

Modified garlic straws as new adsorbents for removing ionic dyes from aqueous solutions

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ABSTRACT

In this study, garlic straws (GS) from agricultural by-products were chemically modified by sodium hydroxide and citric acid to yield potential adsorbents for the removal of ionic dyes. Firstly, the physical and chemical properties of obtained adsorbents were characterized by component analysis, X-ray diffraction, scanning electron microscopy and Fourier transform infrared spectroscopy. Then the cationic dye crystal violet (CV) and anionic dye Congo red (CR) were applied to evaluate the adsorption capacity of adsorbents under different conditions such as initial solution pH (2–12), adsorbent dose (0.5–10 g/L), initial dye concentration (0.1–6 g/L) and contact time (up to 120 min). Results showed that sodium hydroxide and citric acid treatments could enhance the adsorptions of CV and CR probably through increasing the hydroxyl groups and carboxyl groups on the surface of GS. The maximum adsorption capacities of CV and CR on modified GS at 308.15 K were 63.69 and 998.3 mg/g, respectively. Furthermore, a kinetics study revealed that the adsorption processes could be described by the pseudo-second-order kinetic model. Thermodynamic parameters indicated that the adsorption processes were spontaneous and endothermic. Generally, these results confirmed that sodium hydroxide and citric acid treatments were effective methods to improve the adsorption capacities of GS for ionic dyes.

Keywords: Garlic straws; Chemical modification; Crystal violet; Congo red; Adsorption mechanism

1. Introduction

Dyes from industrial effluents such as textiles, pulp and leather are mostly synthetic with complex aromatic structure molecules that make them persistent to light, oxidation and biodegradation [1–3]. Many dyes have been reported not only to interfere with light penetration and reduce photosynthetic action, but also to have toxic as well as

carcinogenic, mutagenic and teratogenic effects on aquatic life and human beings [4,5]. Among these dyes, crystal violet (CV) is a cationic dye and is widely used in the textile industry, manufacture of paints and printing inks. Crystal violet has been found to be carcinogenic and highly toxic to mammalian cells [6]. Congo red (CR) is an anionic dye and is widely used in the textile industry, plastics, paper and leather. Its intermediary metabolites were reported to

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generate carcinogenic amines which affect DNA and induce apoptosis in HL-60 cells [7].

Therefore, researchers have been trying to find ways to remove dyes from wastewater [8–10]. Various methods of dye removal have been developed, including coagulation, filtration, ion exchange, biological treatment, advanced oxidation processes, electrolysis, activated sludge, adsorption and solvent extraction [11–13]. Among these methods, adsorption is considered to be the simplest, most effective and economical method for dye removal [14]. Adsorption is a superficial phenomenon, which is defined as an increase in the concentration of a specific component at the surface or interface between two phases [15–17]. Highly functional porous materials with high surface areas are often used as suitable adsorbents to evaluate the adsorption efficiency of dye removal [18,19].

In the past few years, by-products of agricultural and food industries have been deemed to be potential adsorbents because they are abundant, inexpensive and environmentally friendly [20–22]. Garlic is consumed globally on a large scale, leading to a large amount of garlic straw (GS) waste. GS are a promising substitute as a biological adsorbent for various pollutants [23]. It has been used for the adsorption of Methylene blue, Direct pink 12 B, phenol and heavy metals (such as Cu^{2+} , Ni^{2+} , Pb^{2+} and Au^{3+}) [16]. However, no modification method has been reported to improve the adsorption capacity of GS for the removal of ionic dyes. On the other hand, sodium hydroxide and citric acid have been widely used to modify agricultural waste-derived adsorbents, such as sodium hydroxide modified rice straw for adsorption of Methylene blue (MB) [24], citric acid modified wheat straw for adsorption MB and CV [25], as well as sodium hydroxide and citric acid-modified garlic peels for adsorption of Rhodamine B [26].

Therefore, the purpose of this research is to investigate the potential use of sodium hydroxide and citric acid-modified GS to remove ionic dyes CV and CR from aqueous solutions. The physical and chemical properties of adsorbents were characterized by component analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). Then the effects of various parameters (such as initial solution pH, adsorbent dose, initial dye concentration and contact time) on the adsorption capacities of adsorbents were evaluated. Finally, the adsorption kinetics, thermodynamics and isotherms properties of adsorption processes were discussed.

2. Materials and methods

2.1. Reagents and materials

GS was purchased from Jiangsu Foodmeritt Biotech Inc., (Jiangsu, China). Analytically pure CV, CR, sodium hydroxide and citric acid were purchased from Sinopharm Chemical Reagent Co., Ltd., (China).

2.2. Component analysis of GS

According to the Van Soest method [27], the components of GS were detected using a fiber analyzer (Model: FIWE6, Manufacturer: VELP, Italy) and a muff furnace (Model:

KSY6D16, Manufacturer: Shenyang Energy-Saving Electric Furnace Factory, China).

2.3. Preparation of the adsorbent

Unmodified GS: 50 g of GS powder was blended with 500 mL deionized water in a beaker at room temperature (25°C) for 24 h. After filtration, the residue was cleaned, flattened and dried in an oven at 80°C for 12 h. Subsequently, it was ground with a ball mill and sieved through a 50-mesh sieve (approximately 0.28–0.3 mm) for use [10].

Modified GS: 50 g of GS powder was blended with 0.6 mol/L citric acid solution (500 mL) or 1% sodium hydroxide solution (500 mL) at room temperature (25°C) for 2 h. After filtration, the residue was washed with deionized water until the pH of the wash water was neutral. Subsequently, the residue was dried in an oven at 80°C for 12 h, ground with a ball mill and sieved through a 50-mesh sieve for use [26].

2.4. Characterization of the adsorbent

Morphology and microstructure of the adsorbents were analyzed by SEM. Functional group compositions of the adsorbents were characterized by FT-IR. Structures of adsorbents were analyzed by XRD.

