# UTILIZATION OF HYDROXYAPATITE/CRAB SHELL CHITOSAN COMPOSITES IN REMOVAL OF AQUEOUS CONGO RED: INFLUENCE FACTORS, ADSORPTION KINETICS AND ISOTHERM

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#### **Article Info**

#### Abstract

Volume: 7 Issue: 2 Jun: 2025 Received: Mar. 17<sup>th</sup>, 2025 Accepted: Apr. 11<sup>th</sup>, 2025 Page No: 254-264 Due to the limitations of traditional adsorbents for dveing wastewater, this study combined natural adsorbent (CS, chitosan) and hydroxyapatite (HAp) to form a composite for enhancing the adsorption of aqueous Congo red (CR). The chitosan was prepared from crab shells (Somanniathelphusa sinensis) with a deacetylation degree of about 89%. The HAp and HAp-CS composites were prepared by precipitation in high pH (~10) with the help of concentrated ammonia water (25%). The crab shell chitosan and chitin were characterized by the FTIR method, and the HAp and HAp-CS composites were analyzed using the SEM method. The CR adsorption experiments were carried out in batch form and sampled once for each condition. The results showed that the characteristic peaks in the FTIR spectrum confirmed the success of the crab shell chitosan preparation. The HAp and HAp-CS composites possess porous structures and seem to have a high surface area. The CR adsorptions reached optimal after 5-15 min. contacting, the adsorption efficiency tended to decrease with the initial concentration of CR and increase with the adsorbent dosage. The initial pH of the solution affected the adsorption efficiency for the 70%HAp-CS and 30%HAp-CS composites but had almost no effect on the adsorption capacity of 0%HAp-CS and 50%HAp-CS. The 50% HAp-CS composite had the best adsorption capacity among the synthesized composites (qmax = 769.2mg/g). The adsorption isotherm and kinetics best fit the Langmuir isotherm and pseudo-second-order kinetics model.

Keywords: adsorption, chitosan, composite, Congo red, hydroxyapatite

## **1. Introduction**

Pollution of dye wastewater is a major environmental issue, particularly in regions where textile dyeing industries are concentrated. Wastewater from these industries frequently contains various hazardous materials, including synthetic dyes, heavy metals, and treatment chemicals (Premkumar et al., 2018), which detrimentally affect the environment and human health. CR is among the most prevalent and harmful dyes in

textile industries. It may irritate the skin, eyes, and respiratory system, and studies have shown that it can induce gene changes and cancer (Hemashenpagam & Selvajeyanthi, 2023). It can also build up in organisms and result in long-term health issues. Dye wastewater that has not been adequately handled will have major negative effects on human health, including soil and water pollution. Toxic compounds can enter the body through food, breathing, and skin contact, leading to digestive, skin, and respiratory disorders, as well as cancer. As a result, dyeing wastewater treatment is crucial and necessitates stringent control procedures to guarantee adherence to environmental protection.

Effective treatment techniques are necessary for dye wastewater because of its hazardous and complicated composition. Conventional methods include membrane treatment (nanofiltration, reverse osmosis), biological treatment (activated sludge, biofiltration), and physicochemical treatment (coagulation, precipitation, oxidation) (Ahmed et al., 2021). These techniques might, however, be limited in their capacity to address certain contaminants, cost, and efficiency. A possible remedy that has surfaced recently is the use of composite adsorbents. Materials composed of two or more phases, at least one of which adsorbs contaminants, are composite adsorbents. Increased surface area, enhanced adsorption capacity, improved mechanical and chemical stability, and reusability (Liu et al., 2022) are just a few of the many exceptional benefits that this combination provides. Composite adsorbents can be targeted for various dye types, including those that are challenging to break down. Reducing the environmental impact of wastewater treatment is another benefit of using natural and recyclable materials to make composite adsorbents.

