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# One-step preparation of a novel SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> nano-composite and its application in selective adsorption of crystal violet

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A novel kind of nanoparticle SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> was prepared using strontium carbonate (SrCO<sub>3</sub>) and melamine (C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>) as raw materials *via* one-step calcination. The formation of SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> was confirmed from the X-ray diffraction (XRD), Fourier transform infrared spectra (FT-IR), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Brunauer–Emmett–Teller (BET) and X-ray photoelectron spectroscopy (XPS) analysis. Its selective adsorption performance was evaluated towards crystal violet (CV), rhodamine B (RhB) and methylene blue (MB). The results showed that the SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> had selective adsorption ability of CV. Furthermore, adsorption measurements of CV were conducted to investigate the influences of contact time, initial concentration, initial dye solution pH value and adsorbent dosage. The maximum removal rate of CV was 98.56% when the initial concentration was 1600 mg L<sup>-1</sup>. The kinetic study indicated the adsorption of CV followed the pseudo-second-order model well. The adsorption efficiency of SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> was greater (97.46%) than that of g-C<sub>3</sub>N<sub>4</sub> (31.30%) and SrCO<sub>3</sub> (17.30%). It could be deduced that the synergistic effect of conjugation interaction of g-C<sub>3</sub>N<sub>4</sub> and the electrostatic attraction of SrCO<sub>3</sub> might be the main driving force for the superb adsorption of CV.

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## 1 Introduction

Nowadays, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has gained considerable research attention because it possesses excellent advantages such as high chemical and thermal stability under ambient temperature, cost-effective, non-toxic and simple preparation.<sup>1,2</sup> g-C<sub>3</sub>N<sub>4</sub>, as a new intriguing class of graphite analogue, consists of conjugated planes containing highly ordered tri-s-triazine (C<sub>6</sub>N<sub>7</sub>) units. The layered structure of the tri-s-triazine is connected by weak forces-van der Waal forces. It has been widely used in the photocatalysis field for it has an energy band gap of 2.7 eV which makes it is capable of the visible adsorption.<sup>3–6</sup> As a photocatalyst, it has been widely used in water splitting,<sup>7,8</sup> organic pollutants degradation,<sup>9,10</sup> CO<sub>2</sub> reduction,<sup>11</sup> and other fields.<sup>12,13</sup>

Crystal violet (CV, C<sub>25</sub>H<sub>30</sub>ClN<sub>3</sub>, IUPAC name is *N*-[4-[bis[4-dimethyl-amino]-phenyl]methylene]-2,5-cyclohexadien-1-ylidene]-*n*-methylmethanaminium chloride), a typical triphenyl-methane dye, is widely used in cell biology, paper, leather and textile industry.<sup>14–16</sup> The wastewater containing CV is low

biodegradability and high stability (complex aromatic structure) and it could be absorbed through the skin and causing the skin, eye, digestive irritation and even cancer.<sup>17–19</sup> From the aspect of environmental safety and health of life, it is vital to develop an effective way to abate CV in wastewater. Various methods have been adopted for eliminating dye pollution from water, including chemical oxidation,<sup>20,21</sup> photo-catalytic decomposition,<sup>22,23</sup> electro-catalytic degradation<sup>24,25</sup> and non-thermal plasma.<sup>26–28</sup> These methods usually have some defects, such as slow degradation rate, complex, heavy expenses and usually causing secondary pollution. The adsorption technique is gaining more attention for it is high efficiency, simple design, cost-effective and adaptable.<sup>29–35</sup> There have been various kinds of adsorbents developed, such as carbon materials,<sup>36–38</sup> natural clay minerals,<sup>39–42</sup> and bioadsorbents.<sup>43–45</sup> However, certain deficiencies including costly, intricate pre-treatment and low adsorption capability limited the use of some certain adsorbents.<sup>46–53</sup>

Due to the conjugated region, stacking structure and the weak forces of g-C<sub>3</sub>N<sub>4</sub>, it has the potential for aggregating functional groups or materials to form nanocomposite with multiform favorable properties.<sup>54–56</sup> This distinctive structure has drawn great interesting in improving the photocatalytic performance.<sup>57,58</sup> But the research of using modified g-C<sub>3</sub>N<sub>4</sub> as adsorbent for clearing up dye pollutant is rarely been reported.<sup>59,60</sup> As far as we know, there has been no report of using

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g-C<sub>3</sub>N<sub>4</sub>-based composite as an adsorbent in dye wastewater treatment. Strontium carbonate (SrCO<sub>3</sub>), a typical alkaline earth metal carbonate, has been widely used as additives in industrial production.<sup>61–63</sup> Meanwhile, some research has been reported on its adsorption performance attributed to its various architectures.<sup>64,65</sup>

In this work, we firstly induced SrCO<sub>3</sub> to incorporate with g-C<sub>3</sub>N<sub>4</sub> *via* one-step calcination method to fabricate a novel adsorbent SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>. The morphology and structure of the composite was characterized by XRD, FT-IR, SEM, TEM, BET and XPS, and its adsorptive capacity and selectivity of CV in aqueous solution were investigated. To the best of our knowledge, this work represents the first example employing g-C<sub>3</sub>N<sub>4</sub>-based composite for selective adsorption of CV.

## 2 Experimental

### 2.1 Synthesis of SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>

SrCO<sub>3</sub>, melamine and CV are all AR grade and purchased from Chengdu Kelong Chemical Agents (China), without any further purification. SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> was synthesized by one-step calcination process in a muffle furnace. SrCO<sub>3</sub> and melamine (mass ratio = 1 : 1) were dissolved with deionized water in alumina crucible, and then the mixed solution was dispersion with ultrasonic irradiation for 20 min under ambient temperature. The final solution was transferred into muffle furnace and maintained at 600 °C for 4 hours at heating rate of 5 °C min<sup>-1</sup> to obtain the prepared nanocomposite. SrCO<sub>3</sub> and melamine were also treated as the forward route for making comparison.