2.5. Preparation of ionic dye solutions

A cationic dye CV ($\text{C}_{25}\text{H}_{30}\text{ClN}_7$, MW = 407.98) and an anionic dye CR ($\text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2$, MW = 696.66) were selected to study the adsorption behaviors of GS. Their molecular structures are shown in Fig. 1a and b.

To prepare stock solutions of CV (10 g/L) and CR (10 g/L), 10 g each of CV and CR powder were separately dissolved in deionized water and stabilized to 1,000 mL. The experimental solutions were prepared by diluting dye stock solutions.

2.6. Adsorption of ionic dyes

To study the adsorption properties of CV and CR on GS under different conditions (including initial solution pH, adsorbent dose, initial dye concentration and contact time), the adsorbents were added to conical flasks containing 100 mL CV or CR solution. After blending, the conical flasks were placed in a constant-temperature shaker at 35°C with a rotational speed of 150 rpm. The concentrations of residual dyes in the solutions at different time were determined by sampling 2 mL of solutions and centrifuging at 3,000 rpm for 5 min. Then the dye concentrations in the supernatant were determined using an ultraviolet-visible spectrophotometer (Model: UV-5500PC, Manufacturer: Shanghai Metash, China). The wavelengths of CV and CR were 595 and 498 nm, respectively. Dye removal rate was calculated using the equation as below:

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of dye solutions (mg/L).

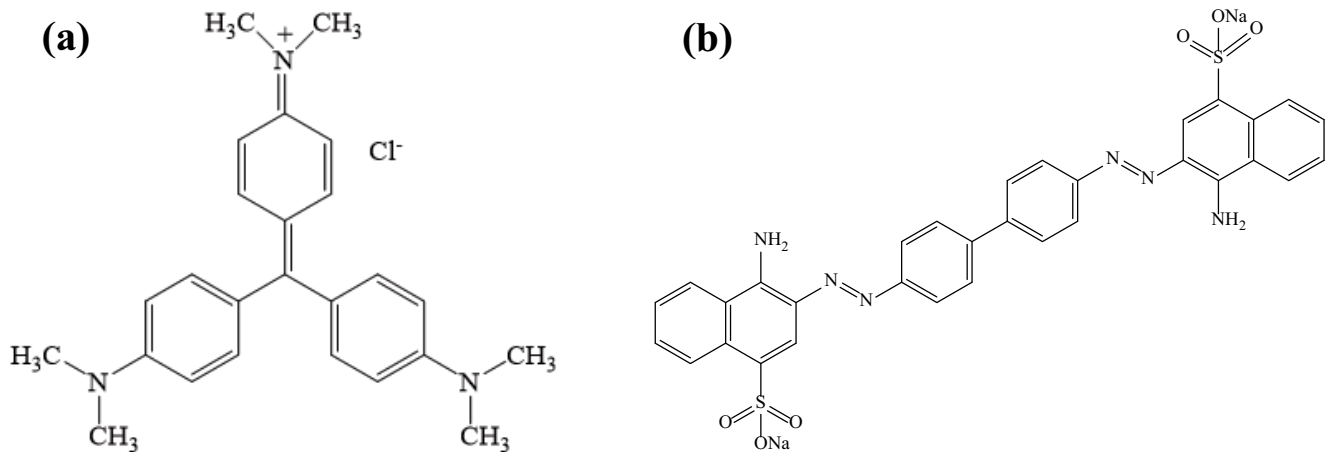


Fig. 1. Molecular structures of two dyes, (a) crystal violet (CV) and (b) Congo red (CR).

2.7. Adsorption kinetics

Pseudo-first-order and pseudo-second-order kinetic models were applied to study the time dependence of adsorption processes and mechanisms. The equations used were as follows:

Pseudo-first-order kinetic equation [28]:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (2)$$

where Q_t (mg/g) is the amount of adsorbed adsorbate per unit mass of adsorbent at time t , Q_e is the adsorption capacity at equilibrium (mg/g), k_1 is the pseudo-first-order kinetic rate constant (min^{-1}) and t is the adsorption time (min).

Pseudo-second-order kinetic equation [29]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (3)$$

where k_2 is the pseudo-second-order kinetic rate constant (g/mg/min).

2.8. Adsorption thermodynamics

Adsorption thermodynamics study was used to identify the affinity of adsorbent for the adsorbate. The thermodynamic parameters for the adsorption of CV and CR on GS were calculated using the following van't Hoff equations [30]:

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

$$\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5)$$

where $K_D = Q_e/C_e$, ΔG is Gibbs free energy, ΔH is enthalpy, ΔS is entropy change, R is the universal gas constant (8.314 J/mol/K) and T is temperature (K).

2.9. Adsorption isotherms

Adsorption isotherm was investigated to correlate the adsorption capacity and the residual concentration of the adsorbate. Langmuir's equation was employed in this study

since it is the most frequently used model for the adsorption of dyes in aqueous solution.

The Langmuir equation [31]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{\max} K_L} + \frac{1}{Q_{\max}} C_e \quad (6)$$

where Q_{\max} is the maximum adsorption capacity (mg/g), K_L is the Langmuir constant (L/mg).

The essential characteristic of adsorption isotherm could be expressed by a dimensionless constant called equilibrium parameter R_L , defined by Hameed [32] as follows:

$$R_L = \frac{1}{1 + C_0 K_L} \quad (7)$$

where C_0 is the highest dye concentration (mg/L). The value of R_L indicates the type of the isotherm. Adsorption isotherm is considered to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

3. Results and discussion

3.1. Component analysis of GS

According to the component analysis, GS contained 36.83% cellulose, 29.51% neutral detergent fiber, 16.03% hemicellulose, 15.72% lignin and 1.91% inorganic salt. Cellulose, hemicellulose and lignin were the main chemical components of GS, and similarly results could be found in other literatures [2,33].

