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TiO₂/CTS/ATP adsorbent and its application in Adsorption- Ultrafiltration Process for dye wastewater purification

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Abstract: Industrial dyeing produces highly polluting wastewater and threatens the environment. Effective treatment of dyeing wastewater is a crucial step to prevent toxic chemicals from entering receiving waters. This study aimed to assess a modified attapulgite (ATP)-based adsorbent for dyeing wastewater purification by introducing chitosan (CTS) and titanium dioxide (TiO_2) into the adsorbent material named $\text{TiO}_2/\text{CTS}/\text{ATP}$. It was found that, after modification, the adsorbent showed a lower hydrophilicity, as demonstrated by an increase in the water contact angle from 9.1° to 42° , which could reduce the water adsorption tendency and potentially facilitate contaminants adherence. The modification also led to a significantly increased specific surface area of $79.111 \text{ m}^2/\text{g}$ from $3.791 \text{ m}^2/\text{g}$, and exhibited more uniform and smaller particle size (reduced to $2.52 \mu\text{m}$ from $3.99 \mu\text{m}$). When the $\text{TiO}_2/\text{CTS}/\text{ATP}$ adsorbent was applied to the adsorption of Congo red solution, the adsorption efficiency was observed to reach to 97.6% at the dosage of 0.5 g/L. Furthermore, the combination of adsorption and ultrafiltration was able to achieve 99% Congo red removal. Adsorption pretreatment prior to the ultrafiltration also enabled to reduce membrane fouling, increased the reversible membrane fouling and resulted in a considerably lower transmembrane pressure as compared with the direct ultrafiltration filtration system.

Keywords: $\text{TiO}_2/\text{CTS}/\text{ATP}$ adsorbent; Ultrafiltration; Membrane fouling; Dyeing wastewater; Modified attapulgite

1 Introduction

Over the past few decades, rapid population growth and accelerated globalization have led to a marked upsurge in the production of drugs, food, cosmetics and, textiles etc. ([Guerranti et al. 2019](#), [Wei et al. 2020](#)). The discharge of untreated wastewater containing these products into surface waters known to severely damage the ecological environment ([Samsami et al. 2020](#)). As one of the highly polluting industrial effluents, dye wastewater features a high chromatic and toxic level, low biodegradability and significant mutagenicity and carcinogenicity ([A et al. 2020](#)). It has been reported that more than 7×10^5 tons of dyes are produced each year, and about 10% originated from textile and related industries ([Shahanaz et al. 2019](#)). Therefore, it is important to develop reliable technologies for remediating textile dying wastewater. To date, multiple treatment options, such as membrane filtration ([Abdel-Karim et al. 2020](#)), electrochemical method ([V et al. 2018](#)), biological process ([Paz et al. 2017](#)), photocatalysis ([Wang et al. 2019](#)), adsorption ([Xiaoduo et al. 2019](#)), have been studied. Among these methods, the adsorption method has been widely considered for dying wastewater treatment due to low cost, high pollutant removal efficiency, uncomplicated design and operation ([Abdulhameed et al. 2019b](#), [Jawad et al. 2020](#)).

Various adsorbents have been used to eliminate dyes from water ([Hassan et al. 2019](#)). Attapulgite (ATP), a typical low-cost adsorbent material with abundant reserves on the Earth, has attracted increased interest ([Pan et al. 2017](#), [Wang et al. 2017](#)). ATP is a mineral with unique layered chain structure, mainly composed of hydrous magnesium

56 aluminum silicate, and is widely used as an adsorbent in wastewater treatment due to
57 its considerably porous structure, high specific surface area and excellent physico-
58 chemical properties ([Zhang et al. 2009](#)). However, impurities are commonly
59 encountered in natural ATP, which increase the tendency of pore blockage, decrease
60 the specific surface area and thus negatively affect the adsorption performance ([Wang
61 et al. 2017](#)). Therefore, modifications are often critical in order to achieve enhanced
62 water treatment efficiency. For instance, chitosan @ ATP composite was prepared by a
63 self-assembly method and this modified ATP adsorbent greatly improved the removal
64 efficiency of uranium pollutants ([Pan et al. 2017](#)). The unique structure of CS is
65 attributed to the presence of re-active amino($-NH_2$) and hydroxyl($-OH$) groups which
66 are considered active adsorption sites for unlimited types of organic and inorganic water
67 pollutants([Abdulhameed et al. 2019a](#), [Abdulhameed et al. 2019b](#)). In another study,
68 Zhou *et al.* ([Zhou et al. 2015](#)) adopted a hydrothermal carbonization method to
69 synthesize a chitosan@ATP composite and successfully used it to remove methylene
70 blue from wastewater.