### 2.2 Characterization

X-ray diffraction (XRD, Shimadzu, XRD-6100) patterns were detected with Cu K $\alpha$  radiation (40 kV, 30 mA, 2 $\theta$  = 10–80°) to investigate the crystal structures of the samples. Fourier transform infrared spectra (FT-IR, Shimadzu, IR Prestige-21), were recorded in the range of 4500–400 cm<sup>-1</sup>, using KBr technique to analyze the functional groups on the surface of the composite. Scanning electron microscope (SEM, JEOL, JSM-7800F) and Transmission Electron Microscopy (TEM, JEOL, JEM-2100) were used to observe the morphologies and the microstructures of the samples. The N<sub>2</sub> adsorption apparatus (Micromeritics, ASAP 2020) were used to obtain the Brunauer–Emmett–Teller (BET) surface area of the samples. X-ray photoelectron spectroscopy (XPS, Thermo Scientific, ESCALAB 250xi) was used to determine the binding energy.

### 2.3 Adsorption experiments

The concentration of CV in the solution was determined at the maximum absorbance ( $\lambda_{\text{max}}$  = 580 nm) by UV-vis spectrophotometer (UV-vis spectrometer, Tianmei, UV1102). For high concentration, the samples were diluted before measurements. And the initial pH of the dye solution was measured by pH meter (pH meter, Sartorius, PB10).

The adsorption experiments were conducted by a batch method. All experiments were conducted at 7.0 pH value, except those that investigated the effect of initial pH of dye solution.

And 0.08 g adsorbent was dispersed in 80 mL CV solution, except that were used to study the effect of the dosage. Similarly, the initial concentration is 1600 mg L<sup>-1</sup>, except those that investigate the same parameters. The pH of the initial dye solution was adjusted with HCL (0.1 mol L<sup>-1</sup>) and NaOH (0.1 mol L<sup>-1</sup>). The kinetic experiments were carried out at the initial concentration of 500, 1000, 1200, 1400, and 1600 mg L<sup>-1</sup>. It performed on an air bathed shaker. The solution was separated by centrifugation at 5000 rpm for 5 min.

The adsorption capacity at time  $t$   $q_t$  (mg g<sup>-1</sup>) and removal rate (%) were calculated using the following equation:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

$$\text{Removal rate (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where  $C_0$  and  $C_t$  are the liquid-phase concentrations of the CV (mg L<sup>-1</sup>) at initial time and time  $t$ , respectively.  $V$  is the volume of the solution (mL) and  $m$  is the mass of the used adsorbent (mg).

## 3 Results and discussion

### 3.1 Characterization of the samples

The XRD patterns of the prepared samples are shown in Fig. 1. The g-C<sub>3</sub>N<sub>4</sub> displayed a typical diffraction peaks at 27.46° and 12.96°, corresponding to the (002) and (100) diffraction planes, which represented the interlayer stacking reflection and in-plane structure of aromatic system, respectively.<sup>66,67</sup> This indicated that the g-C<sub>3</sub>N<sub>4</sub> was synthesized by polycondensation approach with pure melamine. Meanwhile, the observed diffraction peaks of calcined SrCO<sub>3</sub> are located at 2 $\theta$  angles = 25.28°, 25.91°, 29.73°, 31.62°, 34.64°, 35.22°, 36.64°, 41.42°, 44.18°, 45.74°, 46.68°, 47.80°, 50.03° which correspond to the planes of (111), (021), (002), (012), (102), (200), (130), (220), (221), (041), (202), (132), (113), respectively. It could be unambiguously indexed to the orthorhombic phase of SrCO<sub>3</sub> (JCPDS card no. 05-0418).<sup>68,69</sup> There is no observation of the typical

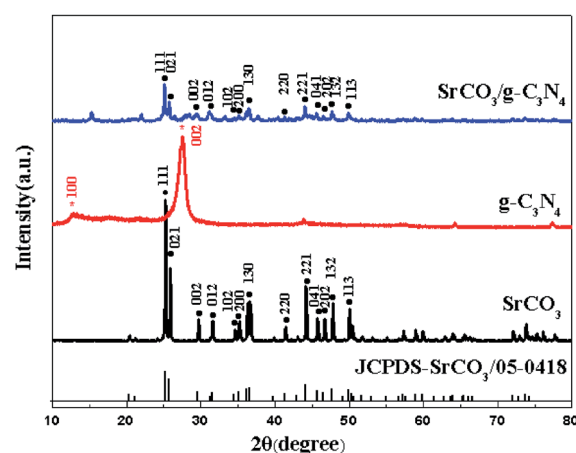


Fig. 1 XRD patterns of the g-C<sub>3</sub>N<sub>4</sub>, SrCO<sub>3</sub> and SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>.



diffraction of  $g\text{-C}_3\text{N}_4$  in the synthesized composite, the diffraction peaks were mostly the same as the  $\text{SrCO}_3$ , but the feature peaks positions of  $\text{SrCO}_3$  shifted slightly toward a lower diffraction angle. And the impure peaks of the composite might be the carbonization of the raw materials or the melamine did not condense completely.

