Adsorption of Reactive Brilliant Red X-3B from Aqueous Solution by Polypyrrole/Calcium Rectorite Composites: Adsorption Behavior and Mechanism

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Abstract. In this study, polypyrrole/calcium rectorite clay composites (PPy/REC composites) were prepared by in-situ polymerization of pyrrole monomer to adsorb reactive brilliant red X-3B from aqueous solution. The results of XRD showed that the clay flakes exfoliated in the prepared composites. The SEM results showed that PPy had good dispersibility on clay sheets. The adsorption mainly depended on the initial pH value of the solution, and the optimal adsorption of reactive brilliant red X-3B was achieved when the pH value was 2.0. The removal rate of PPy/REC composite was much higher than that of PPy homopolymer. The adsorption kinetic data of reactive brilliant red X-3B at three initial concentrations (100, 150 and 200 mg/L) were best fitted by the pseudo-second-order model, indicating that the concentration gradient of the adsorbent was the driving force of the adsorption process. The adsorption isotherm accorded with the Langmuir isotherm model, and the maximum adsorption capacity was 232.56 mg/g at 298 K. The PPy/REC composites could be regenerated and reused for 5 continuous adsorption-desorption cycles without losing the removal efficiency of the original reactive brilliant red X-3B. XPS, zeta potential and FT-IR results showed that the removal mechanism of reactive brilliant red X-3B was related to electrostatic interaction and ion exchange.

Keywords: Organic pollutants; Wastewater treatment; Clay-based materials; Reactive brilliant red X-3B removal mechanism; Pyrrolic nitrogen.

1. Introduction
There are more than 10 000 different dyes and pigments in the world, which are utilized in a variety of uses in the paper, textile, food, and cosmetic industries. Azo dyes are the most widely used dyes in industry, accounting for more than 50% of the total dyes. Azo dyes are characterized by the presence of one or more azo groups (-N=N-), which form a conjugated system with other groups and produce color. In the dyeing process, about 10% of the dyes do not bind to the fiber and therefore discharged into the sewage treatment system or the environment. Among the dyes, the reactive brilliant red X-3B is one of the most representative substances of azo dyes. Therefore, the adsorption of reactive brilliant red X-3B has been one of the research hot-spots in the field of environmental protection\textsuperscript{1,2}. 

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Adsorption has been paid more and more attention because of its advantages such as low operating cost, simple operation, feasible process and so on. Traditional adsorbents are widely used in reactive brilliant red X-3B, including activated carbon, polymers, metal oxides, clay minerals, zeolites and agricultural residues. Due to the unsatisfactory removal efficiency, these methods have some shortcomings [3].

Polypyrrole (PPy) has been paid more and more attention for dyes removal because of its non-toxic, environmental protection, low price, easy synthesis, ion exchange and other advantages [4]. PPy has pyrrolidine nitrogen structure and shows good adsorption performance for reactive brilliant red X-3B. However, due to the aggregation of π-π stacked PPy particles, it is difficult for doped anions to be dispersed from the polymer, which will limit the removal ability of reactive brilliant red X-3B.

In order to overcome this disadvantage and increase the specific surface area of PPy, synthetic composites are considered to be one of the most effective modification methods of PPy. The combination of PPy and clay minerals has attracted wide attention. Rectorite (REC) has higher aspect ratio and longer interlayer spacing than some clays (such as montmorillonite). REC can form promising interlaminar exfoliated polymer nanocomposites with better properties and hard-to-reach positions on the layers. In addition, there are a lot of calcium rectorite (Ca-REC) reserves in the natural environment. Therefore, the development of Ca-REC-based composites has a broad application prospect, which can increase the adsorption capacity and expose inaccessible sites [4].

In this study, PPy coated Ca-REC composites were prepared by in-situ polymerization of pyrrole monomer in the existence of Ca-REC. PPy showed special adsorption properties for the reactive brilliant red X-3B dissolved in aqueous medium, while the existence of Ca-REC can solve the problem of agglomeration and dispersion of PPy in aqueous solutions. The adsorption capacity and mechanism of PPy/Ca-REC composite as an active adsorbent to remove reactive brilliant red X-3B from aqueous solution were discussed.

2. Materials and Methods

2.1. Materials

Ca-REC was purchased from Zibo Kangnengda Rare Earth Materials Co., Ltd. Ammonium persulfate, o-phosphoric acid, pyrrole monomer, cetyltrimethylammonium bromide, potassium dichromate, anhydrous ethanol, sodium hydroxide and diphenyl carbazide were obtained from Sinopharm Chemical Reagent Co., Ltd. Sulfuric acid was acquired from Xilong Scientific Co., Ltd. Sulfuric acid was acquired from Xilong Scientific Co., Ltd.