71 Additionally, titanium dioxide (TiO_2) is commonly considered in adsorption
72 processes and is often combined with clay for the treatment of dye wastewater ([Djellabi
73 et al. 2014](#)). This combination can not only enhance the light absorption capacity of
74 TiO_2 , but also increase the specific surface area and the dye adsorption capacity
75 ([Setthaya et al. 2017](#)). Previous research has demonstrated that kaolin/ TiO_2 ([Wongso
76 et al. 2019](#)), montmorillonite/ TiO_2 ([Djellabi et al. 2014](#)), and zeolite/ TiO_2 ([Setthaya et](#)

[al. 2017](#)) have the ability to effectively adsorb dye from wastewater. Combining chitosan with TiO_2 is also beneficial; the composite can not only reduce the risk of agglomeration, but also expand the optical reaction range of TiO_2 from the ultraviolet region to the visible region, thus enabling TiO_2 to play a better role in water treatment ([Karthikeyan et al. 2017](#)).

Solid-liquid separation is an important process after adsorption, and it affects numerous aspects of the treatment process, such as operating cost and recycling of adsorbents and adsorbates. Among all the separation techniques, ultrafiltration (UF) is often a preferred option due to its high solid removal efficiency, operational simplicity, and low energy consumption([Chen et al. 2019](#)), and ultrafiltration is widely used in the treatment of dye ([Lin et al. 2016](#)). Nevertheless, wastewater treatment using a standalone ultrafiltration is usually not able to achieve the removal of some low molecular weight dissolved pollutants, and severe fouling is likely to occur([Chen et al. 2019](#)). Combining ultrafiltration and an adsorption pretreatment process can effectively solve these problems([Hammami et al. 2017](#)). For example, during dyeing wastewater treatment, adding an adsorbent in a ultrafiltration unit is expected to enhance the removal of some pigment molecules that are not rejected by the membrane. In addition, the adsorbent retained on the membrane surface can form a filtrate cake to prevent foulants adhering to the membrane([Dong et al. 2011](#), [Hammami et al. 2017](#)).

In this study, an adsorbent material is prepared via modifying ATP with TiO_2 and chitosan, and is termed $\text{TiO}_2/\text{CTS}/\text{ATP}$. The adsorbent is subjected to comprehensive

characterization prior to being applied to remove Congo red. Then, the $\text{TiO}_2/\text{CTS}/\text{ATP}$ adsorbent is combined with the ultrafiltration membrane to treat a synthetic dye wastewater. Both treatment efficiency and membrane performance will be examined to demonstrate the benefits of combining the $\text{TiO}_2/\text{CTS}/\text{ATP}$ adsorption coupled with ultrafiltration process for dyeing wastewater treatment

2 Materials and methods

2.1 Materials

Attapulgite (ATP) was purchased from the Xuyi Botu Attapulgite Co. Ltd., Jiangsu, China. Terabutyl titanate ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}_2$), nitric acid (HNO_3), and acetic acid (CH_3COOH) were all obtained from Honghui Reagent Co. Ltd., Hunan, China. Chitosan ($\text{C}_6\text{H}_{11}\text{NO}_4\text{X}_2$), hydrochloric acid (HCl), absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$) was provided by Qingdao BZ Oligo Biotech Co. Ltd., China. Congo Red ($\text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2$) dye was acquired from Kemi Reagent Co. Ltd., Tianjin, China. All the chemicals used were of analytical grade and without further treatment. Deionized water was used throughout the experimental work to prepare solutions and synthetic wastewater.

2.2 Solutions

Congo red solution was prepared by dissolving Congo red into deionized water, and the concentration was 100 mg/L. A synthetic dyeing wastewater was produced according to the characteristics of the secondary effluent at one printing and dyeing plant in Guangzhou. The water quality indexes of the actual dyeing wastewater are shown in [Table 1](#). It can be seen from the table that the COD concentration of dyeing

wastewater after biological treatment was still higher than First class effluent standard of China's "Discharge Standard of Water Pollutants for Dyeing and Finishing of Textile Industry" (GB4287-1992).

Table 1 The characteristic of dyeing wastewater

Parameter	Untreated wastewater	Biochemical effluent
Conductivity /($\mu\text{S}\cdot\text{cm}^{-1}$)	4800	4300
Turbidity /(mg/L)	195	57.3
COD/(mg/L)	1900	250
pH	7.34	7.06
SO_4^{2-} /(mg/L)	1281.9	326.0
Cl^- /(mg/L)	1646.4	589.3

2.3 Modification of Attapulgite

2.3.1 ATP acidification

As show in Fig.1, 100 mL HCl at a concentration of 3 mol/L was used to treat 25 g ATP. The mixture was shaken for 3 h at a constant temperature of 25 °C, and then centrifuged, washed and dried for 12 h.

2.3.2 Synthesis of CTS/ATP

As show in Fig.1, CTS of different masses (0.08 g, 0.16 g, 0.32 g) was dissolved into 100 mL CH_3COOH (2.0%), and 16 g acidified ATP was then added into the solution. Subsequently, the mixture was stirred for 30 min, dried and grinded to obtain 0.5%, 1.0% and 2.0% (w/w) CTS/ATP.

2.3.3 Synthesis of TiO_2 /ATP and TiO_2 /CTS/ATP

As show in Fig.1, 10 mL Terabutyl titanate was added slowly into 30 mL absolute ethanol. Then, the solution was subjected to magnetic stirring and 60 °C water bath for 15 min. During the process, 2 mL CH_3COOH was added to control the hydrolytic rate.