The FT-IR spectra of the prepared materials are shown in Fig. 2. For the calcined melamine, the typical adsorption peaks in the  $1200\text{--}1700\text{ cm}^{-1}$  range and at  $808\text{ cm}^{-1}$  of  $g\text{-C}_3\text{N}_4$  could be observed. They are assigned to the typical skeletal stretching vibrations of aromatic C–N heterocycles and the out-of-plane bending vibration of tri-*s*-triazine rings, respectively.<sup>70,71</sup> The peaks at  $698$ ,  $858$ ,  $1070$ ,  $1458$  and  $1774\text{ cm}^{-1}$  corresponding to the  $\text{CO}_3^{2-}$  of the calcined  $\text{SrCO}_3$  were observed.<sup>50</sup> In case of the  $\text{SrCO}_3/g\text{-C}_3\text{N}_4$ , the typical skeletal stretching vibrations of tri-*s*-triazine were hardly observed; it might be the adsorption intense of  $\text{SrCO}_3$  was so strong in order to impede the peaks of  $g\text{-C}_3\text{N}_4$ . Meanwhile, the peak at  $808\text{ cm}^{-1}$  presented in  $g\text{-C}_3\text{N}_4$  shifted to  $821\text{ cm}^{-1}$ , the peak at  $856\text{ cm}^{-1}$  presented in  $\text{SrCO}_3$  shifted to  $858\text{ cm}^{-1}$ , the peaks at  $1070\text{ cm}^{-1}$  and  $1774\text{ cm}^{-1}$  were disappeared, these might due to the strong interactions

between the carbonate of  $\text{SrCO}_3$  and tri-*s*-triazine rings of  $g\text{-C}_3\text{N}_4$ . Furthermore, the new peak at  $2112\text{ cm}^{-1}$  corresponding to C≡N groups appeared after calcination indicating that the incorporation of  $\text{SrCO}_3$  has intense interaction during the condense process of melamine.<sup>72</sup>

To make further investigation of the constitution of the prepared composite, the calcined product was treated with HCl ( $0.5\text{ mol L}^{-1}$ ) and deionized water, because  $g\text{-C}_3\text{N}_4$  possessed fascinating acid stability. The treatment was terminated until the pH value was neutral, and then the treated nanocomposite was dried at  $60\text{ }^\circ\text{C}$  for 24 h. The XRD patterns and FT-IR spectra of the HCl-treated product are characterized in Fig. 3. The feature diffraction peak of  $g\text{-C}_3\text{N}_4$ , indicating the interlayer stacking, changed from  $27.46^\circ$  to  $27.92^\circ$  is explicitly observed in Fig. 3a. The change of the diffraction peak was corresponded to the stacking distance reduced from  $0.325$  to  $0.319\text{ nm}$ . The above results implied that the interlayer stacking order was improved. And FT-IR spectra of the product were well matched with the pure  $g\text{-C}_3\text{N}_4$  except the weak intensity (Fig. 3b). So, it could be indicated that the  $\text{SrCO}_3/g\text{-C}_3\text{N}_4$  was formed with the raw materials  $\text{SrCO}_3$  and melamine.

SEM and TEM images of the calcined samples are displayed in Fig. 4. It revealed the morphology and microstructure of  $\text{SrCO}_3/g\text{-C}_3\text{N}_4$ . In Fig. 4a, it could be seen the calcined melamine was predominantly composed of plate-like sheets,<sup>73</sup> and the morphology of calcined  $\text{SrCO}_3$  was irregular polyhedrons with smooth surface is shown in Fig. 4b. In Fig. 4c, it could be seen clearly that the  $g\text{-C}_3\text{N}_4$  covered on the  $\text{SrCO}_3$  incompletely. Further structural details of  $\text{SrCO}_3/g\text{-C}_3\text{N}_4$  are shown in Fig. 4d. There were some step edges of the layered  $g\text{-C}_3\text{N}_4$  and rods-like  $\text{SrCO}_3$  with some parts overlapping. It might be the amount of  $g\text{-C}_3\text{N}_4$  was not enough to disperse on the entire surface of  $\text{SrCO}_3$ ; and some areas cannot be wrapped by the  $g\text{-C}_3\text{N}_4$ . The SEM and TEM image could reveal that there existed some interactions between these two materials. Meanwhile, the specific surface areas of the clained samples were measured. As shown in Table 1, compared with  $g\text{-C}_3\text{N}_4$  the composite BET surface area gets smaller with the addition of  $\text{SrCO}_3$ , this might be the  $\text{SrCO}_3$  interacted with the stacking structure of  $g\text{-C}_3\text{N}_4$ . These results

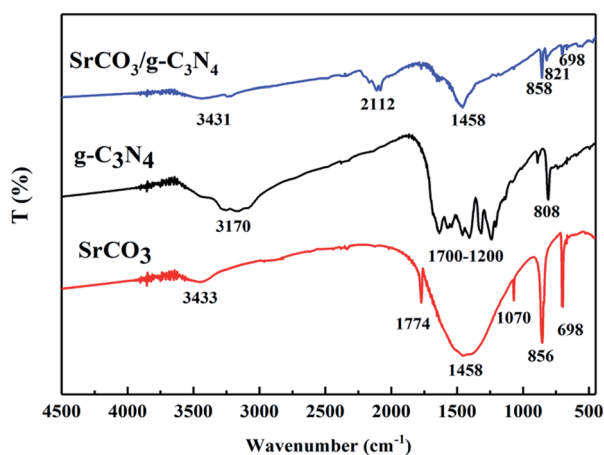


Fig. 2 FT-IR spectra of the  $g\text{-C}_3\text{N}_4$ ,  $\text{SrCO}_3$  and  $\text{SrCO}_3/g\text{-C}_3\text{N}_4$ .