3.2. Characterization of GS and modified GS

The SEM images for surface morphologies of the unmodified and modified GS before and after dyes adsorption are shown in Fig. 2. The unmodified GS in Fig. 2a was characterized by a tight lamellar surface structure, while modified GS showed larger lamellar structure and small pores irregularly distributed on the surface, indicating that sodium hydroxide and citric acid significantly change the morphology of GS. Similar studies have been reported that

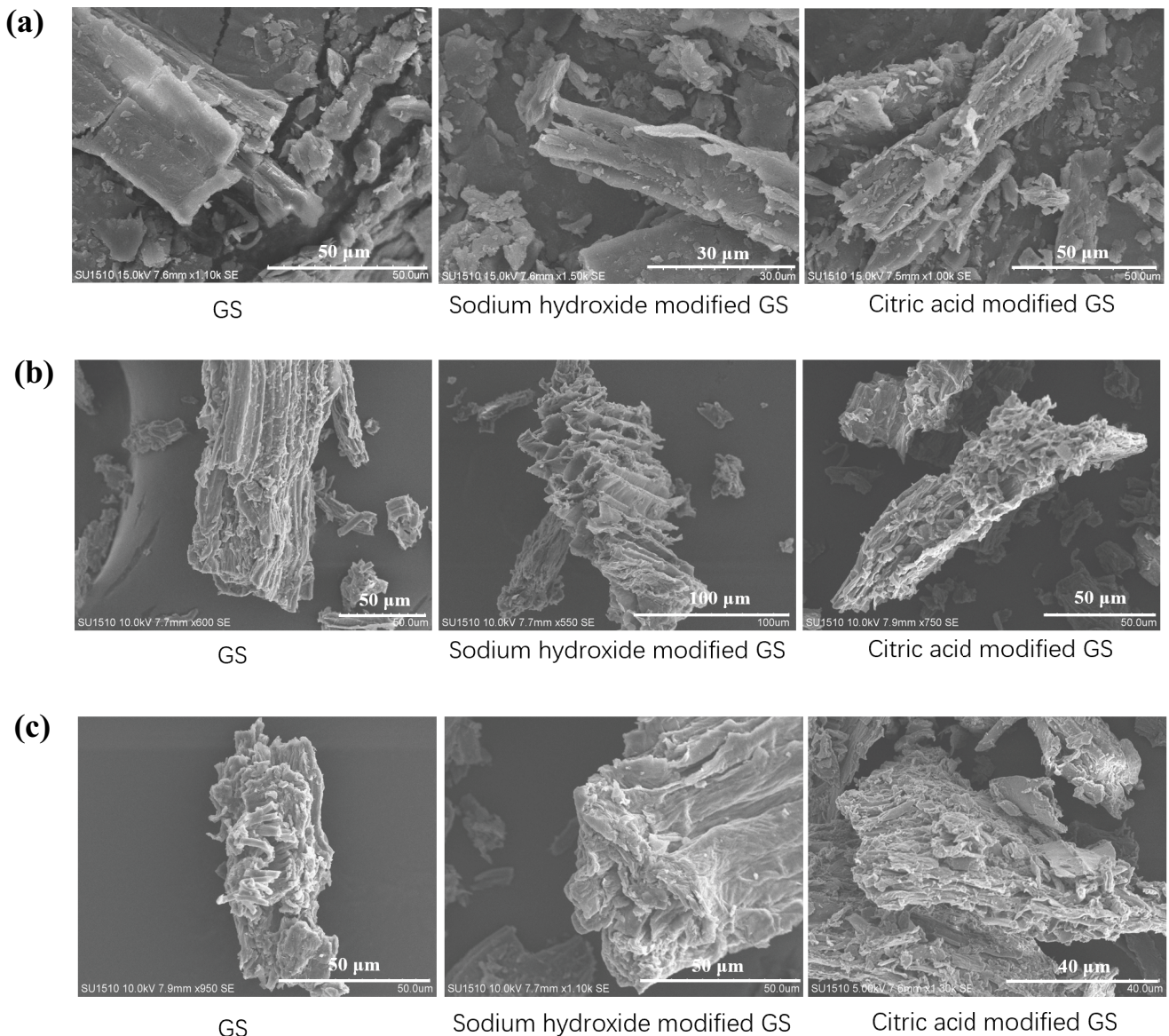


Fig. 2. SEM images of adsorbents with different modifications before and after adsorptions of CV and CR: (a) unmodified and modified GS before adsorption, (b) unmodified and modified GS after CV adsorption, and (c) unmodified and modified GS after CR adsorption.

the chemical treatments such as alkalization, silanization, acetylation and etherification treatment lead to changes in crystallinity, pore structure, stiffness, unit cell structure and orientation of fibrils [34–36]. Fig. 2b and c present the surface morphologies of GS after the adsorption of CV and CR, respectively. It clearly showed that pores on the surface of GS were more densely filled with CV and CR dyes.

To observe changes in the functional groups of GS after different treatments, the GS before and after chemical modifications with sodium hydroxide or citric acid were characterized via FT-IR at 4,000–500 cm^{-1} (Fig. 3). The wide and strong absorption peak in the spectrum of 3,740–3,008 cm^{-1} was attributed to the OH stretching vibration of alcohols and carboxylic acids or the NH stretching

vibration of amines [37]. The peaks at 2,851 and 2,919 cm^{-1} were characteristic of the stretching vibration of C–H [38]. The peaks at 1,736 and 1,735 cm^{-1} in both spectra were attributed to the strengthening vibration of carboxylic acid C=O, and that the peaks at 1,620 and 1,641 cm^{-1} were assigned to C=C or C=N [33]. The adsorption of GS in the spectrum range of 1,530–1,201 cm^{-1} is related to the stretching of the C=C bond in the aromatic ring [39,40]. In addition, the peaks at 1,056 and 1,064 cm^{-1} in the two spectra represent bending changes of C–O in –COOH [41,42]. Two significant changes in the FT-IR spectra were observed after citric acid treatment that the peaks at 1,736 and 1,641 cm^{-1} were relatively strong compared with the corresponding peaks in the spectrum of unmodified GS. This phenomenon suggested that citric acid might oxidize some unreacted groups to –COOH [42].