The solution was then mixed with 8 g acidified ATP or 8 g CTS/ATP (1.0%) and a buffer solution composed of 0.5 mL HNO₃, 10mL ethanol as well as 5 mL distilled water. The mixture was stirred for 30 min and then dried and grinded to get TiO₂/ATP or TiO₂/CTS/ATP powder.

2.3.4 Synthesis of CTS/TiO₂/ATP

As show in Fig.1, 0.08 g CTS was dissolved in 100 mL CH₃COOH (2%), and then 8 g TiO₂/ATP was added. Subsequently, the mixture was stirred for 30 min, dried and grinded to obtain CTS/TiO₂/ATP.

Fig. 1. Material preparation.

2.4 Experimental setup and operating condition

2.4.1 Adsorption experiments with different types of modified ATP as variable

0.05 g acidified ATP, 0.5% CTS/ATP, 1.0% CTS/ATP, 2.0% CTS/ATP, TiO₂/ATP, TiO₂/CTS/ATP and CTS/TiO₂/ATP was added into 7 beakers containing 100 mL Congo red solution (100 mg/L) with a pH of 7 at 25 °C, respectively. The experiments were run for 60 min on a plate shaker at a constant shaking speed of 200 r/min. After the experiments, supernatant samples were collected using centrifugation and then

analyzed in a by ultraviolet spectrophotometer at a wavelength of 498 nm (see Section 2.6 for details).

2.4.2 Adsorption experiments at different TiO₂/CTS/ATP doses

In this experiment, certain amounts (0.01, 0.03, 0.05, 0.07 and 0.1 g) of TiO₂/CTS/ATP were added in 5 beakers with 100 mL Congo red solution (100 mg/L); the experimental condition and operation were the same as Section 2.4.1.

2.4.3 Adsorption of Congo red solution with pH as a variable

The experiment was carried out by adding 0.05 g TiO₂/CTS/ATP into 9 beakers containing 100 ml Congo red solution (100 mg/L) with the adjustment of pH to 3, 4, 5, 6, 7, 8, 9, 10 and 11, respectively. The pH of the raw water was adjusted to the initial target pH by the addition of dilute 0.1 M HCl or NaOH as necessary. The experimental conditions were the same as above.

2.4.4 Adsorption-ultrafiltration treatment of synthetic dying wastewater

The flat membrane ultrafiltration rig was mainly composed of an ultrafiltration vessel, a circular plate membrane, peristaltic pump and pressure acquisition and control device (Fig. 2). The disc flat sheet membrane (ϕ 76mm, PVDF), with the nominal molecular weight cut-off value was 100 kDa, was placed at the bottom of the 200 mL ultrafiltration vessel. The pressure acquisition device and peristaltic pump was connected at the outlet of the ultrafiltration vessel. In this experiment, a constant flux ($J=120 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) of dead-end filtering was adopted and the pressure acquisition device automatically recorded the data in a computer every 10 s. The transmembrane pressure data recorded

could reflect the fouling of ultrafiltration membrane under the constant flux condition.

Fig. 2. Experimental device diagram of adsorption and ultrafiltration.

The combined process started with treating the synthetic wastewater with $\text{TiO}_2/\text{CTS}/\text{ATP}$ (1.5 g/L) adsorption for 1 h at a shaking speed of 200 r/min. The mixture was fed into the ultrafiltration vessel at a constant flux of $J=120 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and the filtration process continuously operated for 30 min (Fig. 2).

2.5 Membrane fouling evaluation method

Membrane fouling calculation was calculated using the model of resistance-in-series as shown in Eq. (1)(Cheng et al. 2017).

$$J_f = \frac{TMP}{\mu R_t} = \frac{TMP}{\mu(R_m + R_r + R_{ir})} \quad (1)$$

Where, TMP is the transmembrane pressure (Pa); μ is the dynamic viscosity ($\text{Pa} \cdot \text{s}$); J is the permeate flux (m^3/s); R_t , R_m , R_{ir} and R_r are the total hydraulic fouling resistance, intrinsic membrane resistance, hydraulic irreversible fouling resistance and hydraulic reversible fouling resistance (m^{-1}), respectively.

2.6 Analytical methods

pH was measured using a Starter 3100 pH meter. The level of Congo red in the supernatant was determined by measuring the ultraviolet absorbance at 498 nm wavelength in an ultraviolet spectrophotometer using distilled water as reference. The concentration and removal of Congo red were then calculated using Eq. (2) and Eq. (3). In Eq. (2), A is the ultraviolet absorbance data, and C denotes the concentration of Congo red, In Eq. (3), C_0 denotes the initial concentration of Congo red, and C_e denotes the final concentration of Congo red.

$$A = 0.0201C + 0.0308 \quad (2)$$

$$R = \frac{(C_0 - C_e)}{C_e} \times 100 \% \quad (3)$$

Contact angle measuring instrument (OCA15Pro) was used to analysis the wettability of the adsorbents. Distilled water was used as the reagent and the contact angle was measured by the hanging drop method. For particle size analysis, a small amount of adsorbent was initially subjected to ultrasonic dispersion in ultra-pure water for 20 min, and a portion of the upper liquid was then transferred to laser particle size analyzer (Mastersizer2000, Malvern Instruments Ltd., UK) for analysis. Surface Area and Porosity Analyzer (ASAP2460) was used to measure the specific surface area of adsorbent samples. Before testing, the sample was vacuumed at 100 °C for about 4 h. N_2 was used as adsorption molecules for the tests.

