 Å), 40.2° (2.2 Å), 42.3° (2.1 Å), 50.1° (1.8 Å), 54.8° (1.6 Å), 59.9° (1.5 Å), 68.1° (1.3 Å), and 75.6° (1.2 Å), which are characteristic for quartz (JCPDS no. 46-1045). The reflections at 2θ = around 12.2° (7.2 Å), 19.8° (4.4 Å), 24.9° (3.5 Å), 34.9° (2.5 Å), 38.4° (2.3 Å), 45.7° (1.9 Å), 62.1° (1.4 Å), and 64.0° (1.4 Å) indicate the presence of kaolinite (JCPDS no. 29-1488). Accordingly, it can be concluded that NC is mainly composed of quartz and kaolinite. The quantification of the phase's percentage indicates that quartz was the dominant phase (89.52%), while kaolinite was the minor phase (7.11%). The XRD patterns of CAPB-NC prepared at different conditions are very similar to that of NC. This observation indicates that the modification of NC by CAPB did not cause any changes in the clay fraction diffractogram.

Arrangement of CAPB and NC in the CAPB-NC Samples. The potential of CAPB intercalation between the interlayer of the NC was investigated using the XRD technique. According to XRD analyses, modification by CAPB did not change either the d(001) values or the intensity of the reflection peaks. Thus, CAPB molecules are not intercalated into the interlayer of NC but adsorbed on its surface. Kaolinite, the minor component of the NC, is a nonswelling layered clay mineral consisting of silica and alumina and develops intrinsic negative surface charge at its edge surface. 28,29 The length of the alkyl chain of CAPB, the exchangeability of interlayer cations, and/or the nonswelling nature of kaolinite could hinder the intercalation of CAPB into kaolinite interlayers. On the other hand, the surface charge of kaolinite could promote the adsorption of CAPB on the surface via electrostatic interactions. Therefore, the driving forces for the adsorption of CAPB on NC could be electrostatic attraction between the positively charged group of CAPB and negative surface of NC. Similar trend has been reported before. For example, Liu et al. reported that the modification of a commercial vermiculite with the amphoteric surfactants dodecyl dimethyl(3-sulfonate)ammonium and dodecyl dimethyl(N-carboxylate)ammonium occurs via adsorption on the surface not via intercalation into the interlayer. 30 Similarly, Mudzielwana et al. found that the cationic surfactant hexadecyltrimethylammonium bromide gets adsorbed on the surface of South African natural kaolin clay and did not intercalate into the layers. 30 Also, Jin et al. concluded that the cationic surfactant hexadecyltrimethylammonium...
monium chloride covers the surface of a commercial kaolinite and did not enter into the layers.31

**Thermogravimetric Analysis.** The TGA profiles of NC and CAPB-NC are displayed in Figure 2. Generally, the structure of clay materials has three types of water molecules: (a) physisorbed and interlayer water: these are loosely bound and mobile and removed below 200 °C; (b) water molecules in the first coordination sphere of the interlayer ions: these are strongly bonded and are removed at 300–500 °C; and (c) structural hydroxyl groups: these dehydrate at 500–800 °C.23,32 In this study, NC shows the aforementioned three weight loss events; specifically, loss of physisorbed water and volatile matters (below 200 °C), slow dehydration of coordinated water (200–400 °C), and dehydroxylation of the crystal network (400–600 °C). Modifying NC with CAPB has a significant effect on the TGA profile. First, the mass loss below 200 °C decreases as the CAPB concentration increases because of the removal of physisorbed water during modification.24,33 Second, the two decomposition events at 200–400 and 400–600 °C overlap and the mass loss above 200 °C increases significantly with increasing CAPB concentration. Finally, the total mass loss steeply increases with increasing CAPB concentration, indicating the successful modification of the clay.

On the other hand, it is argued that because there are three types of binding between the modifier and clay (surface adsorption, interlayer adsorption, and intercalation), the modifier would decompose at different temperatures.24 In the current study, both NC and CAPB-NC show the same decomposition events, and no additional decomposition events were observed in the TGA curves of CAPB-NC, indicating that only one type of binding between CAPB and the clay takes place. Combining this observation with XRD results, it can be inferred that CAPB is adsorbed on the surface of NC.