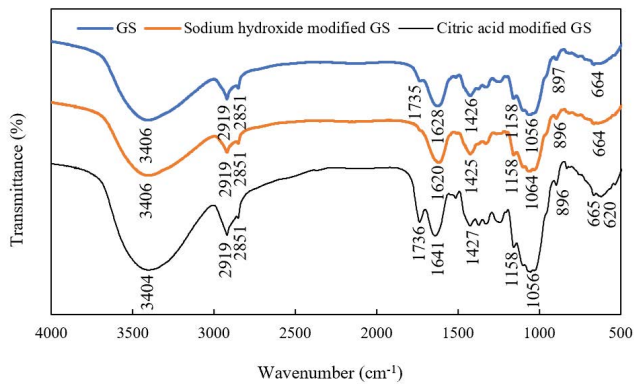


Fig. 3. FT-IR spectra of unmodified, sodium hydroxide and citric acid-modified GS.

Due to interactions of hydrogen bonds and van der Waals forces between adjacent molecules, cellulose could be characterized by a crystal structure [39], whereas, amorphous cellulose, hemicellulose and lignin constitute amorphous components [41]. According to XRD detecting, no significant differences in peak position and peak width were observed among unmodified, sodium hydroxide and citric acid modified GS (data was not shown here), indicating that the pretreatment of GS with sodium hydroxide or citric acid did not destroy the ordered structure of the crystal cellulose region [42].

3.3. Dye adsorption under different pH conditions

The effect of initial solution pH on the adsorption of dyes was firstly investigated using 0.5 g/L CV, 0.5 g/L CR and 0.6 g adsorbents. The initial pH value of both dye solutions ranged from 2 to 12. As shown in Fig. 4a, the dye removal rate was extremely low when the initial pH of CV solution was 2. With increasing initial pH value, the proportion of absorbed dyes increased because the attraction between the cationic dye and the negatively charged sites of the adsorbent increased, and thus enhanced the adsorption [43,44]. However, the adsorption

rate decreased slightly at pH = 10 because CV underwent color changes and flocculation at this pH value. Finally, the dye removal rate reached its highest value at pH = 12. Considering the actual situation and operational feasibility, the pH = 8 was selected as optimum pH of CV solution for subsequent experiments. In addition, the removal rate of sodium hydroxide modified GS was higher than that of citric acid modified and unmodified GS. Findings from previous studies suggested that alkaline treatment could remove a certain amount of lignin, wax and oils covering the external surface of fiber cell walls [34], and thus increase the number of possible reaction sites and activate the hydroxyl groups of cellulose and lignin in the fiber for CV adsorption [35,45].

As shown in Fig. 4b, the CR removal rate was relatively high at pH = 2. It was speculated that a lower pH led to an increase in the concentration of H⁺ in solution, which gave the material a positive surface charge that resulted in increasing electrostatic attraction between anionic dye and GS surface, and thus enhanced the adsorption of CR [10,44]. Therefore, considering the operational feasibility, pH = 4 was selected as optimum pH of CR solution for subsequent experiments. On the other hand, the results also demonstrated that the adsorption capacity of GS for removal of CR increased significantly after modification with citric acid. According to previous studies, esterification by citric acid caused significant changes to physical and chemical properties of fiber surfaces [46], and thus improved the adsorption of anionic dyes by both physical and chemical processes, including chelation, hydrogen bonding and fixation, due to the active adsorption sites (hydroxyl group and carboxyl group) of citric acid [47,48]. This is also correlated well with our FT-IR results that the carboxyl groups of GS were increased after citric acid treatment.

3.4. Dye adsorption under different adsorbent doses

The effect of adsorbent doses on dye removal rate is shown in Fig. 5. As the adsorbent doses increased from 0.5 to 10 g/L, the removal rates of CV increased from 47.4% to 73.0% on unmodified GS, from 59.4% to 75.3% on sodium

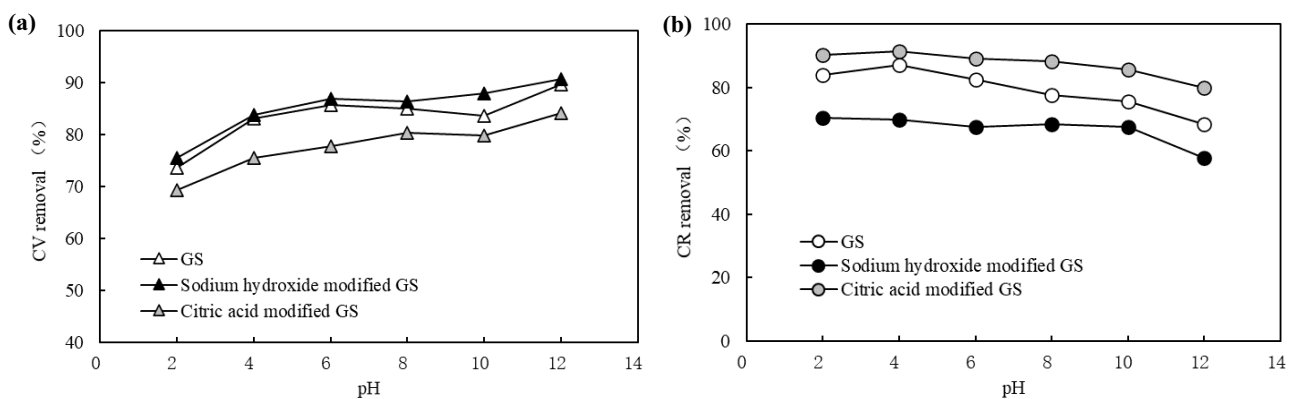


Fig. 4. Removal rates of (a) cationic dye CV and (b) anionic dye CR by unmodified and modified GS under different initial solution pH (adsorbent dose: 0.6 g unmodified or modified GS; dye concentration: 0.5 g/L for CV and CR; contact time: 20 min for CV and CR).

hydroxide modified GS, and from 38.0% to 68.1% on citric acid modified GS. The removal rate remained nearly unchanged after a dose of 6 g/L for the unmodified and sodium hydroxide modified GS. The removal rate of CR increased from 51.8% to 90.9% for unmodified GS, from 63.2% to 96.3% for citric acid modified GS, and from 31.7% to 70.9% on sodium hydroxide modified GS. The removal rate remained nearly unchanged after a dose of 8 g/L for the unmodified and citric acid modified GS.