3 Result and discussion

3.1 Modified attapulgate

It can be seen from [Fig. 3a, b and c](#) that modifying ATP achieved considerably enhanced Congo Red removal. Among 0.5%, 1.0% and 2.0% CTS/ATP, the 1.0% had the best Congo red adsorption efficiency ([Fig. 3a](#)). The lower Congo red removal at the lower CTS concentration (0.5%) was likely attributed to the lower availability of adsorption-related functional groups, such as amino and hydroxyl groups([Abdulhameed et al. 2019a](#), [Abdulhameed et al. 2019b](#)). On the other hand, the higher CTS proportion (2%) could lead to increased viscosity of solution, inhibiting the uniform dispersion of solid particles and resulting in the agglomeration of CTS/ATP which reduced the absorption efficiency of Congo red. Therefore, CTS with a mass fraction of 1.0% was used in the later trials. [Fig. 3\(b\)](#) shows the importance of the sequence of adding CTS and TiO₂ when preparing the adsorbents, and it was found that TiO₂/CTS/ATP (for which CTS was added before TiO₂) achieved better Congo Red removal than CTS/ TiO₂/ATP (for which TiO₂ was added before CTS). It was likely that CTS was positively charged after protonation and it performed ion exchange with ATP, resulting in the inner-sphere complexes ([Pan et al. 2017](#)). As a result, the interval between layers increased, so more TiO₂ particles could be absorbed. However, in the case of TiO₂ being initially loaded, agglomeration occurred to a greater extent, limiting the adsorption and adhesion of CTS([Salameh et al. 2014](#)). According to [Fig. 3\(c\)](#), ATP modified with both CTS and TiO₂ was significantly more effective in Congo red

removal in comparison with the ATP modified by CTS or TiO_2 alone.

Fig. 3. Comparison of adsorption properties under (a) different chitosan content, (b) different load sequence of CTS and TiO_2 and (c) varied modification conditions.

3.2 Analysis of surface characteristics of modified attapulgite

The N_2 adsorption-desorption isotherms of ATP and TiO_2 /CTS/ATP are shown in Fig. 4 (a). According to the IUPAC classification, the adsorption process was a type II isotherm, reflecting a typical multilayer adsorption occurring on non-porous or macro porous adsorbent as the adsorption equilibrium was reached (Nodehi et al. 2020), the amount of gas adsorbed by TiO_2 /CTS/ATP was significantly higher than that of ATP. According to the BET equation (Peng et al. 2020), modification could increase the surface area, and the specific surface area of TiO_2 /CTS/ATP increased by 20.8 times, from $3.791 \text{ m}^2/\text{g}$ to $79.111 \text{ m}^2/\text{g}$.

Fig. 4(b) shows that the pore size distribution of ATP was relatively uniform, with the main peak at 0-2 nm. By contrast, the pore size distribution of TiO_2 /CTS/ATP exhibited double peaks, with the dominant peak at 120-140 nm and the secondary peak at 0-2 nm. The finding suggests that ATP modification created considerably larger pores that were expected to enhance the adsorption capacity of the material (Liu et al. 2008).

Fig. 4. N₂ adsorption-desorption isotherms of ATP (a-1) and TiO₂/CTS/ATP (a-2), pore distribution of ATP and TiO₂/CTS/ATP (b), particle size distribution of ATP, CTS/ATP, TiO₂/ATP and TiO₂/CTS/ATP (c) and contact angle photograph of ATP (d-1), CTS/ATP (d-2) and TiO₂/CTS/ATP (d-3).

The particle size distribution of TiO₂ before and after modification is shown in Fig. 4(c). The average particle size of ATP, TiO₂/ATP, CTS/ATP was 3.99 μm , 12.62 μm , 14.16 μm respectively, indicating that particle agglomeration occurred in the system after the ATP was treated separately by TiO₂ or CTS. In comparison, the TiO₂/CTS/ATP adsorbent displayed the lowest average particle size of 2.52 μm . The result suggests that treating ATP with both TiO₂ and CTS can not only solve the agglomeration problem,

but also distribute adsorbents more uniform in size ([Siripatrawan &Kaewklin 2018](#)).

[Fig. 4\(d\)](#) illustrates the water contact angle of the laminates of ATP, CTS/ATP and TiO₂/CTS/ATP. ATP had the strongest hydrophilicity with a water contact angle of 9.1°, followed by CTS/ATP (11.7°). By contrast, the water contact angle of TiO₂/CTS/ATP soared to 42° and thus its hydrophobicity was improved substantially ([Cieśliński &Krygier 2014](#), [Ku et al. 2011](#)). Therefore, the TiO₂/CTS/ATP modification a hindered was anticipated to hinder the adsorption of water molecules during the treatment process, which facilitated the removal of Congo red.