The amount of CAPB incorporated into CAPB-NC was estimated by subtracting the mass loss at 200–600 °C from NC to CAPB-NC.22,34 CAPB represents about 0.8, 1.8, 3.6, and 7.7 m % of the whole NC mass of CAPB-NC0.5-60-24, CAPB-NC1.6-60-24, CAPB-NC2.6-60-24, and CAPB-NC4.6-60-24, respectively.

**Morphological Analysis.** The morphologies of NC and CAPB-NC are shown in Figure 3. Both NC and CAPB-NC presented large agglomerated particles built up of smaller nonporous particles. The agglomerated particles have irregular shapes and uneven sizes. Similar morphology for Chilean kaolin has been reported before.35 The surface of NC is rough and contains numerous interparticle cavities (Figure 3a). Such surface is favorable for adsorption because of the predicted high surface area and ease of pollutant diffusion through cavities.36 In contrast, the surface of CAPB-NC is smooth with less interparticle cavities (Figure 3b). Therefore, the surface area of CAPB-NC is predicted to be less than that of NC. It is obvious that the surface of CAPB-NC was wrapped by a layer of the CAPB surfactant, which indicates the adsorption of CAPB molecules on the surface of NC. This observation is in support of the aforementioned XRD and TGA findings. The adsorption of CAPB on the NC surface occurs via two consecutive mechanisms: first, electrostatic interaction between the positively charged quaternary ammonium ions of CAPB and the negatively charged surface of NC and second, hydrophobic interactions between the alkyl chains of CAPB. Liu et al.20 reported similar behavior upon modifying vermiculites by amphoteric surfactants.

**Textural Characteristics.** Figure 4 shows the nitrogen adsorption–desorption isotherms and the pore size distribution curves of NC and CAPB-NC. The NC adsorption isotherm (Figure 4a) presents a sharp knee and unrestricted adsorption up to high p/p0. Therefore, the NC adsorption isotherm can be classified as type II according to the International Union of Pure and Applied Chemistry (IUPAC) classification.37 Type II adsorption isotherm is typical for nonporous or microporous materials and indicates multilayer N2 adsorption. On the other hand, the CAPB-NC2.6-60-3 adsorption isotherm (Figure 4a) has no knee, and the amount of N2 adsorbed remains finite at p/p0 = 1. Thus, the CAPB-NC2.6-60-3 adsorption isotherm is type III based on the IUPAC classification.37 Type III is characteristic of nonporous or macroporous solids. Both NC and CAPB-NC2.6-60-3 adsorption isotherms present type H3 hysteresis loop which is given by either nonrigid aggregates of platelike particles or macropores partially filled with a pore condensate.37 The pore size distribution curves (Figure 4b) indicate that the pores of NC and CAPB-NC2.6-60-3 have average sizes of 7 and 2 nm, respectively. Thus, both NC and CAPB-NC2.6-60-3 are mesoporous; however, CAPB-NC2.6-60-3 is narrower. The calculated SRET and total pore volume (Vtot) of NC are 28 m2/g and 0.06 cm3/g, respectively. This value of SRET is higher than the values reported for other NCs26 and comparable to others.24,27 The SRET and Vtot 2 m2/g and 0.01 cm3/g, respectively, of CAPB-NC2.6-60-3 are substantially lower than that of NC.

Correlating the results of textural analysis and FE-SEM indicates that NC and CAPB-NC are basically nonporous particles which agglomerate into larger particles having mesoporous structures resulting from the interparticle void spaces. The adsorption of CAPB on the surface of NC leads to clogging the interparticle void spaces and makes the surface of...
CAPB-NC smooth; consequently, it decreases the specific surface area, total pore volume, and average pore size. Similar trend has been documented in the literature.

**FTIR Spectral Analysis.** Figure 5 depicts the FTIR spectra of NC and different CAPB-NC samples. The absorption band at 3697 cm$^{-1}$ is assigned to combined in-phase and out-of-phase stretching frequency of hydroxyl groups of kaolinite. Bands around 3438 and 1625 cm$^{-1}$ are attributed to adsorbed water stretching and bending vibration, respectively. The bands at 2970 and 2920 cm$^{-1}$ are attributed to the asymmetric stretching vibration of C–C in the alkyl chain, while the bands at 2856 and 1390 cm$^{-1}$ are attributed to the symmetric stretching and bending mode, respectively, of the same group. The intense band at 1045 cm$^{-1}$ with a shoulder at 1090 cm$^{-1}$ is ascribed to perpendicular stretching vibrations of the Si–O–Si group, while the bands at 685 and 468 cm$^{-1}$ are the bending mode of the same group. Absorption bands at 920 and 534 cm$^{-1}$ are ascribed to Al(IV)–OH and Si–O–Al(VI) stretching vibrations, respectively. The band at 790 cm$^{-1}$ corresponds to Si–O symmetric stretching.