Besides, these results also demonstrated that the adsorption capacities of adsorbents (the amount of adsorbed adsorbate per unit mass of adsorbent) for both dyes decreased with increasing adsorbent doses, which could be attributed to a reduction in total surface area available to dyes and increase in diffusion path length, as a result of the aggregation of adsorbents [48]. Therefore, adsorbent doses of 6 and 8 g/L were selected in subsequent experiments for CV and CR adsorption, respectively.

3.5. Dye adsorption under different initial dye concentrations

Regarding the effects of the initial dye concentrations on adsorption, as shown in Fig. 6, the removal rate of CV by unmodified GS increased from 81.9% (0.1 g/L) to 85.8% (1 g/L), and then decreased to 26.4% (6 g/L). The removal

rate of CV by sodium hydroxide modified GS increased from 86.0% (0.1 g/L) to 91.3% (1 g/L) and then decreased to 31.8% (6 g/L). The removal rate of CV by citric acid modified GS increased from 71.4% (0.1 g/L) to 79.4% (1 g/L), and then decreased to 27.3% (6 g/L). For unmodified GS under different initial CR concentrations, the removal rate increased from 75.3% (0.1 g/L) to 85.5% (1 g/L), and then decreased to 52.1% (6 g/L). For sodium hydroxide modified GS, the removal rate increased from 63.3% (0.1 g/L) to 62.6% (0.5 g/L) and then decreased to 31.1% (6 g/L). For citric acid modified GS, removal rate increased from 92.4% (0.1 g/L) to 93.9% (0.5 g/L), and then decreased to 63.6% (6 g/L). In general, the increase of removal rate as a function of lower dye concentrations was attributed to the greater driving force to overcome the mass transfer resistance of adsorbate from solution to the adsorbent. For higher dye concentrations, the removal rate decreased significantly due to the saturation of adsorption sites on the adsorbent surface by molecules of the dyes [44,49].

3.6. Dye adsorption under different contact time

The effects of contact time on removal rates of CV and CR by adsorbents were studied for a period of 120 min at initial dye concentrations of 1 and 0.5 g/L, respectively.

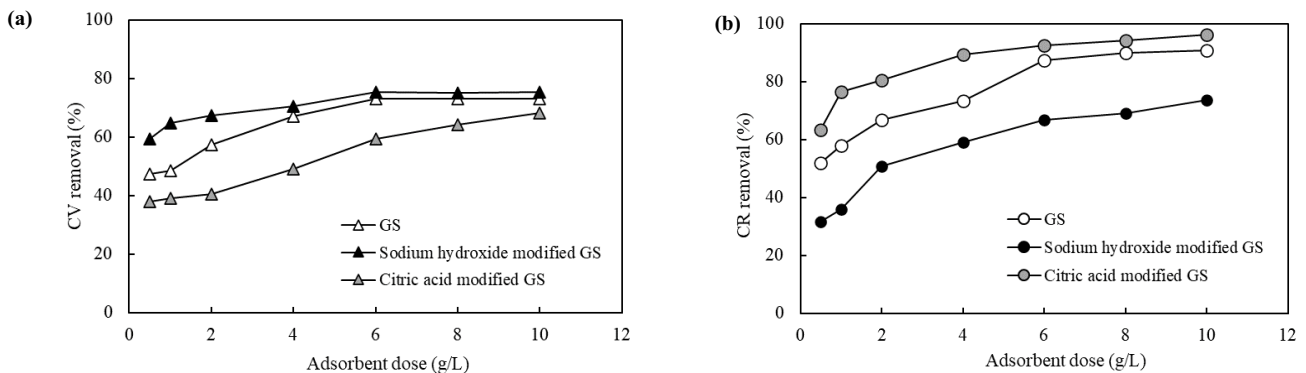


Fig. 5. Removal rates of (a) cationic dye CV and (b) anionic dye CR by unmodified and modified GS under different adsorbent doses (pH = 8 for CV and pH = 4 for CR; dye concentration: 0.5 g/L for CV and CR; contact time: 20 min for CV and CR).

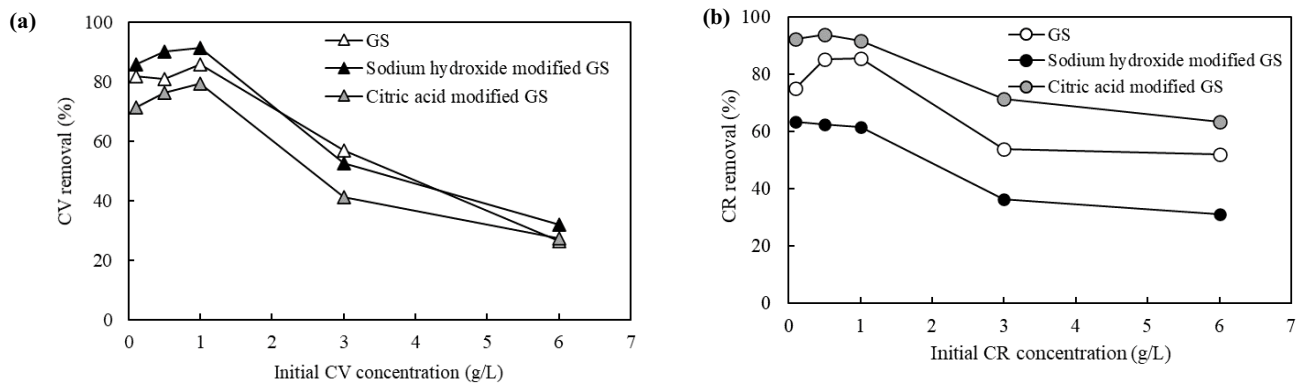


Fig. 6. Removal rates of (a) cationic dye CV and (b) anionic dye CR by unmodified and modified GS under different initial dye concentrations (adsorbent dose: 0.6 g for CV and 0.8 g for CR; pH = 8 for CV and pH = 4 for CR; contact time: 20 min for CV and CR).