Chitosan, a natural polysaccharide, can adsorb dyes due to the amino and hydroxyl groups on the polymer chain. However, pure chitosan has some limitations, such as low mechanical strength and adsorption capacity for some dyes (Saheed et al., 2021). Researchers have developed various chitosan composites by combining chitosan with other materials, such as metal oxides, clays, activated carbons, and synthetic polymers, to overcome these limitations (Nikoshvili et al., 2023). Studies have shown that combining chitosan with these materials can significantly improve the dye adsorption capacity of the composite. For example, chitosan/magnetic iron oxide (Fe<sub>3</sub>O<sub>4</sub>) composites have been shown to effectively remove azo dyes from wastewater (Freire et al., 2020). In addition, chitosan/bentonite composites also showed good adsorption capacity for synthetic dyes (Şenol et al., 2024). Besides, chitosan/hydroxyapatite composite has also been studied for use as a dye adsorbent. (Jamarun et al., 2024) investigated different concentrations of chitosan in this composite and found that at a chitosan concentration of 30%, the optimal adsorption capacity for Rhodamine B was 0.1832mg/g. (Shi et al., 2017) fabricated a chitosan/hydroxyapatite composite membrane and found that the prepared membrane also featured repeated Direct Blue 15 removal (above 80% after 5 cycles of adsorption at a dye concentration of 150mg/L). However, the chitosan used in the above studies was commercially prepared from shrimp shells. In this study, we synthesized chitosan from crab shells (Somanniathelphusa sinensis) and used it as a component to synthesize composites with hydroxyapatite as an adsorbent. The target dye in this study was CR, which has never been used in adsorption studies using chitosan/hydroxyapatite composites. Therefore, our study is novel in the type of chitosan used and target dyesimulating textile wastewater.

# 2. Materials and method

# 2.1. Materials

HCl (36-38%), NaOH (96%), Acetic Acid (CH<sub>3</sub>COOH, 99.5%), Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O (99%), and Congo red (CR, 99%) were provided by Xilong Scientific, China. (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> was bought from Scharlau, Spain. Ethanol (C<sub>2</sub>H<sub>5</sub>OH, 99%) and Acetone (CH<sub>3</sub>COCH<sub>3</sub>, 99%) were purchased from Chemsol Vina, Vietnam. Chemicals were used without further purification, and distilled water was used in all experiments.

# 2.2. Methods

## 2.2.1. Crab shell chitosan preparation

The crab shell chitosan was prepared following the procedure in our published work (Nguyen & Bui, 2020). The washed crab shells were boiled in water for 1 hour. The crab meat was removed, and the crab shells were dried at 80°C for 5 hours. The crab shells were then ground into a fine powder using a grinder. Next, 25g of shell powder and 750mL of 1M HCl were added to a 1000mL beaker and stirred gently for 2 hours. The solid fraction was then filtered, washed to neutral pH, and dried. Next, 25g of the resulting powder was mixed with 750mL of 3M NaOH and stirred gently for 90 minutes. The solid fraction was then filtered, washed to neutral pH, and dried. 25g of the resulting powder was mixed with 375mL of acetone and stirred gently for 10 minutes for bleaching. The 25g of the dried powder was then reacted with 375mL of 50% NaOH in a 1L reaction vessel at 120°C for 3 hours. Finally, the obtained solid was filtered, washed to neutral pH, and dried at 70°C for 24h.

# 2.2.2. Preparations of hydroxyapatite and hydroxyapatite/chitosan composites

HAp and HAp–CS composites were synthesized using the precipitation method.  $(NH_4)_2HPO_4$  solution was slowly added to Ca $(NO_3)_2.4H_2O$  solution, contained in a reaction flask placed on a magnetic stirrer at 250rpm, with a molar ratio of Ca/P = 1.67. The pH of the reaction medium was maintained above 10 with a 25% ammonia solution. After adding all the  $(NH_4)_2HPO_4$  solution, the mixture was stirred continuously for 4 hours and then left for 24 hours at room temperature. The obtained HAp was filtered from the reaction mixture and washed with distilled water until the pH of the filtrate was close to 7. Finally, the HAp was washed further with ethanol and dried at 70°C for 12 hours.

To synthesize HAp–CS composites, chitosan was first dissolved in a 2% acetic acid solution, and then  $Ca(NO_3)_2.4H_2O$  was further dissolved into the solution with the mass shown in Table 1. Then,  $(NH_4)_2HPO_4$  solution was slowly added to the above solution, the remaining steps were the same as for HAp synthesis. HAp–CS composite materials with chitosan contents of 0%, 30%, 50%, and 70% were synthesized.