Comparing the spectra of NC and different CAPB-NC samples shows the existence of the same bands in all samples. This observation indicates that the structure of NC was maintained unchanged after CAPB modification. Also, an obvious increase in the relative intensities of the absorption bands at 3438, 2970, 2920, 2856, and 1390 cm$^{-1}$ after CAPB modification can be observed. This increase in the case of the absorption band at 3438 cm$^{-1}$ could be due to overlapping of the N–H stretching of CAPB and the adsorbed water stretching. It has been reported that the N–H stretching vibrations overlap with the adsorbed water stretching and cannot be separately detected. On the other hand, the relative increase in the intensity of the absorption bands related to C–C in the alkyl chain is indicative of highly ordered chains of methylene groups and proves the presence of CAPB and the successful interaction between NC and CAPB during the modification process. Similar behavior has been reported for other organically modified clays.

**Adsorption Properties.** The isometric substitution in the tetrahedral and octahedral sites of the NC endows it negative charge. This negative charge, along with the CEC and pore volume of the NC, makes it a very effective adsorbent of potentially toxic metal cations. Modifying NC with cationic or zwitterionic surfactants occurs via replacing the inorganic cations of the NC with the quaternary ammonium cations of the surfactant. Modification with long carbon chain zwitterionic surfactant such as CAPB makes the NC hydrophobic, which enables the adsorption of nonionic organic compounds (via partitioning into the alkyl chain of CAPB), and had little, if any, effect on their CEC (because CAPB carries both a cationic and an anionic group, each exchanged site on the NC will be replaced by an exchangeable site on the CAPB molecule).

**Effect of CAPB Modification Conditions on the Adsorption Properties.** Figure 6 displays the time-course variation of the adsorption efficiency as a function of CAPB concentration and modification reaction time and temperature. The R% of the RY160 dye increases as the concentration of CAPB increased from 0.5 to 2 times the CEC of NC (Figure 6a). Further increase in CAPB concentration has an insignificant effect on the removal of the RY160 dye. The CAPB molecule contains a quaternary ammonium group, a carboxylate group, and a secondary amide group (Table S1). The modification of NC with CAPB occurs via replacing the inorganic cations of NC with the quaternary ammonium group of CAPB. Thus, each exchanged site on the NC will be replaced by a carboxylate group and an amide group, that is, the potential adsorption sites are increased. At acidic conditions, both the carboxylate and amide groups become protonated and...
electrostatically attract the negatively charged sulfonate (−SO₃⁻) groups of RY160. Increasing the concentration of CAPB results in an increase in the amount of CAPB adsorbed on the NC surface; consequently, the adsorption sites increase, leading to an increase in the R % of the RY160 dye. Similar behavior has been reported before.¹⁹,²⁰ To acquire the best adsorption efficiency and reduce the cost of modification, the sample prepared with CAPB concentration 2 times the CEC of NC was selected as the optimal.

Figure 6e shows that increasing the modification reaction temperature to 60 °C caused an increase in the R % of the RY160 dye, which could be due to an increase in the amount of CAPB adsorbed on the NC surface. Increasing the modification reaction temperature decreases the viscosity of the surfactant;⁴⁵ consequently, it increases its mobility and enables better contact with the active sites on the surface of clay. Also, the CEC of clay increases at higher temperature by releasing some bound functional groups and making it free for ionization.⁴⁶ This observation implies that the modification reaction temperature plays a key role in CAPB adsorption on the NC surface. Hence, a modification reaction temperature of 60 °C was chosen as the optimal. Figure 6c discloses that the time of modification reaction has insignificant effect on the removal of the RY160 dye. Therefore, a time for the modification reaction of 3 h was considered as the optimum.
For Pb^{2+}, it can be observed from Figure 6b,d,f that the studied different modification conditions do not affect the R % of Pb^{2+}. This is due to the fact that the CAPB modification has no effect on the CEC of the clay as stated above. Overall, the sample CAPB-NC_{2-60-3} was chosen as the optimum and will be used in the following studies.