As shown in Fig. 7a and b. The removal rates increased rapidly at the initial stage and then slow down with the extension of contact time until equilibriums were reached at 10 and 20 min for CV and CR, respectively. Similar results have been reported for the adsorption of Methylene blue by GS [43]. This is evident from the fact that large numbers of empty surface sites are available for adsorption in the initial stage, and the remaining empty surface sites become difficult to occupy after a certain time because of repulsive forces between solute molecules. Besides, the adsorption capacities of GS for removal of CV and CR were significantly improved after modification with sodium hydroxide and citric acid.

3.7. Adsorption kinetics analysis

To determine the mechanism of adsorption on GS, the adsorption data of both dyes with different initial concentrations were analyzed. Figs. 8 and 9 show the graphs of pseudo-first-order and pseudo-second-order kinetics for adsorption of CV and CR on GS with different initial concentrations. Related kinetic parameters were listed in Tables 1 and 2, which included equilibrium adsorption capacity Q_e , rate constant k_1 , rate constant k_2 , and correlation coefficient R^2 . For both dyes, the R^2 of the

pseudo-second-order kinetics were found to be closer to 1 than that of the pseudo-first-order dynamics. These results suggested that the adsorption processes of CV and CR on GS might be best described by the pseudo-second-order kinetic model and the chemisorption might be the rate-limiting step controlling the adsorption processes [30].

3.8. Adsorption thermodynamics analysis

Thermodynamic considerations of an adsorption process are required to conclude the spontaneity and feasibility of such process [50]. The thermodynamic parameters of the adsorption of CV on sodium hydroxide modified GS and the adsorption of CR on citric acid modified GS were calculated from Fig. 10 and listed in Table 3. The Gibbs free energy change values were -6.184, -6.991 and -7.798 kJ/mol for CV, -6.739, -9.037 and -11.335 kJ/mol for CR at 298.15, 308.15 and 318.15 K, respectively, indicating that the adsorptions were spontaneous processes for both dyes. The positive values of ΔH further confirmed the endothermic nature of the adsorption processes and the positive ΔS values suggested the increase in randomness at the solid-liquid interface during adsorptions. Similar results were obtained during adsorption of CV on almond shells [51] and adsorption of direct red 80 and Methylene blue on potato peels [44].

Table 1
Parameters of the pseudo-first-order and pseudo-second-order kinetic models for the adsorptions of CV by unmodified and modified GS at different initial CV concentrations

C_0 (g/L)	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
	Q_e (mg/g)	k_1 (min ⁻¹)	R^2	Q_e (mg/g)	k_2 (g/mg/min)	R^2
Unmodified GS						
0.03	4.432	0.1573	0.9022	4.109	0.3653	0.9221
0.05	7.021	0.0957	0.9063	6.805	0.2152	0.9315
0.10	14.76	0.0876	0.8947	13.51	0.0791	0.9300
0.15	20.75	0.0627	0.8595	21.31	0.0330	0.9097
0.20	26.91	0.0533	0.9231	26.46	0.0300	0.9677
0.30	42.97	0.0289	0.8275	40.51	0.0101	0.9147
Sodium hydroxide modified GS						
0.03	4.561	0.0946	0.8158	4.453	0.1961	0.9284
0.05	7.136	0.0880	0.9394	7.381	0.1373	0.9658
0.10	15.02	0.0723	0.9355	14.92	0.1031	0.9611
0.15	21.81	0.0502	0.9034	22.74	0.0427	0.9488
0.20	28.93	0.0427	0.8672	27.85	0.0196	0.9451
0.30	44.64	0.0397	0.8672	43.97	0.0154	0.9428
Citric acid modified GS						
0.03	3.716	0.0256	0.8813	3.073	0.3664	0.9298
0.05	6.868	0.0244	0.8054	7.069	0.0834	0.9138
0.10	13.54	0.0179	0.9010	14.18	0.0577	0.9508
0.15	19.11	0.0043	0.8680	20.25	0.0227	0.9653
0.20	26.36	0.0033	0.8833	25.74	0.0174	0.9882
0.30	39.98	0.0030	0.8802	37.16	0.0010	0.9780

Table 2

Parameters of the pseudo-first-order and pseudo-second-order kinetic models for the adsorptions of CR by unmodified and modified GS at different initial CR concentrations

C_0 (g/L)	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
	Q_e (mg/g)	k_1 (min^{-1})	R^2	Q_e (mg/g)	k_2 (g/mg/min)	R^2
Unmodified GS						
0.1	9.345	0.1659	0.8754	9.610	0.1156	0.9877
0.5	52.59	0.1486	0.8573	58.37	0.0278	0.9999
1	108.3	0.0782	0.8910	100.7	0.0037	0.9998
3	206.6	0.0708	0.8947	202.8	0.0016	0.9998
6	390.6	0.0456	0.8628	414.3	0.0003	0.9991
10	687.1	0.0594	0.8717	604.3	0.0002	0.9976
Sodium hydroxide modified GS						
0.1	7.745	0.1032	0.8463	7.601	0.0934	0.9763
0.5	39.59	0.0994	0.9103	32.59	0.0365	0.9942
1	76.27	0.0684	0.8346	78.07	0.0028	0.9721
3	141.6	0.0532	0.9061	134.6	0.0012	0.9852
6	223.6	0.0291	0.8304	214.3	0.0003	0.9937
10	375.1	0.0203	0.8452	354.3	0.0001	0.9842
Citric acid modified GS						
0.1	11.45	0.2031	0.9032	10.61	0.1932	0.9942
0.5	59.59	0.1992	0.8856	52.59	0.0353	0.9743
1	112.3	0.1436	0.9033	116.7	0.0136	0.9943
3	261.6	0.1057	0.8842	280.5	0.0073	0.9891
6	483.6	0.0842	0.8739	504.3	0.0008	0.9903
10	740.1	0.0763	0.8992	775.3	0.0005	0.9991