HAp-CS (%)	Chitosan (g)	$Ca(NO_3)_2.4H_2O(g)$	$(NH_4)_2HPO_4(g)$
0	0.00	11.76	3.946
30	1.50	8.232	2.762
50	2.50	5.880	1.793
70	3.50	3.528	1.184

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## 2.2.3. CR adsorption experiment

The CR adsorption experiment was performed in 25ml of CR solution; each condition of the adsorption experiment was conducted in a separate experiment. A CR solution of the desired concentration is diluted from a 1000mg/L stock solution. The CR concentration in the experiments was 200mg/L. However, the initial solutions had varying concentrations in the CR concentration-based adsorption experiment. The amount of adsorbent used is 50mg. However, the amount of adsorbent varied for dose-based adsorption experiments. First, 25ml of CR solution and a certain amount of adsorbent were added to a 100-ml Erlenmeyer flask and placed on a circular shaker at a speed of 300rpm. At a certain time, 1ml of the solution was withdrawn with a syringe equipped with a filter membrane. Next, the filtered solution was measured for optical absorbance at a wavelength of 497nm. The standard curve of CR solution was constructed with the same but known concentrations of CR (Figure 1).

The CR adsorption efficiency is calculated based on the following equation:

$$R\% = \left(1 - \frac{C_t}{C_0}\right) \times 100\%$$

Where R% is adsorption efficiency (%),  $C_t$  is the CR concentration (mg/L) at time t, and  $C_0$  is the initial CR concentration (mg/L).

The CR adsorption capacity is calculated by:

$$q = \frac{(C_0 - C_t)V}{m_{ad}}$$

Where q is the adsorption capacity (mg/g), V is the volume of CR solution (L),  $m_{ad}$  is the mass of adsorbent (g)



Figure 1. The standard curve of CR solution at a wavelength of 497nm

# 3. Result and discussion

# 3.1. Materials characterization

3.1.1. FTIR of crab shell chitosan and chitin



Figure 2. FTIR spectra of prepared crab shell chitosan and chitin

Infrared spectroscopy is a qualitative technique for locating vibrations and particular chemical functional groups in a molecule. The distinctive infrared spectra of chitin and chitosan have long been published in the context of fundamental research. The FTIR spectra of the chitosan and chitin from crab shells that were produced and utilized in this investigation are shown in Figure 2. The distinctive vibration ranges of chitosan and chitin (Dara et al., 2020) are occupied by the unique peaks in Figure 2. The deacetylation degree of chitosan is also demonstrated by the low-intensity peaks that correspond to the C-H vibrations (2800-2900cm<sup>-1</sup>), amide II, and bonding stretch vibrations of C=O in acetyl (1661cm<sup>-1</sup>), and bonding stretch vibrations of N-H in amide I and amide II (1563cm<sup>-1</sup>).





Figure 3. SEM images of the prepared HAp

Figure 3 shows HAp particles with fibrous or needle-like morphology, clustered into highly porous clusters. As the magnification increases from 20.0k (Figure f) to 120k (Figure a), the fibrous structure and distribution of HAp particles can be more clearly observed. At low magnifications (20.0k, 30.0k, 40.0k), the HAp clusters appear as large aggregates, while at higher magnifications (60.0k, 80.0k, 120k), the individual fibrous structures become more evident, indicating the formation of HAp nanowires or nanorods. The HAp clusters and fibers were observed depending on the magnification, with larger clusters seen at low magnifications and individual fibers seen more clearly at high magnifications. This suggests that increasing the magnification allows for a more detailed observation of the materials' nanostructure.