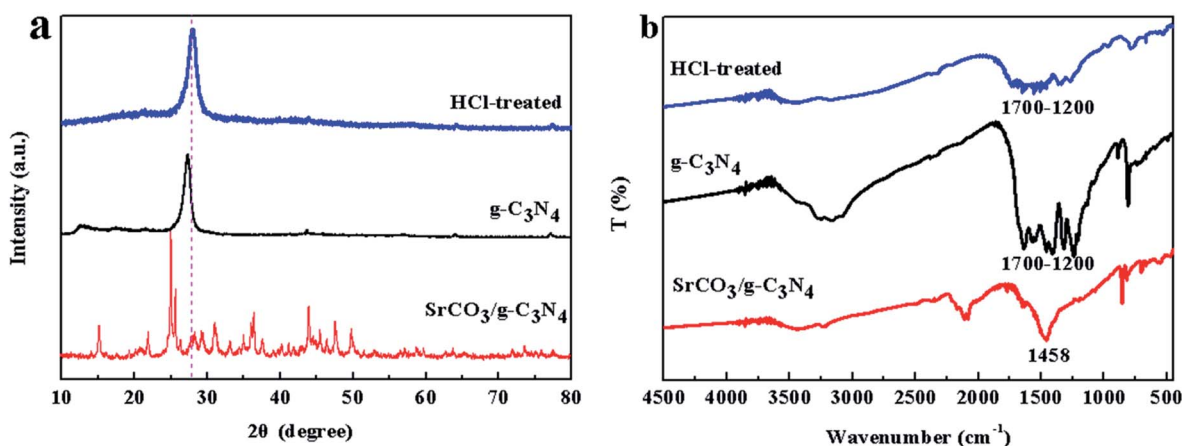


Fig. 3 XRD patterns (a) and FT-IR spectra (b) of the HCl-treated  $\text{SrCO}_3/g\text{-C}_3\text{N}_4$ .





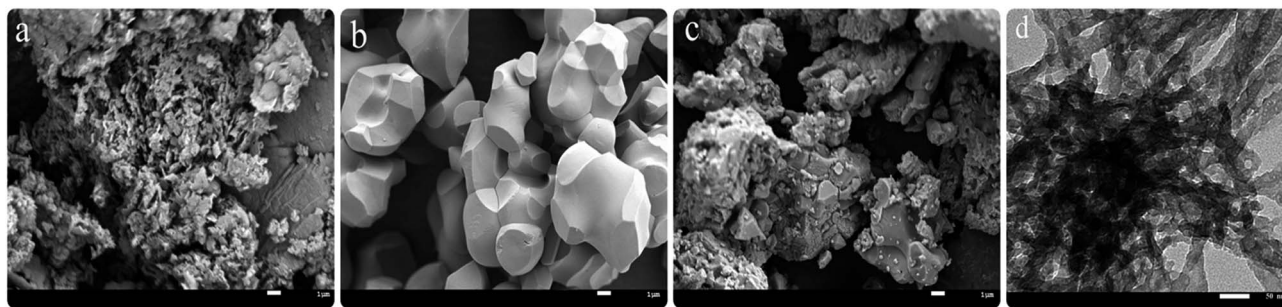


Fig. 4 SEM images of the g-C<sub>3</sub>N<sub>4</sub> (a), SrCO<sub>3</sub> (b) and SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> (c); TEM images of the SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> (d).

Table 1 Textural properties of g-C<sub>3</sub>N<sub>4</sub>, SrCO<sub>3</sub> and SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub><sup>a</sup>

Sample	$S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{\text{total}}$ (cm <sup>3</sup> g <sup>-1</sup> )	$D$ (nm)
g-C <sub>3</sub> N <sub>4</sub>	27.4	0.126	17.5
SrCO <sub>3</sub>	1.93	0.003	8.72
SrCO <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	5.86	0.016	9.69

<sup>a</sup>  $S_{\text{BET}}$ : BET surface area,  $V_{\text{total}}$ : total pore volume,  $D$ : average pore diameter calculated using BJH method.

consistent with SEM results which could further prove that there have been some interactions between SrCO<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub>.

To further study the chemical state of SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>, the XPS measurements were carried out. Fig. 5a is the general XPS

spectra of calcined materials, indicating the presence of C, N, O and Sr in SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>. The XPS spectra of C 1s are shown in Fig. 5b. For pristine g-C<sub>3</sub>N<sub>4</sub> the peaks at 284.2 eV, 287.7 eV were corresponding to sp<sup>2</sup>-hybridized carbon in C-C group or the adventitious hydrocarbon<sup>74</sup> and sp<sup>2</sup>-bond carbon in form of C=C=N.<sup>75</sup> But after the blended calcinations, the peak at 284.2 eV shifted to 284.6 eV. The N 1s spectra are shown in Fig. 5c. The peak at 398.2 eV was attributed to sp<sup>2</sup>-hybridized nitrogen in N atom aromatic rings in form of C=N=C,<sup>76</sup> and the nearly peaks at 399.3 eV and 401.0 eV were regarded as tertiary nitrogen (N-(C)<sub>3</sub>) and amino functional groups, respectively.<sup>77</sup> After incorporation, the binding energy peaks slightly shifted. The peaks at 531.1 eV and 533.2 eV of O 1s spectra corresponding to the SrCO<sub>3</sub> have no significant change in Fig. 5d. The XPS spectra of Sr 3d at 133.1 eV and 134.6 eV for calcined SrCO<sub>3</sub> were observed in Fig. 5e. These peaks were corresponding to the Sr 3d<sub>5/2</sub> and Sr 3d<sub>3/2</sub>, and the peak at 134.6 eV shifted to 134.7 eV after calcination. All these changes after co-calcination suggested that there were strong interactions between the two raw materials. Therefore, according to the analysis of XPS and the above results of XRD, FT-IR, SEM, TEM and BET measurements, it could be concluded that the SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> was synthesized using SrCO<sub>3</sub> and melamine by one-step calcination.

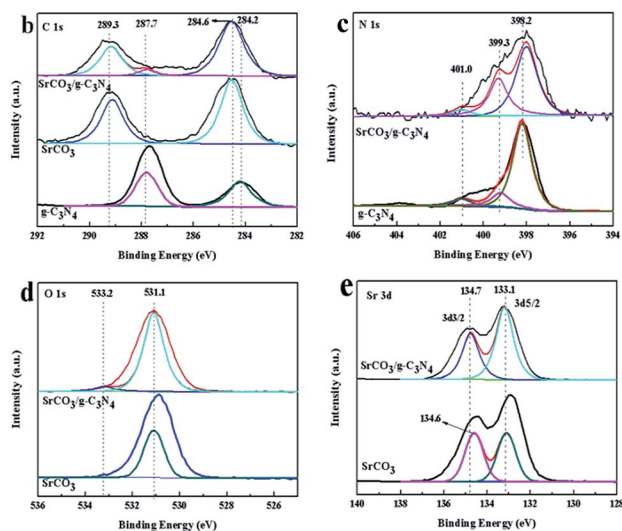
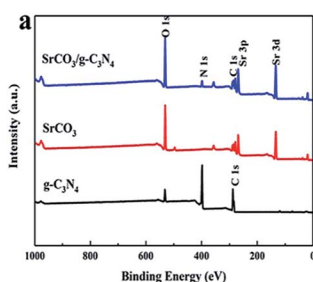


Fig. 5 XPS survey spectra of g-C<sub>3</sub>N<sub>4</sub>, SrCO<sub>3</sub> and SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> (a) and high-resolution XPS spectrum: C 1s (b), N 1s (c), O 1s (d) and Sr 3d (e).