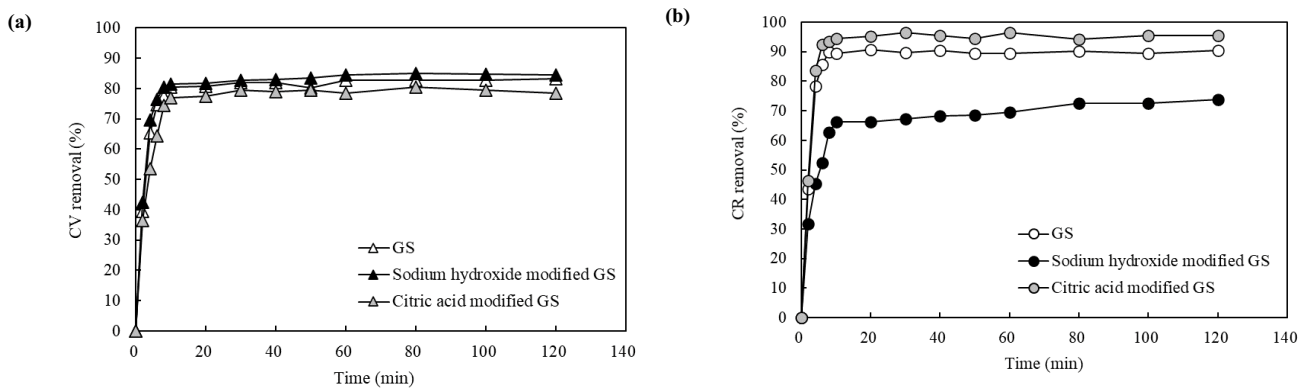


Fig. 7. Removal rates of (a) cationic dye CV and (b) anionic dye CR by unmodified and modified GS under different contact time (adsorbent dose: 0.6 g for CV and 0.8 g for CR; pH = 8 for CV and pH = 4 for CR; dye concentration: 1 g/L for CV and 0.5 g/L for CR)

3.9. Adsorption isotherm analysis

As shown in Table 4, the maximum adsorption capacities of CV and CR by GS at 308.15 K were 63.69 and 998.3 mg/g, respectively. The equilibrium parameter R_L calculated from the Langmuir constant (K_L) were 0.1202 and 0.1190 for CV and CR, respectively. The values of R_L for CV and CR were between 0 and 1 indicated that the adsorptions of CV and CR on modified GS are favorable.

4. Conclusion

In this study, novel biosorbents were prepared by modifying GS with sodium hydroxide and citric acid. Their adsorption capacities were investigated by adsorption of ionic dyes CV and CR. The results showed that the adsorption capacities of adsorbents could be significantly increased by treatment with sodium hydroxide and citric acid. The maximum adsorption capacities were 63.69 and 998.3 mg/g