Figure 4. SEM images of the 50% HAp-CS

Figure 4 shows that the HAp-CS composites possess heterogeneous morphology, with fibrous and bulk structures. Large composite clusters with rough surfaces can be observed at low magnifications (20.0k, 30.0k, 40.0k), indicating the HAp particles' aggregation and the chitosan coverage. As the magnification increases (60.0k, 80.0k, 120k), the fibrous structure of HAp becomes more evident; however, they are covered by a chitosan layer, creating an uneven surface. The size of the composite clusters ranges from a few micrometers to several tens of micrometers, while the size of the HAp fibers can be in the nanometer range. The presence of chitosan helps to bind the HAp particles together, forming a highly porous composite structure. The chitosan coating on HAp particles in the 50% HAp-CS composite may play an important role in enhancing the adsorption efficiency of Congo red. The chitosan layer, with positively charged amino and hydroxyl groups, can strongly interact with the negatively charged sulfonic groups in the structure of the Congo red dye, thereby enhancing the retention of the dye on the material surface. At the same time, the good dispersion of HAp particles due to the chitosan coating can increase the contact surface area of the composite with the dye solution, creating conditions for more adsorption sites. In addition, chitosan can also create porosity for the material, helping the dye to diffuse into the composite structure, not just limited to the outer surface. The combination of the electrostatic interaction of chitosan and the large surface area and porosity of the composite may account for the superior Congo red adsorption efficiency of the 50% HAp-CS composite compared to other ratios or single materials.

## 3.2. CR adsorption

Figure 5 shows the adsorption efficiency over contact time of the synthesized HAp-CS with different chitosan ratios. It can be seen that the adsorption efficiency of all mixtures increased rapidly in the initial stage (5-15 min.) and gradually reached equilibrium after 120 min. The 50% HAp-CS composite showed the highest adsorption efficiency, reaching 98.8% after 120 min, indicating that the appropriate HAp ratio enhanced the adsorption capacity. The 70% HAp-CS composite had the lowest adsorption efficiency, which could increase the connectivity of HAp and reduce the contact surface area. The 0% HAp-CS composite (pure HAp) also showed good adsorption efficiency but was lower than the 30% and 50% HAp-CS composites, indicating the synergy of the two components in improving the adsorption capacity.



Figure 5. CR adsorption efficiency versus contact time



Figure 6. CR adsorption efficiency versus initial CR concentration.

Figure 6 shows the adsorption efficiency of different HAp-CS composites for CR at various initial concentrations. The highest adsorption efficiency was observed at low concentrations (100mg/L) and gradually decreased as the concentration increased. The 50%HAp-CS composite shows the highest adsorption efficiency at all concentrations, reaching 100% at 100, 200, and 300mg/L. The 0%HAp-CS composite (pure HAp) also showed good adsorption efficiency, but it was lower than the 50%HAp-CS composite,

especially at high concentrations. The 70% HAp-CS composite had the lowest adsorption efficiency at high concentrations, possibly due to the low HAp content and the aggregation of HAp reducing the contact surface area. This suggests that the appropriate HAp ratio is important to achieve maximum adsorption efficiency. The 50% HAp-CS composite has an optimal ratio of chitosan and hydroxyapatite, which balances the electrostatic binding ability of chitosan with Congo red and the large surface area due to the good dispersion of HAp. This ratio can prevent excessive aggregation of HAp (as in 70% HAp-CS), maintain porosity, and the number of effective adsorption sites, making the composite perform well at various concentrations.



Figure 7. CR adsorption efficiency versus adsorbent dosage



Figure 8. CR adsorption efficiency versus initial pH of CR solution

Figure 7 shows the adsorption efficiency of different HAp-CS composites at different adsorbent dosages. The adsorption efficiency increased with increasing adsorbent dosage, reaching a maximum value and decreasing slightly. The 50% HAp-CS composite showed the highest adsorption efficiency at most dosages, reaching 100% at 100mg. The 0% HAp-CS composite (pure HAp) also showed good adsorption efficiency, but it was lower than the 50% HAp-CS composite, especially at low dosages. The 70% HAp-CS composite had a lower adsorption efficiency than the 50% HAp-CS composite at most dosages, possibly due to the aggregation of HAp reducing the contact surface area.

Figure 8 shows the adsorption efficiency of different HAp-CS composites at different initial pHs. In general, the adsorption efficiency of 50% HAp-CS composite was the highest at most pH values, especially at neutral pH (pH 7), reaching 99.9%. This shows that 50% HAp-CS composite performed best in a neutral environment. 0% HAp-CS composite (pure HAp) also showed good adsorption efficiency at all pH values, but lower than 50% HAp-CS composite. 30% HAp-CS composite had the lowest adsorption efficiency at all pH values, especially at acidic pH (pH 4 and 5). The 70% HAp-CS composite had good adsorption efficiency at acidic and neutral pH, but lower than the 50% HAp-CS composite. This shows that pH significantly affects the adsorption efficiency of HAp-CS composites, and the appropriate HAp ratio is crucial to achieve maximum adsorption efficiency.