2.2. Synthesis of the PPy/REC Composites

PPy/REC composites were prepared by the chemical oxidation method, 2 g of REC was dispersed in 100 mL of DI water for the first time. Then, 3 mL pyrrole monomer was added and stirred for 30 min. The polymerization was initiated by dropping APS solution (adding 10.2 g APS into 50 mL of 5 M hydrochloric acid). In order to ensure the completion of the polymerization, an overnight reaction was allowed. The resultant solid matter was filtered and then washed with DI water and industrial alcohol until the filtrate was clear. Finally, the product was dried at 60 °C.

2.3. Batch Adsorption Experiment

The effects of the pH value, adsorption kinetics and isotherms on the reactive brilliant red X-3B removal were investigated. The original solution (500mg/L) was diluted with water to obtain different concentrations of reactive brilliant red X-3B solution. The adsorption study was carried out in a temperature-controlled shaking bath at 200 rpm. The initial pH value of the solution pH was adjusted by adding NaOH solution and H2SO4 solution.

The batch adsorption experiment of PPy/REC composite was carried out, 20 mg of PPy/REC composites were mixed with 20 mL of the reactive brilliant red X-3B solution at different concentrations. The adsorption solution was shaken at 298 K for a predetermined time interval. The solution was then filtered through a 0.22-μm filter after the adsorption reaction. The reactive brilliant red X-3B adsorption efficiency (% removal) and adsorption capacity (q_e) were calculated from the following equations.
3. Results and Discussion

3.1. Characterization of the PPy/REC Composites

The XPS spectrum of PPy/REC composites is shown in Fig. 1. The XPS survey spectrum of PPy/REC composites displays energy bands attributable to Cl 2p (199 eV), C 1s (284 eV), N 1s (400 eV) and O 1s (532 eV). In addition, the N 1s core energy spectrum of PPy/REC composites (Fig. 2) could be deconvoluted into three peaks at 399.5 eV, 399.9 eV and 401.85 eV which are attributed to electronic states of the quinoimine (=N-), phenylamine (-NH-) and doped imine (-NH·+-), respectively[5].

![](image1.png)

**Figure 1.** XPS survey scans of the PPy/REC composites.

![](image2.png)

**Figure 2.** N 1s spectrum of the PPy/REC composites.

3.2. Effect of the Initial pH

The pH value of the solution was one of the most significant factors to control the adsorption of dye molecule on the adsorbent sites. The adsorption efficiency of reactive brilliant red X-3B on PPy/REC composites, REC and PPy varies with pH (2-10) as shown in Fig. 3, the maximum adsorption capacity

\[
\%\text{Removal} = \left( \frac{C_0 - C_e}{C_0} \right) 
\]

(1)

\[
qu_e = \left( \frac{C_0 - C_e}{m} \right)V
\]

(2)

where \(C_0\) and \(C_e\) are the initial and equilibrium concentrations (mg/L), \(m\) is the adsorbent mass (g) and \(V\) is the volume of solution (L).
of PPy/REC composites for reactive brilliant red X-3B was 96.03 mg/g, and the removal rate of reactive brilliant red X-3B decreased gradually with the increase of pH value. For PPy/REC composites, the adsorption capacity decreased from 96.03 mg/g (pH 2) to 55.93 mg/g (pH 10). In addition, with the increase of pH value, the content of OH\(^-\) in the solution increased, which would compete with Cr(VI) for the adsorption active sites on the surface of PPy\[^7\]. When the Zeta potential was positive (pH 2-10), the reactive brilliant red X-3B could be adsorbed by PPy/REC composites. When the zeta potential became negative (pH > 11), there was no adsorption capacity for reactive brilliant red X-3B.

![Figure 3. PH-dependent adsorption capacity of X-3B of the PPy/REC composites.](image)

### 3.3. Adsorption Kinetics

Therefore, the effect of contact time on the adsorption of reactive brilliant red X-3B by PPy/REC composites at three initial Cr (VI) concentrations (100, 150, 200 mg/L) is shown in Fig. 4. The pre-5min adsorption of reactive brilliant red X-3B on PPy/REC composites increased rapidly. As the reaction approaches equilibrium, the adsorption rate slowed down obviously due to the decrease of adsorption active sites. With the increase of initial concentration, the adsorption capacity of PPy/REC composites to reactive brilliant red X-3B increased. Adsorption is a process in which the concentration gradient of the adsorbed species played a driving role. Accordingly, a higher initial concentration led to a higher adsorption driving force, thus increasing the adsorption capacity\[^7\].