3.3 Adsorption efficiency of modified attapulgite for Congo red

It can be seen from [Fig. 5\(a\)](#) that the amount of adsorbent exhibited a great influence on the removal effect of Congo red. As the dose of TiO₂/CTS/ATP increased from 0.1 g/L to 0.5 g/L, the removal efficiency of Congo red soared from 5% to 97.6%. Further increase in adsorbent dose showed an insignificant impact on Congo red removal. Therefore, the optimal dosage under this test condition was 0.5 g/L. Mansor *et al.* ([Mansor et al. 2020](#)) also reported that increasing the adsorbent dosage from 1.5 g/L to 2.5 g/L increased the removal efficiency from 72.6% to 96% after 50 min of adsorption time using composite membrane for dye adsorption and filtration.

The effect of different pH on the absorption of Congo red by TiO₂/CTS/ATP is shown in [Fig. 5\(b\)](#). The removal of Congo red by TiO₂/CTS/ATP remained above 95% when pH was between 3 and 8, and a higher pH (8-10) led to a slight decrease in removal. Increasing pH beyond 10 sharply decreased the Congo red adsorption

efficiency. This finding can be explained by the electrostatic interaction between Congo red and the adsorbent. At pH of 3-10, Congo red was negatively charged. The TiO₂/CTS/ATP adsorbent was positively charged when pH was lower than 6.26 according to the Zeta Potential (Fig. 5(c)), and electrostatic attraction served as a major pathway for Congo red removal. In the meantime, the sulfonate groups of Congo red readily formed hydrogen bonds with the hydroxyl groups of TiO₂/CTS/ATP, thus facilitating the adsorption process (Nodehi et al. 2020). With pH increased in the range of 6.28-10, electrostatic repulsion became more significant (Chatterjee et al. 2007), leading to a decrease in the adsorption efficiency of Congo red. At the highest pH of 11, in addition to the strongest electrostatic repulsion, the large number of hydroxides (OH⁻) present in the solution competed with Congo red for adsorption sites (Feng et al. 2012), resulting in a sharp decrease in Congo red removal.

Fig. 5 Effects of doses (a) and pH (b) on Congo red sorption capacity and (c) Zeta

Potential of TiO₂/CTS/ATP adsorbent

3.4 Simulated actual dye wastewater

It can be seen from Fig. 6, in the case of stand-alone ultrafiltration treatment, the

removal of Congo red from synthetic dyeing wastewater was only 22%. Severe membrane fouling was observed, with TMP rising by 51 kPa within 30 minutes. The resistance R_f , representing irreversible pollution, caused by adsorption or blockage accounted for 70% of the membrane fouling resistance. The filter cake resistance R_c , representing reversible fouling, was only responsible for 30% of the membrane fouling resistance. When the adsorption-ultrafiltration process was combined, the removal of Congo red was as high as 99%. Previous research also reported that a hybrid adsorption membrane process also achieved More than 97 % dye removal in removing dyes from contaminated water([Alardhi et al. 2020](#)). Compared with ultrafiltration alone, membrane fouling was considerably mitigated, as demonstrated by a minor TMP increase of 6 kPa in 30 minutes. In addition, pretreatment with adsorption increased the reversibility of the fouling, with R_c playing a greater role (67%) compared with R_f (33%). Dong *et al.* ([Dong et al. 2011](#)) also reported that UF process enhanced with powdered activated carbon (PAC) adsorption showed the good application potential in the dye wastewater treatment, and they emphasized that PAC enabled to form an intact filter cake and exhibited the high adsorption ability of PAC toward dye molecules.

[Fig. 7](#) indicates the deposition of pollutants on the membrane surface. Comparison between [Fig. 7b](#) shows an uneven sludge layer formed on the surface of the membrane, and some membrane pores on the surface were still visible. Pretreatment with $\text{TiO}_2/\text{CTS}/\text{ATP}$ before ultrafiltration led to the generation of a compact cake layer that covered almost all the pores on the membrane surface. Comparison of [Fig. 7 \(c\)](#) and

Fig. 7 (e) demonstrates that the cleaned membrane of the adsorption-ultrafiltration unit had clearer pores as compared with that of direct ultrafiltration, on which blocked pores were still found, which was in accordance with that in Fig. c.

Fig. 6. Effect of adsorption pretreatment on CR removal efficiency (a), TMP (b) and resistance distribution of membrane fouling (c).

Fig. 7. Deposition maps and SEM micrographs ($\times 500$ magnification) of membrane surface pollutants (a-Virgin, b- cake by ultrafiltration, c- cake by ultrafiltration after cleaning, d- cake by adsorption-ultrafiltration; e- cake by adsorption-ultrafiltration after cleaning).

As shown in Fig.8, the comparison between the adsorption-ultrafiltration process and the controlled ultrafiltration process reveals that the levels of C, Na, which were the main element of Congo red on ultrafiltration membrane, and the element on the ultrafiltration membrane without pretreatment were higher than those measured for the adsorption-UF membrane. This finding indicates that the adsorption-ultrafiltration process alleviated the fouling of Congo red on the ultrafiltration membrane.