# 3.3. CR adsorption isotherm and kinetics



*Figure 9.* The adsorption isotherms: Freundlich model (a) and Langmuir model (b) *TABLE 2.* Correlation coefficients R<sup>2</sup> for Freundlich and Langmuir model

Madal	<b>R</b> <sup>2</sup>		
WIOUEI	50%HAp-CS	НАр	CS
Freundlich model	0.9381	0.2508	0.9877
Langmuir model	0.9915	0.9924	0.9945

Figure 9a shows the fit of the experimental data to the Freundlich isotherm adsorption model, which describes multilayer adsorption on a heterogeneous surface. The linear curves show the relationship between Lnqe and LnCe, with different correlation coefficients R<sup>2</sup> for each adsorbent (50%HAp-CS, HAp, CS) and smaller than the R<sup>2</sup> of the Langmuir model (Figure 9b). Figure 9b shows a good fit of the experimental data to the Langmuir isotherm adsorption model, which describes monolayer adsorption on a homogeneous surface. The linear curves show the relationship between Ce/qe and Ce, from which the maximum adsorption capacity (qmax) and the Langmuir constant (KL) can be determined. The qmax was calculated as 588.2mg/g and 769.2mg/g from the Langmuir regression equation for CS and 50%HAp-CS composite, respectively. The high R<sup>2</sup> values (0.9924, 0.9915, and 0.9945) showed that the Langmuir model fitted the experimental data better, indicating that monolayer adsorption was the main mechanism in the adsorption of CR by these materials.

Figure 10a shows the fit of the experimental data to a pseudo-first-order adsorption kinetic model, in which  $log(q_e - q_t)$  is plotted versus time. Figure 10b shows the fit of the experimental data to a pseudo-second-order adsorption kinetic model, in which t/qt is plotted versus time. Based on the correlation coefficient R<sup>2</sup>, it can be seen that the pseudo-second-order model fits the experimental data better for both the 50%HAp-CS and 70%HAp-CS

composites, with  $R^2$  of 0.9999 and 0.9942, respectively. This suggests that the adsorption of CR by these composites follows pseudo-second-order kinetics, i.e., the adsorption rate depends on the square of the number of vacant adsorption sites. Furthermore, the linear curves in the pseudo-second-order model show a better fit than those in the pseudo-first-order model ( $R^2$  of 0.9185 and 0.9791), further reinforcing this conclusion.



*Figure 10.* The adsorption kinetics: pseudo-first-order model (PFO) (a) and pseudo-second-order model (PSO) (b)

TABLE 3. Correlation coefficients R <sup>2</sup> for PFO and PSC	) model
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Madal	R <sup>2</sup>		
WIOUEI	50%HAp-CS	70%HAp-CS	
PFO model	0.9185	0.9791	
PSO model	0.9999	0.9942	

### 4. Conclusion

This study successfully synthesized HAp-CS composites from HAp and crab shell chitosan. SEM images showed that HAp particles had a highly porous structure, with nanowire or nanorod shapes of nanometer sizes assembling into large clusters. The morphology of HAp-CS composites was quite uneven, with chitosan covering the outside of HAp nanorods or nanowires. Overall, the materials were highly porous and appeared to have a large surface area. CR adsorption studies under different conditions showed that 50% HAp-CS composite had the best adsorption capacity among the synthesized composites, with a theoretical maximum adsorption capacity of 769.2mg/g. In addition, the adsorption capacity reached its maximum in the initial 5-15 min; the adsorption efficiency tended to decrease with the initial concentration of CR and increase with the adsorbent dosage. The initial pH of the solution affected the adsorption efficiency for the 70%HAp-CS and 30%HAp-CS composites but had almost no effect on the adsorption capacity of 0%HAp-CS and 50% HAp-CS in the investigated pH range. The adsorption of CR onto the materials fits the Langmuir adsorption isotherm model better than the Freundlich model. Finally, the adsorption kinetics of the materials also fit the pseudo-second-order kinetics better than the pseudo-first-order kinetics. In the future, further studies should focus on investigating the reusability of the HAp-CS composite adsorbent through multiple adsorption and desorption cycles to evaluate the economic and sustainability of the material. Besides, testing the performance of this composite in treating actual dye wastewater, which has a more complex composition than a single dye solution, is necessary to evaluate the potential for the materials' practical application in environmental pollution treatment.