Comparing the Adsorption Efficiency of NC and Optimal CAPB-NC. Figure 7a shows that NC was inefficient to adsorb the RY160 dye and the adsorbed amount was very less (2 mg/g). Modifying NC by CAPB induced a great enhancement in the adsorption efficiency, and the adsorbed amount became 12 mg/g for CAPB-NC_{2-60-3}. Correlating this observation to the results of textural analysis suggests that the inserted functional groups on the surface of the clay as a result of CAPB modification play a key role in the adsorption of RY160 not the S_{BET}. This result highlights the importance of CAPB modification and indicates that it is a key factor in the RY160 adsorption. This trend is consistent with the previous literature. On the other hand, Figure 7b shows that both NC and CAPB-NC_{2-60-3} can efficiently adsorb Pb^{2+}. The adsorbed
amount of Pb\textsuperscript{2+} by CAPB-NC\textsubscript{2,60,3} (40 mg/g) was comparable to that of NC (43 mg/g). This comparable efficiency in spite of the lower $S_{\text{BET}}$ of CAPB-NC indicates that the adsorption of Pb\textsuperscript{2+} depends mainly on the CEC rather than on the $S_{\text{BET}}$. Ma et al. reported that modifying clay with the zwitterionic surfactant had little, if any, effect on their CEC.\textsuperscript{23} Similar behavior has been reported before.\textsuperscript{23} It is noteworthy that the adsorption of Pb\textsuperscript{2+} on NC was faster than that on CAPB-NC\textsubscript{2,60,3}. NC reached equilibrium within 30 min and achieved about the same amount of Pb\textsuperscript{2+} adsorbed on CAPB-NC\textsubscript{2,60,3} after 60 min. It seems that the steric effect of CAPB long alkyl chains hinders the interaction between Pb\textsuperscript{2+} and the surface of CAPB-NC\textsubscript{2,60,3} and slows down the adsorption process.\textsuperscript{35,47} Based on these results, the study of the effects of adsorbent dosage on the adsorption process was performed using the sample CAPB-NC\textsubscript{2,60,3} for RY160 dye and the NC for Pb\textsuperscript{2+}.

**Effects of Adsorptive Solution Chemistry on the Adsorption Process.** The adsorption time profile of RY160 on CAPB-NC\textsubscript{2,60,3} and Pb\textsuperscript{2+} on NC as a function of material dosage is illustrated in Figure 8a,b, respectively. It is evidently perceived that the R % of RY160 and Pb\textsuperscript{2+} increased with increasing adsorbent dosage up to 1.5 g/L (87%) and 1.0 g/L (96%), respectively, and then it remained constant. Intuitively, increasing the adsorbent dosage ensures an increase in the adsorption sites on NC, so the R % tremendously decreases. However, the adsorbent particles agglomerate when high dosage is used. This agglomeration hides some adsorption sites, decreases the surface area available for adsorption, increases the diffusion path length, and ultimately causes a decrease in the adsorption amount.\textsuperscript{15,48,49} Accordingly, the optimum dosage was 1.5 g/L for RY160 adsorption on CAPB-NC\textsubscript{2,60,3} and 1.0 g/L for Pb\textsuperscript{2+} adsorption on NC.