Furthermore, the levels of O, Al, Si and Ti on the adsorption-ultrafiltration membrane was significantly higher than its counterpart, as expected due to these four elements being the main components of TiO₂/CTS/ATP (Fig. 8 a). When the adsorption-ultrafiltration membrane was cleaned, the levels of these four elements decreased significantly, suggesting that these elements contributed to reversible membrane fouling (Fig. 8 b).

Fig. 8 EDS analysis of membrane surface (a) before and (b) after physical cleaning

4 Mechanism and implication

As shown in Fig. 9(a), when ultrafiltration was used to remove dye molecules, membrane pores were easily blocked by dye molecules due to direct contact. To address the fouling issue, pretreatment with adsorption was considered Fig. 8(b). The adsorbent was produced by modifying ATP with CTS and TiO₂. After modification, the water contact angle of ATP increased from 9.1° to 42° (Fig. 4 (d)), indicating a decrease in hydrophilicity, which reduced the adsorption of water molecules and improved Congo red removal. The specific surface area also increased from 3.791 m²/g to 79.111 m²/g, providing more adsorption sites for pollutants. In the process of TiO₂/CTS/ATP

adsorption, pollutants attached with $\text{TiO}_2/\text{CTS}/\text{ATP}$ through electrostatic interaction and hydrogen bonds [Fig. 5](#). During filtration of pre-adsorbed wastewater, a cake layer containing abundant adsorbents was formed on the ultrafiltration membrane. When approaching the membrane, pollutants were intercepted by the cake layer without entering and blocking the membrane pore ([Fig. 9 b](#)). As a result, not only enhanced treatment efficiency (99% congo red removal) but also minimized membrane fouling and improved water permeability were achieved.

Fig. 9 Schematic of mechanism for ultrafiltration in dye wastewater treatment (a) and $\text{TiO}_2/\text{CTS}/\text{ATP}$ adsorbent combined with ultrafiltration in dye wastewater treatment (b).

5 Conclusion

In current work, $\text{TiO}_2/\text{CTS}/\text{ATP}$ adsorbent was developed and applied for adsorption-ultrafiltration process for dye wastewater purification. Our finding was summarized as follows:

(1) TiO₂/CTS/ATP composites were prepared by modifying ATP with CTS and TiO₂. Characterization of TiO₂/CTS/ATP showed that modification significantly increased hydrophobicity and specific surface area of the adsorbent, and decreased the average particle size, which was conducive to adsorption of Congo red.

(2) When the dosage of TiO₂/CTS/ATP was 0.5 g/L, the removal of Congo red was 97.6%. Under acidic conditions, the removal of Congo red was almost not impacted. Increasing pH over 10 was found to greatly reduce the treatment efficiency due to the strongest electrostatic repulsion.

(3) The removal of Congo red was notably enhanced and reached up to 99% during treatment with by the adsorption-ultrafiltration process. Membrane fouling was considerably mitigated due to adsorption. Adsorption also increased the reversibility of the fouling components.

These aforementioned benefits demonstrate that the combination of TiO₂/CTS/ATP adsorption and ultrafiltration is a promising approach to dyeing wastewater treatment.

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Authors' contributions

390 **Zhihong Wang**: Experimental design, Writing- Original draft preparation. **Zekun Wu**:
391 Sample analysis and Graph editing. **Xujun Zhi**: Reactor operation and sample analysis,
392 Data curation. **Tianfu Tu** : Sample analysis. **Jinxu Nie** : Reactor design and
393 Experimental design. **Xing Du**: Reactor design, Writing- Reviewing, and Editing.
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405 A VS, A TSK, B CM, C MA (2020): An over review on recently developed techniques,
406 mechanisms and intermediate involved in the advanced azo dye degradation for
407 industrial applications J. Mol. Struct. 1224, 129195
408 Abdel-Karim A, El-Naggar ME, Radwan EK, Mohamed IM, Kenawy ER (2020): High-
409 performance mixed-matrix membranes enabled by organically/inorganic
410 modified montmorillonite for the treatment of hazardous textile wastewater.
411 Chem. Eng. J. 405, 126964
412 Abdulhameed AS, Jawad AH, Mohammad A-T (2019a): Synthesis of chitosan-ethylene

glycol diglycidyl ether/TiO₂ nanoparticles for adsorption of reactive orange 16
dye using a response surface methodology approach. *Bioresour. Technol.* 293,
122071

Abdulhameed AS, Mohammad A-T, Jawad AH (2019b): Application of response
surface methodology for enhanced synthesis of chitosan tripolyphosphate/TiO₂
nanocomposite and adsorption of reactive orange 16 dye. *Journal of Cleaner
Production* 232, 43-56

Alardhi SM, Albayati TM, Alrubaye JM (2020): A hybrid adsorption membrane process
for removal of dye from synthetic and actual wastewater. *Chemical Engineering
and Processing - Process Intensification* 157, 108113