The values of \(q_e\) and \(k_1\) and the correlation coefficients (\(R^2\)) obtained from the pseudo-first-order model as shown in Table 1. The results showed that the values of \(R^2\) were in the range of 0.7310-0.9357. Although the \(R^2\) values of some studies were higher, the calculated \(q_e\) values were still lower (21.81-22.26 mg/g) than the corresponding experimental values (94.46-147.75 mg/g). For the pseudo-second-order kinetic model, the \(R^2\) values varied from 0.9994 to 0.9999, and the calculated \(q_e\) values are in good agreement with the experimental values. The values of \(q_e\) and \(R^2\) indicated that the adsorption kinetics of reactive brilliant red X-3B adsorption accorded well with the pseudo-second-order model. Table 1 also showed that the pseudo-second-order rate constant \(k_2\) decreased with the increase of reactive brilliant red X-3B concentration. These results implied that when the initial concentration of reactive brilliant red X-3B was 100 mg/L, the removal rate of reactive brilliant red X-3B by PPy/REC composite was slower than that of 150 and 200 mg/L.
Figure 4. Kinetics of X-3B adsorption onto PPy/REC composites from simulated solutions with different initial concentrations.

Table 1. Kinetic parameters for the reactive brilliant red X-3B adsorption by PPy/REC composites.

| C_0/(mg/L) | pseudo-first-order | pseudo-second-order |
|------------|--------------------|---------------------|
|            | k_1/(1/min)        | q_e/(mg/g)          | R^2   | k_2/(g/mg/min) | q_e/(mg/g) | R^2   |
| 100        | 0.0463             | 21.81               | 0.9357| 0.0064         | 95.24      | 0.9999|
| 150        | 0.0562             | 22.26               | 0.7310| 0.0060         | 126.58     | 0.9994|
| 200        | 0.0578             | 21.84               | 0.8309| 0.0088         | 144.93     | 0.9999|

3.4. Adsorption Isotherm

Adsorption isotherm plays an important role in the study of chemical interactions between homogeneous and non-uniform adsorbents [8]. The adsorption isotherm of reactive brilliant red X-3B adsorption at three different temperatures is shown in Fig. 5. In order to predict the adsorption capacity of the adsorbent, which was the most important parameter for designing the adsorption system, the analysis of the adsorption isotherm data of two widely used isotherm models (Langmuir and Freundlich) were verified.

The Freundlich and Langmuir isotherm parameters (slope and intercept) determined from the linear equations were given in Table 2. The values of q_m, K_F, and b increased with the increase of temperature, which indicated that the adsorption process was endothermic, and the R^2 value of Langmuir model (0.9937) was much higher than that of Freundlich model (0.9895). The maximum adsorption capacity was increased from 232.56 mg/g at 298 K. Therefore, it is measured that the adsorption of the reactive brilliant red X-3B was achieved through the formation of monolayers on a limited number of the same adsorption sites on a uniform surface.
Figure 5. Equilibrium isotherms of X-3B adsorption onto the PPy/REC composites.

Table 2. Langmuir and Freundlich isotherm parameters for the reactive brilliant red X-3B adsorption by PPy/REC composites.

| Temperature (K) |   | 298  |
|----------------|---|------|
| Langmuir isotherm | q_m (mg/g) | 232.56 |
|                  | b (L/mg)   | 0.0714 |
|                  | R^2        | 0.9937 |
| Freundlich isotherm | K_F (mg/g) | 75.78 |
|                  | 1/n        | 0.1978 |
|                  | R^2        | 0.9895 |

4. Conclusion
The removal of the reactive brilliant red X-3B was explored by batch adsorption method using PPy/REC composites as an adsorbent. The adsorption mainly depended on the initial pH values of the solution, and the optimal the reactive brilliant red X-3B adsorption was achieved at pH 2.0. The adsorption kinetics followed the pseudo-second-order kinetic model. The adsorption isotherm data were well described by Langmuir isotherm model with a maximum adsorption capacity of 232.56 mg/g at 298 K.

Acknowledgments
This work was supported by the National Natural Science Foundation of China (No.51374157), the Program for New Century Excellent Talents in University (NCET-12-0713), the Presidential Research Fund of Wuhan Institute of Technology (2018115) and Graduate Innovation Fund of Wuhan Institute of Technology (CX2018141).

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