The initial pH (pHi) of the adsorptive solution is a decisive factor in the adsorption process because it controls the extent of adsorption by controlling the surface charge of the adsorbent and the ionization of the adsorbate.\textsuperscript{2,9,20,30} Figure 8c,d depicts the effect of pHi on the R % of RY160 and Pb\textsuperscript{2+} with time. It is evident that the amount of RY160 and Pb\textsuperscript{2+} removed depends on the solution pH. A steeper increase in R % can be observed upon raising the pHi of the RY160 solution from 2 (87%) to $\geq5$ (43%) (Figure 7c). The sulfonate groups of RY160 are very weak bases and stable anions in aqueous solutions. On the other hand, at pHi 2, the functional groups on the surface of CAPB-NC\textsubscript{2,60,3} become protonated and acquire net positive charges. The electrostatic interactions between the sulfonate groups of RY160 and the positively charged surface functional groups of CAPB-NC\textsubscript{2,60,3} drive the adsorption process and result in high R %. Raising the pHi to $\geq5$ reduces the protonation of the functional groups on the surface of CAPB-NC\textsubscript{2,60,3}; consequently, repulsion between the anionic RY160 and the surface functional groups of CAPB-NC\textsubscript{2,60,3} takes place and leads to a sharp reduction in R %. This result agrees with the previously published literature.\textsuperscript{51} In contrast, a steeper increase in R % can be observed upon raising the pHi of the Pb\textsuperscript{2+} solution from 2 (8%) to 4 (75%) and then to 6.2 (96%) (Figure 8d). At pHi 2, the hydronium ions exist in the solution and compete with Pb\textsuperscript{2+} for the adsorption sites on NC, so R % tremendously decreases. Raising the pHi to 4 or 6.2 decreases or diminishes, respectively, the presence of hydronium ions; hence, the adsorption sites on NC become available for Pb\textsuperscript{2+} and R % increases. Above pH 6.5, Pb\textsuperscript{2+} would precipitate.\textsuperscript{48,52} Similar findings have been reported earlier.\textsuperscript{11,49,52} Further experiments were performed at pHi 2 for RY160 and 6.2 for Pb\textsuperscript{2+}.

**Effect of Contact Time and Kinetic Study.** The effect of contact time on RY160 and Pb\textsuperscript{2+} adsorption is shown in Figure 9. The adsorption of RY160 is fairly rapid and reaches equilibrium within 20 min (Figure 9a). This fast adsorption indicates strong adsorption interaction between CAPB-NC\textsubscript{2,60,3} and RY160. On the other hand, Figure 9b shows that the adsorption of Pb\textsuperscript{2+} is a gradual process that occurs via three stages: a fast adsorption in the initial period up to 5 min, followed by slower adsorption up to 45 min and finally reaches equilibrium within 60 min.

The kinetic data were analyzed by the PFO and PSO models. The fitting parameters are listed in Table 1. For both adsorbents, in the R$^2$ values indicate that both PFO and PSO fit well the kinetic data, but the values of $\chi^2$ and SSE indicate PSO as the best model that can accurately describe the kinetic data. Therefore, the assumption of the chemisorptive nature of adsorption is valid for RY160/CAPB-NC\textsubscript{2,60,3} and Pb\textsuperscript{2+}/NC adsorption systems.

**Isotherm Study and Adsorption Capacity.** The adsorption isotherms of RY160 by CAPB-NC\textsubscript{2,60,3} and Pb\textsuperscript{2+} by NC along with the fitted models are presented in Figure 10, and the calculated isotherm parameters are summarized in Table 2. The adsorption isotherm of both RY160/CAPB-NC\textsubscript{2,60,3} and
gives the best fitting of the Langmuir model. This suggests a strong affinity between the adsorptive and the adsorbent. Comparing the values of \( R^2, \chi^2 \), and SSE in Table 2, it can be concluded that among the different investigated isotherm models, the Freundlich model gives the best fit to RY160 adsorption on CAPB-NC-2-60-3-y. Therefore, the assumption of multilayer adsorption and heterogeneous distribution of active sites is valid for RY160/CAPB-NC-2-60-3-y. The value of 1/\( n \) is <1, indicating that the adsorption is a favorable and physical process.50 This situation is analogous to the adsorption behavior on other organically modified clays.53 It is worth pointing out that the suggestion of physical adsorption conflicts with that of chemical adsorption from fitting to PSO kinetics model. However, it has been reported that both physisorption and chemisorption can occur simultaneously. In this case, a layer of molecules is physically adsorbed above the chemisorbed layer.54

On the other hand, the adsorption process of Pb\( ^{2+} \) on NC was better fitted by the R–P model according to the values of \( R^2, \chi^2 \), and SSE. The R–P model consolidates the characteristics of both Langmuir and Freundlich isotherms and overcomes their inaccuracy in some adsorption systems.55,56 The R–P equation is reduced to Langmuir when the value of the exponent g is close to 1 and to Henry’s law when g is close to 0. The value of g calculated in this study (Table 2) is close to 1, indicating that the R–P equation can be reduced to Langmuir. This finding is in line with the high \( R^2 \) and the low \( \chi^2 \) and SSE calculated from the fitting of the Langmuir model.