### 3.2 The selective adsorption of CV

In our previous study, cationic dyes MB, RhB and CV were chosen as the target dye to conduct the adsorption experiments. We found that SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> appeared efficient adsorption capacity for CV except for the other dye solutions. To make further investigation of the selectivity of SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>, mixed solutions of CV/MB, CV/RhB and CV/MB/RhB with equal volume ratio were prepared. The concentration of each dye solution was 10 mg L<sup>-1</sup>, and dosage ratio of SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> and mixed solutions was 1 g L<sup>-1</sup>. The adsorption experiments were carried out under ambient temperature and different pH value for 120 min.

The optical pictures and UV-vis measurements of the adsorption process are shown in Fig. 6. It could be apparently seen that CV was decolorized after the test (Fig. 6b), but in the MB and RhB groups the color slightly changed (Fig. 6a-c). In Fig. 6d, the color of CV/MB mixed solution was changed from dark blue to incipient blue (the color corresponding to the MB). For the CV/RhB group, the end color is very close to RhB



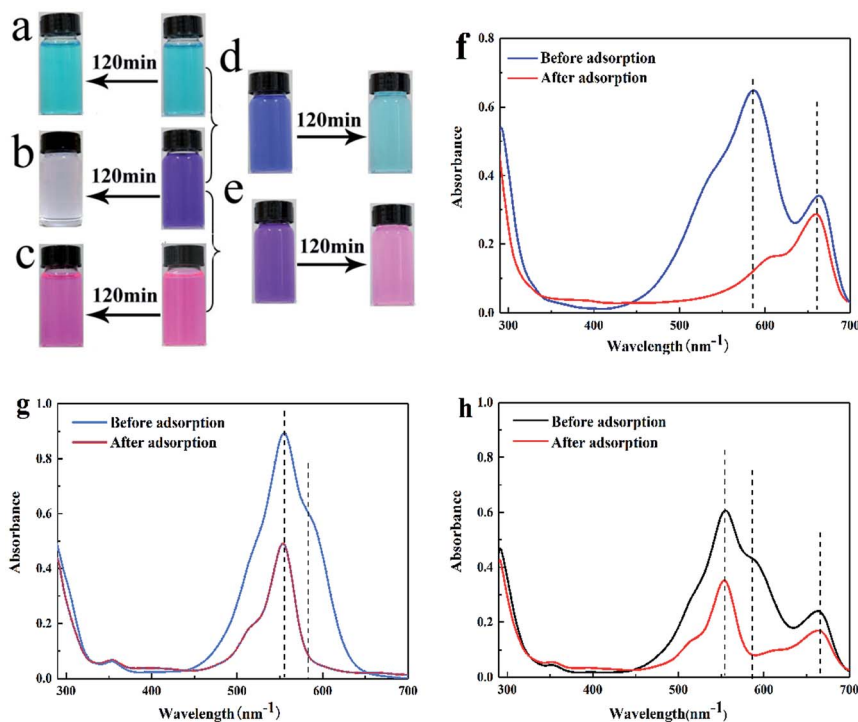


Fig. 6 Optical photographs of single adsorption of MB (a), CV (b) and RhB (c); the selective adsorption of CV from CV/MB (d) and CV/RhB (e) mixture, UV-vis spectra of CV/MB (f), CV/RhB (g) and CV/MB/RhB (h) mixture before and after adsorption.

(Fig. 6e). It suggested that CV in these two mixtures was selectively captured. However, the color in group CV/MB/RhB did not change, because the color of MB and RhB mixed solution is the same as that of CV. To further investigate the selective adsorption of CV, the UV-vis spectra were conducted for the tested groups. In the case of CV/MB, the UV-vis adsorption peaks of CV and MB were at 580 nm and 664 nm before adsorption, respectively. After adsorption, the peak of CV was dropped down drastically while the MB peak was almost unchanged (Fig. 6f). The same situation happened in the CV/RhB group (Fig. 6g). Although the optical of CV/MB/RhB group did not change, but the UV-vis adsorption curve appeared the same situation with the other two mixed groups (Fig. 6h). It could be concluded that the  $\text{SrCO}_3/\text{g-C}_3\text{N}_4$  performed selective adsorption of CV from CV/MB/RhB.

Furthermore, we also evaluated the effect of the initial pH of the dye solution. Fig. 7 shows the tested results. It could be seen that the initial pH (ranged from 4 to 10) of mixed dye solution did not significantly influence the adsorption process in each tested group.

**3.2.1 Effect of contact time.** Fig. 8 shows the effect of different contact time (0–160 min) in the adsorption process. The initial concentration of CV is 1600, 1800 and 2000  $\text{mg L}^{-1}$  and the dosage ratio of  $\text{SrCO}_3/\text{g-C}_3\text{N}_4$  and CV solution was 1  $\text{g L}^{-1}$ . For all concentrations, the removal rate of CV became constant after 120 min. Meanwhile, the group of 1600  $\text{mg L}^{-1}$  reached the equilibrium firstly and the removal rate was up to the other concentration. So, the contact time of 120 min and the initial concentration of CV of 1600  $\text{mg L}^{-1}$  were chosen for the following investigation.