Chatterjee S, Chatterjee S, Chatterjee BP, Guha AK (2007): Adsorptive removal of
congo red, a carcinogenic textile dye by chitosan hydrobeads: Binding
mechanism, equilibrium and kinetics. *Colloids Surf. Physicochem. Eng.
Aspects* 299, 146-152

Chen W, Mo J, Du X, Zhang Z, Zhang W (2019): Biomimetic dynamic membrane for
aquatic dye removal. *Water Res.* 151, 243-251

Cheng X, Liang H, Ding A, Tang X, Liu B, Zhu X, Gan Z, Wu D, Li G (2017): Ferrous
iron/peroxymonosulfate oxidation as a pretreatment for ceramic ultrafiltration
membrane: Control of natural organic matter fouling and degradation of
atrazine. *Water Res.* 113, 32-41

Cieśliński JT, Krygier KA (2014): Sessile droplet contact angle of water–Al₂O₃,
water–TiO₂ and water–Cu nanofluids. *Exp. Therm Fluid Sci.* 59, 258-263

Djellabi R, Ghorab MF, Cerrato G, Morandi S, Gatto S, Oldani V, Michele AD, Bianchi
CL (2014): Photoactive TiO₂–montmorillonite composite for degradation of
organic dyes in water. *Journal of Photochemistry & Photobiology, A: Chemistry*
295, 57-63

Dong Y, Su Y, Chen W, Peng J, Zhang Y, Jiang Z (2011): Ultrafiltration enhanced with
activated carbon adsorption for efficient dye removal from aqueous solution.

441 Chin. J. Chem. Eng. 19, 863-869

442 Feng T, Zhang F, Wang J, Wang L (2012): Application of chitosan-coated quartz sand
 443 for Congo red adsorption from aqueous solution. J. Appl. Polym. Sci. 125, 1766-
 444 1772

445 Guerranti C, Martellini T, Perra G, Scopetani C, Cincinelli A (2019): Microplastics in
 446 cosmetics: environmental issues and needs for global bans. Environ. Toxicol.
 447 Pharmacol., 75-79

448 Hammami A, Charcosset C, Amar RB (2017): Performances of Continuous Adsorption-
 449 Ultrafiltration Hybrid Process for AO7 Dye Removal from Aqueous Solution
 450 and Real Textile Wastewater Treatment. Journal of Membrane Science &
 451 Technology

452 Hassan H, Salama A, El-ziaty AK, El-Sakhawy M (2019): New chitosan/silica/zinc
 453 oxide nanocomposite as adsorbent for dye removal. Int. J. Biol. Macromol. 131,
 454 520-526

455 Jawad AH, Abdulhameed AS, Najwa N, Malek A, Alothman ZA (2020): Statistical
 456 optimization and modeling for color removal and COD reduction of reactive
 457 blue 19 dye by mesoporous chitosan-epichlorohydrin/kaolin clay composite. Int.
 458 J. Biol. Macromol., 4218-4230

459 Karthikeyan KT, Nithya A, Jothivenkatachalam K (2017): Photocatalytic and
 460 antimicrobial activities of chitosan-TiO₂ nanocomposite. Int. J. Biol. Macromol.
 461 104, 1762-1773

462 Ku Y, Huang Y-H, Chou Y-C (2011): Preparation and characterization of ZnO/TiO₂ for
 463 the photocatalytic reduction of Cr(VI) in aqueous solution. J. Mol. Catal. A:
 464 Chem. 342–343, 18-22

465 Lin J, Ye W, Baltaru M-C, Tang YP, Bernstein NJ, Gao P, Balta S, Vlad M, Volodin A,
 466 Sotto A, Luis P, Zydney AL, Bruggen BVd (2016): Tight ultrafiltration
 467 membranes for enhanced separation of dyes and Na₂SO₄ during textile
 468 wastewater treatment. J. Membr. Sci. 514, 217-228

469 Liu Y, Huang J, Wang X (2008): Adsorption Isotherms for Bleaching Soybean Oil with
 470 Activated Attapulgite. *J. Am. Oil Chem. Soc.* 85, 979-984
 471 Mansor ES, Ali H, Abdel-Karim A (2020): Efficient and reusable polyethylene
 472 oxide/polyaniline composite membrane for dye adsorption and filtration.
 473 *Colloid and Interface Science Communications* 39, 100314
 474 Nodehi R, Shayesteh H, Kelishami AR (2020): Enhanced adsorption of congo red using
 475 cationic surfactant functionalized zeolite particles. *Microchem. J.* 153, 104281
 476 Pan D, Fan Q, Fan F, Tang Y, Zhang Y, Wu W (2017): Removal of uranium contaminant
 477 from aqueous solution by chitosan@attapulgite composite. *Sep. Purif. Technol.*
 478 177, 86-93
 479 Paz A, Carballo J, Pérez MJ, Domínguez JM (2017): Biological treatment of model
 480 dyes and textile wastewaters. *Chemosphere* 181, 168-177
 481 Peng L, Chen B, Zhao Y (2020): Quantitative characterization and comparison of
 482 bentonite microstructure by small angle X-ray scattering and nitrogen
 483 adsorption. *Construction and Building Materials* 262, 120863
 484 Salameh S, Scholz R, Seo JW, Mädler L (2014): Contact behavior of size fractionated
 485 TiO₂ nanoparticle agglomerates and aggregates. *Powder Technol.* 256, 345-351
 486 Samsami S, Mohamadi M, Sarrafzadeh MH, Rene ER, Firoozbahr M (2020): Recent
 487 advances in the treatment of dye-containing wastewater from textile industries:
 488 Overview and perspectives. *Process Saf. Environ. Prot.* 143, 138-163
 489 Setthaya N, Chindaprasirt P, Yin S, Pimraksa K (2017): TiO₂ -zeolite photocatalysts
 490 made of metakaolin and rice husk ash for removal of methylene blue dye.
 491 *Powder Technol.* 313, 417-426
 492 Shahanaz P, Kumar BB, Asadur RM, Hafizur RM, Shahyaz AM, Raes UM (2019):
 493 Study on adsorption of Congo red onto chemically modified egg shell
 494 membrane. *Chemosphere* 236, 124326
 495 Siripatrawan U, Kaewklin P (2018): Fabrication and characterization of chitosan-
 496 titanium dioxide nanocomposite film as ethylene scavenging and antimicrobial