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### References

- Ahmed, S., Mofijur, M., Nuzhat, S., Chowdhury, A. T., Rafa, N., Uddin, M. A., Inayat, A., Mahlia, T., Ong, H. C., & Chia, W. Y. (2021). Recent developments in physical, biological, chemical, and hybrid treatment techniques for removing emerging contaminants from wastewater. *Journal of Hazardous Materials*, 416, 125912.
- Dara, P. K., Mahadevan, R., Digita, P. A., Visnuvinayagam, S., Kumar, L. R. G., Mathew, S., Ravishankar, C. N., & Anandan, R. (2020). Synthesis and biochemical characterization of silver nanoparticles grafted chitosan (Chi-Ag-NPs): in vitro studies on antioxidant and antibacterial applications. SN Applied Sciences, 2(4), 665.
- Freire, T. M., Fechine, L. M. U. D., Queiroz, D. C., Freire, R. M., Denardin, J. C., Ricardo, N. M. P. S., Rodrigues, T. N. B., Gondim, D. R., Junior, I. J. S., & Fechine, P. B. A. (2020). Magnetic Porous Controlled Fe3O4–Chitosan Nanostructure: An Ecofriendly Adsorbent for Efficient Removal of Azo Dyes. *Nanomaterials*, 10(6), 1194.
- Hemashenpagam, N., & Selvajeyanthi, S. (2023). Textile Dyes and Their Effect on Human Beings. In A. Ahmad, M. Jawaid, M. N. Mohamad Ibrahim, A. A. Yaqoob, & M. B. Alshammari (Eds.), *Nanohybrid Materials for Treatment of Textiles Dyes*, pp. 41-60. Springer Nature Singapore.
- Jamarun, N., Prasejati, A., Zulhadjri, Z., Caniago, S., Amirullah, T. Y., Wulandari, W., & Sisca, V. (2024). Effect of chitosan concentration on hydroxyapatite/chitosan composite synthesis using the in-situ method as a dye adsorbent. *Kuwait Journal of Science*, 51(4), 100252.
- Liu, X.-q., Zhao, X.-x., Liu, Y., & Zhang, T.-a. (2022). Review on preparation and adsorption properties of chitosan and chitosan composites. *Polymer Bulletin*, 79(4), 2633-2665.
- Nguyen, H. T., & Bui, H. M. (2020). Adsorption of nitrate and phosphate in an aqueous solution on composites of PVA and chitosan prepared from a Somanniathelphusa sinensis shell. *Water Supply*, 21(2), 765-779.
- Nikoshvili, L. Z., Tikhonov, B. B., Ivanov, P. E., Stadolnikova, P. Y., Sulman, M. G., & Matveeva, V. G. (2023). Recent progress in chitosan-containing composite materials for sustainable approaches to adsorption and catalysis. *Catalysts*, 13(2), 367.
- Premkumar, M., Thiruvengadaravi, K., Senthil Kumar, P., Nandagopal, J., & Sivanesan, S. (2018). Eco-friendly treatment strategies for wastewater containing dyes and heavy metals. In T. Gupta, Agarwal, A., Agarwal, R., Labhsetwar, N. (Ed.), *Environmental contaminants: measurement, modelling and control*, pp. 317-360. Springer Nature Singapore.
- Saheed, I. O., Da Oh, W., & Suah, F. B. M. (2021). Chitosan modifications for adsorption of pollutants–A review. *Journal of Hazardous Materials*, 408, 124889.
- Şenol, Z. M., Ertap, H., Fernine, Y., & El Messaoudi, N. (2024). Adsorptive removal of synthetic dye from its aqueous solution by using chitosan-bentonite composite: DFT and experimental studies. *Polymer Bulletin*, 81(14), 12795-12817.
- Shi, C., Lv, C., Wu, L., & Hou, X. (2017). Porous chitosan/hydroxyapatite composite membrane for dyes static and dynamic removal from aqueous solution. *Journal of Hazardous Materials*, 338, 241-249.