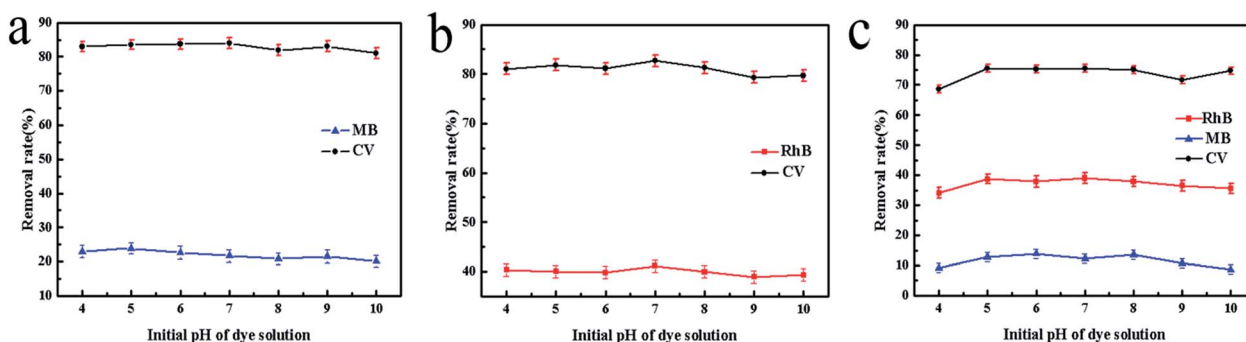


Fig. 7 Effect of the initial pH of mixed dye solution CV/MB (a), CV/RhB (b) and CV/MB/RhB (c).



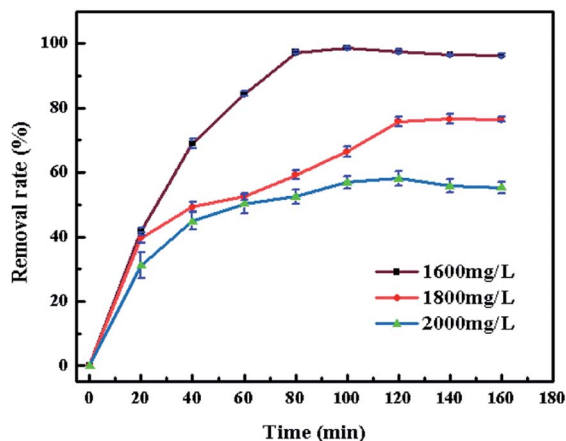
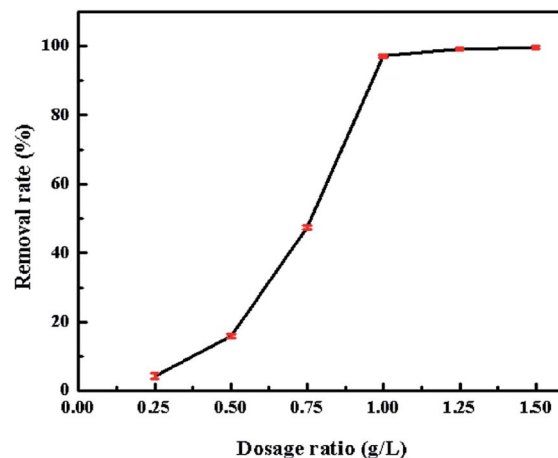


Fig. 8 Effect of contact time.

**3.2.2 Effect of initial concentration of CV.** The effect of initial concentration (50–2000 mg L<sup>-1</sup>) of CV is shown in Fig. 9. From the obtained results, it was found that the removal efficiency kept steadily before the initial dye concentration up to 1800 mg L<sup>-1</sup>. This might be attributed to the higher initial concentration offered more numbers of dye molecules that could contact easily with SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>. However, the removal rate was reduced at higher initial concentration indicating the saturation of SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>.

**3.2.3 Effect of adsorbent dosage.** The dosage of the adsorbents is one of the major parameter which influences the adsorption process; an appropriate amount of adsorbents is in favor of the real industrial treatment. Fig. 10 shows the effect of the adsorbent dosage (0.25, 0.50, 0.75, 1.00, 1.25, 1.50 g L<sup>-1</sup>) of the CV. The removal rate increased with the increased amount of the adsorbent. When the dosage ups to 1.00 g L<sup>-1</sup>, the removal efficiency did not increase with the increasing dosage. It might due to the binding of almost CV ions onto SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>, which made the equilibrium between solution and adsorbents. So the amount of adsorbent 1.00 g L<sup>-1</sup> was the suitable dosage for the adsorption of CV.

Fig. 10 Effect of SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> dosage.

**3.2.4 Effect of pH.** The pH of initial dye solution is a key factor in adsorption process, which could influence the interaction between adsorbent and dye. In order to find out the pH effect, the adsorption test was conducted at initial solution pH ranged from 4 to 10. The results in Fig. 11 show that the initial pH of CV solution had little effect on the adsorption capacity. This observation could demonstrate that SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> is suitable for removing CV in wastewater in a wide pH range, and there is no need to adjust the initial solution pH before treatment.

### 3.3 Adsorption kinetics

In order to study the characteristics of the adsorption process, pseudo-first-order and pseudo-second-order kinetics models were carried out with different concentration (500, 1000, 1200, 1600 mg L<sup>-1</sup>). The pseudo-first-order and pseudo-second-order are expressed by eqn (3) and (4).<sup>78</sup>

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

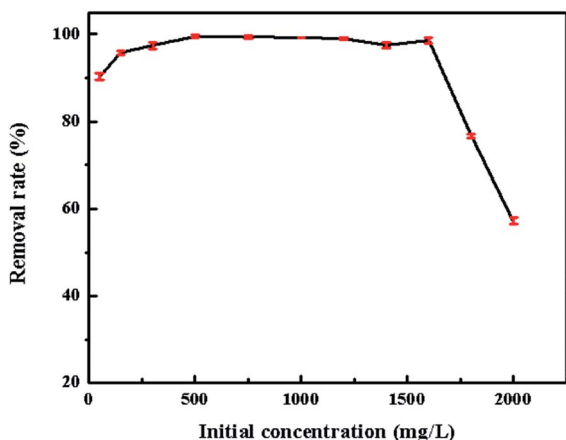


Fig. 9 Effect of initial CV concentration.