active food packaging. Food Hydrocolloids 84, 125-134

V NP, Minghua Z, A OM (2018): An overview on the removal of synthetic dyes from water by electrochemical advanced oxidation processes. Chemosphere 197, 210-227

Wang H, Wang X, Ma J, Xia P, Zhao J (2017): Removal of cadmium (II) from aqueous solution: A comparative study of raw attapulgite clay and a reusable waste—struvite/attapulgite obtained from nutrient-rich wastewater. J. Hazard. Mater. 329, 66-76

Wang H, Sun Y, Wu Y, Tu W, Wu S, Yuan X, Zeng G, Xu ZJ, Li S, Chew JW (2019): Electrical promotion of spatially photoinduced charge separation via interfacial-built-in quasi-alloying effect in hierarchical $\text{Zn}_2\text{In}_2\text{S}_5/\text{Ti}_3\text{C}_2(\text{O}, \text{OH})_x$ hybrids toward efficient photocatalytic hydrogen evolution and environmental remediation. Applied Catalysis B: Environmental 245, 290-301

Wei Y, Cui M, Ye Z, Guo Q (2020): Environmental challenges from the increasing medical waste since SARS outbreak. Journal of Cleaner Production

Wongso V, Chen CJ, Razzaq A, Kamal NA, Sambudi NS (2019): Hybrid kaolin/ TiO_2 composite: effect of urea addition towards an efficient photocatalyst for dye abatement under visible light irradiation. Applied Clay Science 180, 105158

Xiaoduo L, Jiefu T, Yuanyuan L, Ningfei S, Shu M, Yong X, Ziyu C (2019): Enhanced dyes adsorption from wastewater via Fe_3O_4 nanoparticles functionalized activated carbon. J. Hazard. Mater. 373, 397-407

Zhang J, Xie S, Ho Y-S (2009): Removal of fluoride ions from aqueous solution using modified attapulgite as adsorbent. J. Hazard. Mater. 165, 218-222

Zhou Q, Gao Q, Luo W, Yan C, Ji Z, Duan P (2015): One-step synthesis of amino-functionalized attapulgite clay nanoparticles adsorbent by hydrothermal carbonization of chitosan for removal of methylene blue from wastewater. Colloids Surf. Physicochem. Eng. Aspects 470, 248-257

Figures

Figure 1

Material preparation.

Figure 2

Experimental device diagram of adsorption and ultrafiltration.

Figure 3

Comparison of adsorption properties under (a) different chitosan content, (b) different load sequence of CTS and TiO₂ and (c) varied modification conditions.

Figure 4

N₂ adsorption-desorption isotherms of ATP (a-1) and TiO₂/CTS/ATP (a-2), pore distribution of ATP and TiO₂/CTS/ATP (b), particle size distribution of ATP, CTS/ATP, TiO₂/ATP and TiO₂/CTS/ATP (c) and contact angle photograph of ATP (d-1), CTS/ATP (d-2) and TiO₂/CTS/ATP (d-3).

Figure 5

Effects of doses (a) and pH (b) on Congo red sorption capacity and (c) Zeta Potential of $\text{TiO}_2/\text{CTS}/\text{ATP}$ adsorbent

Figure 6

Effect of adsorption pretreatment on CR removal efficiency (a), TMP (b) and resistance distribution of membrane fouling (c).

Figure 7

Deposition maps and SEM micrographs ($\times 500$ magnification) of membrane surface pollutants (a-Virgin, b- cake by ultrafiltration, c- cake by ultrafiltration after cleaning, d- cake by adsorption-ultrafiltration, e- cake by adsorption-ultrafiltration after cleaning).

Figure 8

EDS analysis of membrane surface (a) before and (b) after physical cleaning

Figure 9

Schematic of mechanism for ultrafiltration in dye wastewater treatment (a) and TiO₂/CTS/ATP adsorbent combined with ultrafiltration in dye wastewater treatment (b).