Table 1. Kinetic Parameters for the Adsorption of RY160 on CAPB-NC-2-60-3 and Pb\( ^{2+} \) on NC

| model | parameter | RY160 | Pb\( ^{2+} \) |
|-------|-----------|-------|--------------|
| PFO   | q_{exp}   | 11.61 | 17.40        |
| R^2   | 1.00      | 0.99  |              |
| \( \chi^2 \) | 0.06 | 0.49  |              |
| SSE   | 0.28      | 1.98  |              |
| PSO   | R^2       | 1.00  | 1.00         |
| \( \chi^2 \) | 0.00 | 0.11  |              |
| SSE   | 0.02      | 0.45  |              |

| q_{exp} | 11.34 ± 0.11 | 16.93 ± 0.46 |
| q_{k}   | 0.32 ± 0.02  | 0.11 ± 0.01  |
| k_{l}   | 11.88 ± 0.04 | 19.25 ± 0.41 |
| k_{l}   | 0.06 ± 0.00  | 0.01 ± 0.00  |

Pb\( ^{2+} \)/NC rises very fast over the whole adsorptive concentration range. This suggests a strong affinity between the adsorptives and the adsorbents. Comparing the values of \( R^2, \chi^2 \), and SSE in Table 2, it can be concluded that among the different investigated isotherm models, the Freundlich model gives the best fit to RY160 adsorption on CAPB-NC-2-60-3-y. Therefore, the assumption of multilayer adsorption and heterogeneous distribution of active sites is valid for RY160/CAPB-NC-2-60-3-y. The value of 1/\( n \) is <1, indicating that the adsorption is a favorable and physical process.50 This situation is analogous to the adsorption behavior on other organically modified clays.53 It is worth pointing out that the suggestion of physical adsorption conflicts with that of chemical adsorption from fitting to PSO kinetics model. However, it has been reported that both physisorption and chemisorption can occur simultaneously. In this case, a layer of molecules is physically adsorbed above the chemisorbed layer.54

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Table 2. Isotherm Parameters for the Adsorption of RY160 on CAPB-NC-2-60-3 and Pb\( ^{2+} \) on NC

| model | parameter | RY160 | Pb\( ^{2+} \) |
|-------|-----------|-------|--------------|
| Freundlich | R\( ^2 \) | 0.97 | 0.98 |
| \( \chi^2 \) | 9.49 | 36.65 |
| SSE | 56.91 | 219.92 |
| k_{l} | 12.11 ± 1.82 | 17.36 ± 2.26 |
| l/\( n \) | 0.29 | 0.42 |
| Langmuir | R\( ^2 \) | 0.88 | 0.99 |
| \( \chi^2 \) | 32.19 | 18.45 |
| SSE | 193.11 | 110.70 |
| Q_{L} | 54.61 ± 7.16 | 165.80 ± 6.87 |
| k_{l} | 0.06 ± 0.02 | 0.03 ± 0.00 |
| R_{L} | 0.08–0.45 | 0.10–0.57 |
| D–R | R\( ^2 \) | 0.79 | 0.85 |
| \( \chi^2 \) | 58.45 | 334.00 |
| SSE | 350.72 | 2004.01 |
| q_{D–R} | 42.70 ± 4.17 | 118.31 ± 11.14 |
| L–D–R | 16.88 ± 8.01 | 34.92 ± 12.96 |
| R–P | R\( ^2 \) | 0.96 | 1.00 |
| \( \chi^2 \) | 11.58 | 11.40 |
| SSE | 56.91 | 56.98 |
| k_{R–P} | 1.49 × 10^7 ± 5.33 × 10^{12} | 7.49 ± 1.77 |
| a_{R–P} | 1.23 × 10^7 ± 4.42 × 10^{11} | 0.12 ± 0.07 |
| G | 0.71 ± 0.06 | 0.81 ± 0.07 |
| Temkin | R\( ^2 \) | 0.89 | 0.97 |
| \( \chi^2 \) | 30.48 | 62.97 |
| SSE | 182.90 | 377.80 |
| B | 394.21 ± 74.83 | 80.39 ± 6.29 |
| A | 8.57 ± 8.81 | 0.46 ± 0.10 |