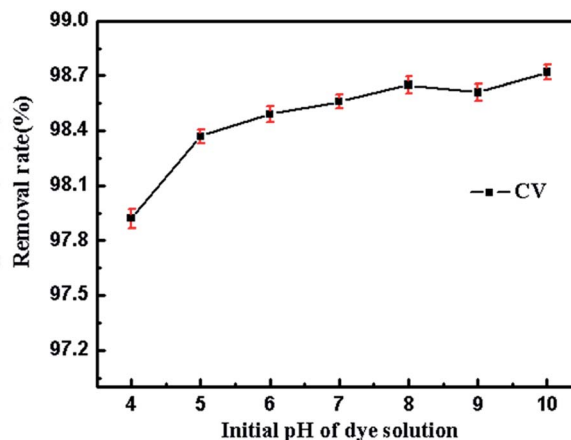


Fig. 11 Effect of the initial pH of CV.



where  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{g}(\text{mg}^{-1}\text{min}^{-1})$ ) are the rate constant of pseudo-first-order and pseudo-second-order model, respectively;  $q_e$  ( $\text{mg g}^{-1}$ ) and  $q_t$  ( $\text{mg g}^{-1}$ ) are the adsorbed amount at equilibrium time and time  $t$ .

The rate constant of adsorption could be calculated from the slope of the plot in Fig. 12 and was listed in Table 2.  $R^2$  of pseudo-second-order model is much higher than the other, indicating that the pseudo-second order equation is more suitable to describe the CV adsorption with  $\text{SrCO}_3/\text{g-C}_3\text{N}_4$ . So the chemisorptions or chemical sorption was the rate-controlling step for the adsorption process.<sup>79</sup>

### 3.4 Desorption and reuse

In order to evaluate the reusability of  $\text{SrCO}_3/\text{g-C}_3\text{N}_4$ , the regeneration process was performed. Adsorption experiment was conducted at the optimal condition as ascribed above in a 250 mL CV solution firstly, after equilibrium the used adsorbent was regenerated by centrifugation and washed several times with methanol and water at room temperature. Finally, the regenerated composite was dried for 24 h at 60 °C for reusing.

It could be seen that the removal rate gradually decreased after regeneration in Fig. 13. It might conclude that the adsorption mechanism of this process is not due to the physical adsorption.

### 3.5 Adsorption mechanism of crystal violet

To further study the adsorption performance of CV, the adsorption experiments were conducted with the calcined  $\text{SrCO}_3$ ,  $\text{g-C}_3\text{N}_4$  and  $\text{SrCO}_3/\text{g-C}_3\text{N}_4$  firstly. 0.08 g tested materials

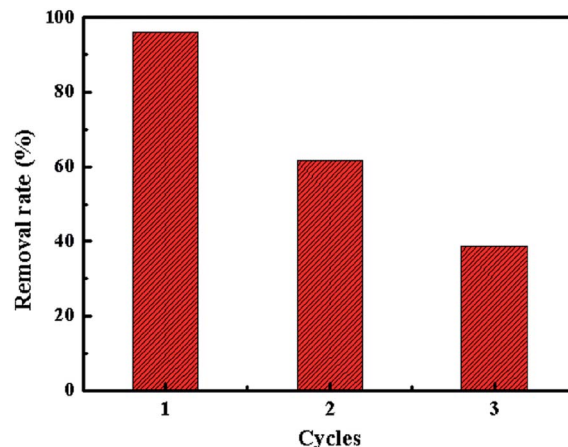


Fig. 13 Reusability of the adsorbent.

were dispersed in 80 mL CV solution ( $10 \text{ mg L}^{-1}$ ), respectively. After 2 h adsorption process, the removal rate of CV for tested materials is exhibited in Fig. 14. It could be seen obviously that the removal ability of  $\text{g-C}_3\text{N}_4$  and  $\text{SrCO}_3$  to CV is much smaller than that of the nanocomposite. The removal rate of  $\text{g-C}_3\text{N}_4$ ,  $\text{SrCO}_3$  and  $\text{SrCO}_3/\text{g-C}_3\text{N}_4$  were 31.30%, 17.30% and 97.46%, respectively. The adsorption mechanism of  $\text{g-C}_3\text{N}_4$  might be attributed to  $\pi$ - $\pi$  interaction between the  $\text{g-C}_3\text{N}_4$  and CV, and that for the  $\text{SrCO}_3$ , the electrostatic attraction between the carbonate generated from the hydrolytic of  $\text{SrCO}_3$  and the cationic chromogenic groups of CV. And for the  $\text{SrCO}_3/\text{g-C}_3\text{N}_4$ , the synergistic effect of  $\pi$ - $\pi$  interaction and electrostatic attraction highly improved the adsorption properties of the