In other words, the Langmuir model can satisfactorily describe the adsorption of Pb\( ^{2+} \) on NC. The good fitting to the Langmuir model indicates that Pb\( ^{2+} \) binds to homogeneous active sites in the form of monolayers on the surface of NC. The separation factor (R_{L}) is usually used to show if the adsorption process is unfavorable (R_{L} > 1), linear (R_{L} = 1), favorable (0 < R_{L} > 1), or irreversible (R_{L} = 0). The value of R_{L} in Table 2 implies that the adsorption of Pb\( ^{2+} \) on NC is favorable. The calculated Langmuir theoretical monolayer saturation capacity for Pb\( ^{2+} \) adsorption on NC was compared to other clay-based adsorbents reported in the literature. Table 3 clearly shows that the NC used in this study has superior

Figure 10. Adsorption isotherms and fitted models of (a) RY160 (CAPB-NC-2-60-3-y, dosage 1.5 g/L, pH 2, contact time 1 h) and (b) Pb\( ^{2+} \) (NC, dosage 1 g/L, pH 6.2, contact time 1 h).
adsorption capacity relative to other clay-based adsorbents; consequently, it could be applied as an excellent adsorbent for removing Pb\textsuperscript{2+} from contaminated water.

**CONCLUSIONS**

In this work, efforts were made to utilize and enhance the adsorption properties of copious low-cost NC. The physical, chemical, and adsorption properties of the NC were assessed before and after modification with the zwitterionic surfactant CAPB. Modification was a key factor in RY 160 adsorption and was ineffectual in Pb\textsuperscript{2+} adsorption. The sample that was heated at 60 °C for 3 h with a concentration of CAPB equal to 2 CEC of NC achieved the highest removal of RY160. The adsorption interaction between RY160 and CAPB-NC was strong and favored at pH 2 and resulted in the formation of multilayers. On the other hand, Pb\textsuperscript{2+} adsorption on NC occurred via monolayer formation and was favored at pH 6.2. To sum up, NC and CAPB-NC can efficiently remove Pb\textsuperscript{2+} and RY160, respectively, from the aqueous medium.

**MATERIALS AND METHODS**

**Materials.** The RY160 dye was provided by a local textile plant. Commercial CAPB was purchased from Mystic Moments and used as received. Table S1 shows some properties of the RY160 dye and CAPB. Analytical grade Pb(NO\textsubscript{3})\textsubscript{2}, NaOH, and HCl were purchased from Sigma-Aldrich (Egypt) and used for the preparation of Pb\textsuperscript{2+} stock and working solutions, and solution pH\textsubscript{i} adjustment. Deionized (DI) water was used during the whole study. The NC was collected from Wadi Kadid, Khulais governorate, Saudi Arabia. (DI) water was used during the whole study. The NC was collected from Wadi Kadid, Khulais governorate, Saudi Arabia. (DI) water was used during the whole study. The NC was collected from Wadi Kadid, Khulais governorate, Saudi Arabia.

**Characterization of NC and CAPB-NC.** The XRD analyses of NC and CAPB-NC were performed using a PANalytical X'Pert Pro diffractometer (The Netherlands) with Cu K\textalpha\ source (\(\lambda = 1.5406 \text{Å}\)). The collected XRD pattern was compared with standard ASTM cards to identify the crystallized phases. Quantitative phase analysis of the NC was performed using DIFFRAC.EVA V4 software. TGA was performed using a Shimadzu TG-50H thermal analyzer. A known weight of the samples was heated from room temperature to 800 °C at a rate of 10 °C/min under the high-purity N\textsubscript{2} atmosphere. FTIR was used to identify the surface functional groups of NC and CAPB-NC. The FTIR spectra of the samples were collected using a Jasco FT/IR-6100A instrument. KBr disks were prepared by pressing a mixture of powdered sample and KBr. All spectra were recorded at room temperature over the range of 400–4000 cm\textsuperscript{-1}. The morphologies of NC and CAPB-NC were observed by a field emission scanning electron microscope (JEOL 6400 F, USA); the accelerating voltage and working distance were 5 kV and 20 mm, respectively. Prior to SEM observation, a small amount of the material was fixed on conductive carbon tape, mounted on the support, and sputtered with gold. Textural analysis was performed using nitrogen adsorption at 77 K by a BELSORP-max (BEL Japan Inc). Before analysis, the samples were degassed for 24 h at 150 °C under a helium flow. The specific surface area and the pore size distribution were obtained by the Brunauer–Emmett–Teller method (S\textsubscript{BET}) and the nonlocal density functional theory (NLDFT) method, respectively.

**Adsorption Studies.** The adsorption experiments were performed in a single component batch mode system. A precisely weighed amount of NC or CAPB-NC was shaken with 100 mL of adsorptive (RY160 dye or Pb\textsuperscript{2+}) solution using a shaking water bath (Mxtrudy18, DAIHAN Scientific Co, Korea) at 26 °C and 120 rpm. At preset times, aliquots were withdrawn and filtered, and the residual concentrations of adsorptives were determined. The RY160 dye was quantified by a UV–vis spectrophotometer (JASCO V630, Japan) at \(\lambda = 425 \text{nm}\) using a standard calibration curve.

Specifically, 0.2 g of the NC was shaken in 100 mL of 1.0 mol/L ammonium acetate for 120 min, and then the concentration of exchangeable cations was measured by inductively coupled plasma-optical emission spectrometry (ICP–OES) (Agilent 5100, USA) following the American Public Health Association (APHA) methods.

**Preparation of the Zwitterionic Surfactant-Modified Clay.** The NC (10 g) was dispersed in DI water (200 mL) by vigorous shaking. An initial amount of CAPB equivalent to 0.5, 1.0, 2.0, and 4.0 times of the NC CEC was added slowly to the suspension at constant temperature (25, 40, 60, or 80 °C) and vigorous shaking. The shaking was continued for 3, 6, 12, or 24 h, and then the mixture was left to equilibrate for 12 h at room temperature. Afterward, CAPB-NC was collected by centrifugation, washed several times with DI water, air-dried at 70 °C, and ground. The samples were denoted as CAPB-NC\(_{a,b,c}\), where the subscripts \(a, b,\) and \(c\) indicate the CEC multiplier, the reaction temperature, and the reaction time, respectively.

**Table 3. Comparison of the Langmuir Theoretical Monolayer Saturation Capacity of Different Clay-Based Adsorbents for Pb\textsuperscript{2+}.**

| adsorbent                      | \(Q_m\) (mg/g) |
|-------------------------------|----------------|
| NC (this work)                | 166            |
| bentonite clay (Morocco)\textsuperscript{57} | 94             |
| montmorillonite–illite clay\textsuperscript{56} | 52             |
| NC (Nigeria)\textsuperscript{59} | 34             |
| acid-activated clay\textsuperscript{59} | 35             |
| thermally activated clay\textsuperscript{59} | 32             |
| NC (India)\textsuperscript{60} | 25             |
| bentonite\textsuperscript{61} | 19             |
| kaolinite–multiwalled carbon nanotube nanocomposite\textsuperscript{62} | 10             |
| acid-activated clay\textsuperscript{63} | 10             |
| nano illite/smectite clay\textsuperscript{64} | 2              |

[\(q_t = (C_i - C_f) \times \frac{V}{w}\)](1)
where \( C_t \) (mg/L) is the concentration of the adsorptive at time \( t \), \( V \) (L) is the volume of the adsorptive solution, and \( w \) (g) is the weight of the material.

The adsorption kinetic data were analyzed by the nonlinear forms of the PFO and PSO equations, while the equilibrium data were analyzed by the nonlinear forms of two-parameter (Langmuir, Freundlich, Dubinin–Radushkevich, Temkin) and three-parameter [Redlich–Peterson (R–P)] models. Table S2 lists the equations and the parameter definition of the used models. The nonlinear regression, chi-square (\( \chi^2 \)) test, sum of squared errors (SSEs), and the kinetic and equilibrium isotherm model constants were calculated using the OriginPro 2016 Ver. 9.3.226 software program. The best model that gives the highest \( R^2 \) value and the lowest \( \chi^2 \) and SSE value is the one that best describes the adsorption data.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00166.

Some properties of the zwitterionic surfactant CAPB and reactive yellow 160 dye, nonlinear form of the studied kinetics and equilibrium isotherm models, UV–visible spectrum of the RY160 dye, and standard calibration curve of RY160 are provided in the Supporting Information.

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**Notes**

The authors declare no competing financial interest.

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