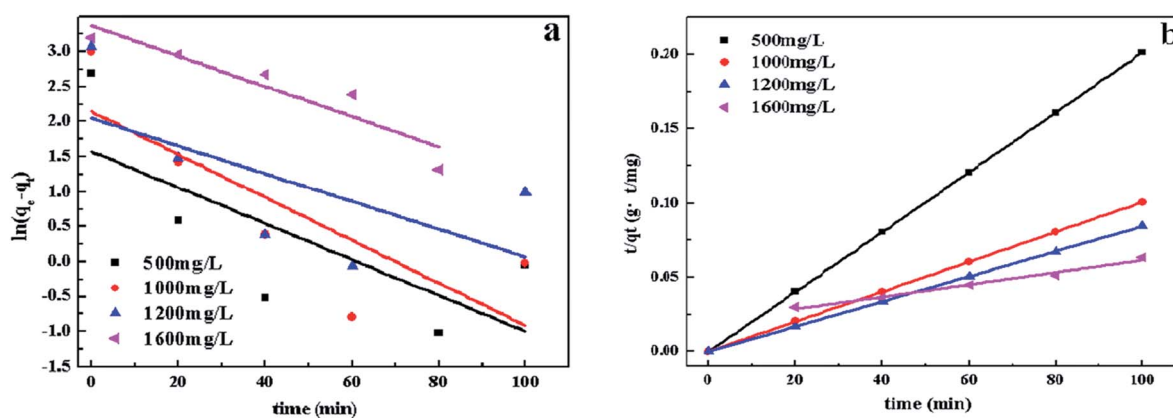


Fig. 12 Pseudo-first-order (a), and pseudo-second-order (b) kinetic plots for adsorption.

Table 2 Kinetic parameters of different initial CV concentration

$C_0$ ( $\text{mg L}^{-1}$ )	Pseudo-first-order			Pseudo-second-order			
	$q_e$ (cal) ( $\text{mg g}^{-1}$ )	$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_e$ (exp) ( $\text{mg g}^{-1}$ )	$q_e$ (cal) ( $\text{mg g}^{-1}$ )	$k_2$ ( $\text{g}(\text{mg}^{-1}\text{min}^{-1})) \times 10^{-5}$	$R^2$
1600	16.91	0.014	0.5357	1576.9	1666.7	3.67	0.9425
1800	28.33	0.016	0.7481	1378.6	1428.5	3.53	0.9577
2000	29.53	0.024	0.7822	1143.4	1250.0	8.10	0.9902





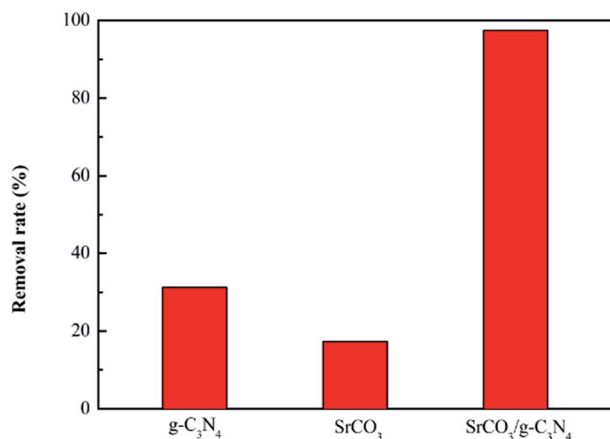


Fig. 14 Comparisons of the adsorption effect of the SrCO<sub>3</sub>, g-C<sub>3</sub>N<sub>4</sub>, and SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>.

nanocomposite on CV.<sup>50</sup> According to the above results and the crystal structures, we could deduce that superb adsorption capacity of CV might attribute to the synergistic interaction of the conjugation of g-C<sub>3</sub>N<sub>4</sub> and the electrostatic attraction of SrCO<sub>3</sub>.

Furthermore, the FT-IR spectra of SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> before and after CV adsorption were recorded. As shown in Fig. 15, the peak at 2112 cm<sup>-1</sup> assigned to the nitrile groups shifted to the 2107 cm<sup>-1</sup> and the peak at 1319 cm<sup>-1</sup> assigned to aromatic C–N heterocycles observed clearly. These results indicate that the previously mentioned groups are involved in the adsorption process. Moreover, the intensity of the peak 1458 cm<sup>-1</sup> corresponding to C–N heterocycle aromatic became stronger, that was for the CV was adsorbed onto the SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>. All the changes of the FT-IR spectra of the SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> before and after adsorption could indicate that there have been intense interactions between dye molecules and SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>. Furthermore, the result of desorption test might indicate that there has been intense chemical adsorption between the composite and CV. It could deduced that SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> performed selective adsorption of CV might due to the chemical

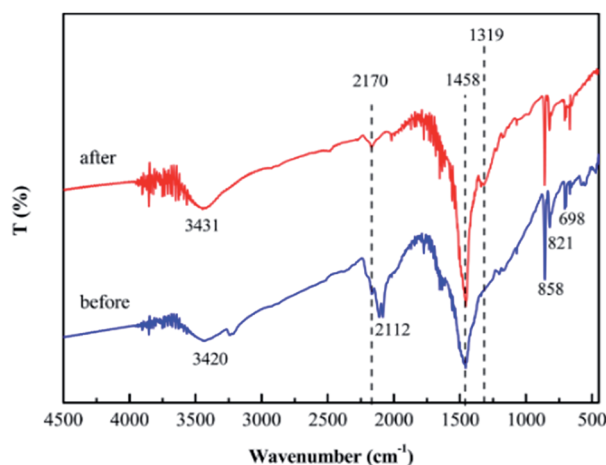


Fig. 15 FT-IR spectra of SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> before and after adsorption.

structure of CV is more symmetrical and conjugation degree is higher than MB and RhB. On the basis of the above analysis, the conjugation and electrostatic interaction would be the driving force for the selective adsorption of CV.

## 4 Conclusions

In summary, a new SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite adsorbent was firstly synthesized with SrCO<sub>3</sub> and melamine *via* a simple one-step calcination method. The SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> performed high and specific selective adsorption for CV. The experiment data was well described by the pseudo-second-order model. According to the crystal structural feature of SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> and the FT-IR analysis of SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> before and after adsorption of CV, it could be deduced that the synergies of  $\pi$  conjugation and electrostatic interaction would be the mechanism for the selective adsorption of CV. Our findings indicate that g-C<sub>3</sub>N<sub>4</sub> based composite SrCO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> could be a promising adsorbent which can potentially be applied for the removal of CV pollutants from aqueous solution.

## Conflicts of interest

There are no conflicts to declare.

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