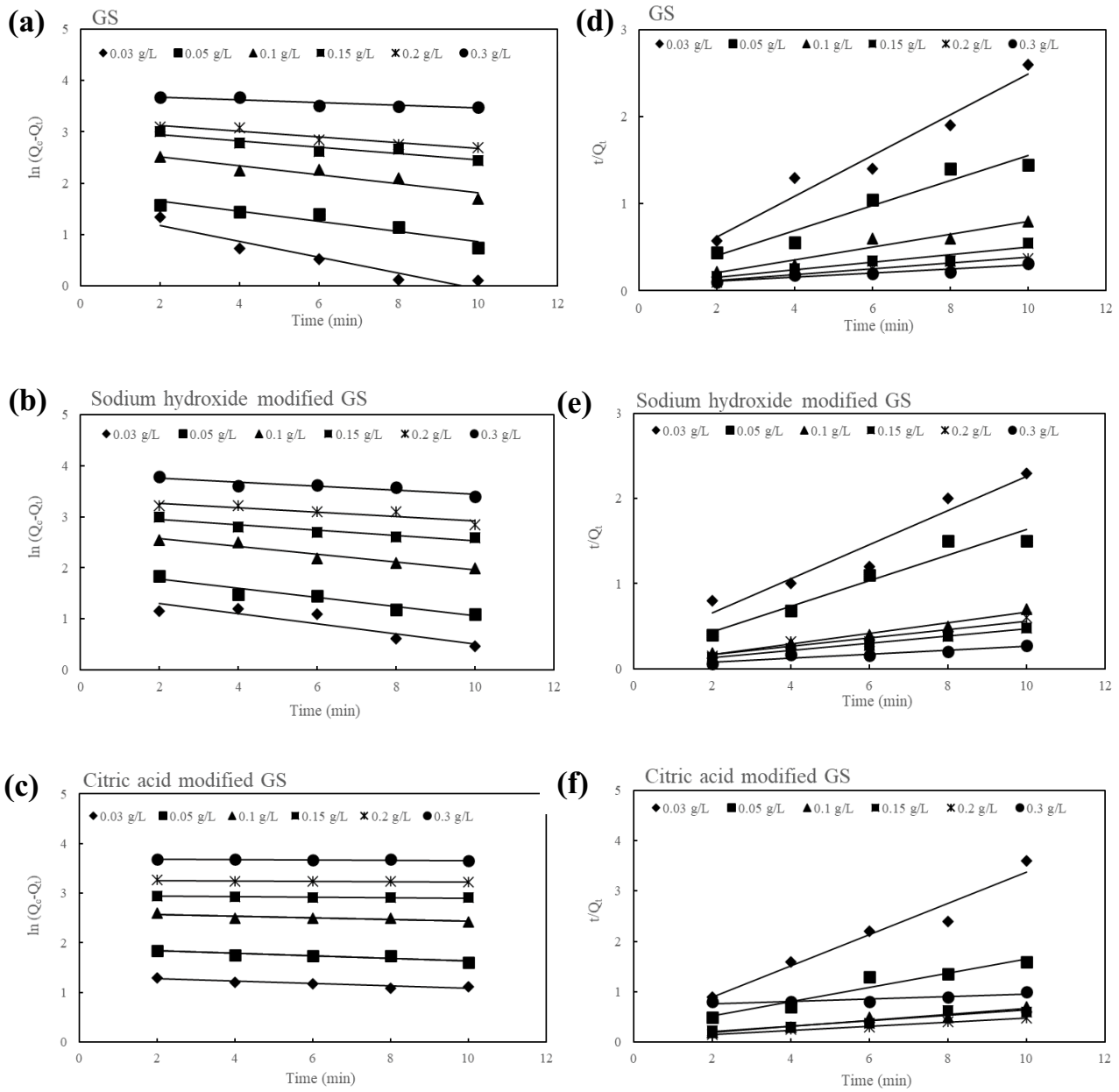


Fig. 8. Pseudo-first-order (a–c) and pseudo-second-order (d–f) kinetics for adsorptions of CV by unmodified and modified GS at different CV concentrations (0.03, 0.05, 0.1, 0.15, 0.2 and 0.3 g/L).

Table 3

Thermodynamic parameters of the adsorption of CV by sodium hydroxide modified GS and the adsorption of CR by citric acid modified GS

Dye	ΔH° (kJ/mol)	ΔS° (J/mol/k)	ΔG° (kJ/mol)		
			298.15 K	308.15 K	318.15 K
CV	17.87	80.73	-6.184	-6.991	-7.798
CR	61.74	229.8	-6.739	-9.037	-11.335

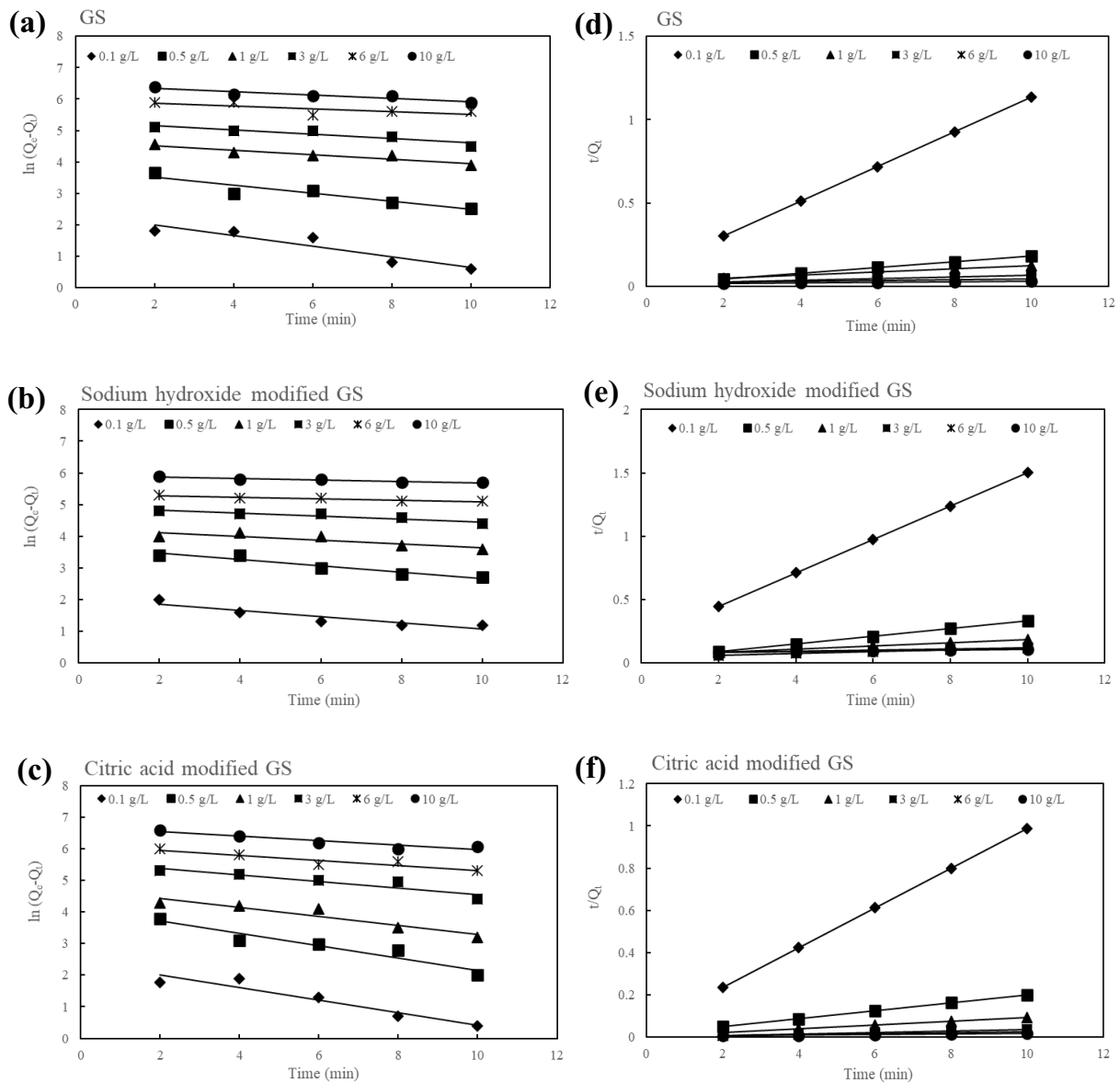


Fig. 9. Pseudo-first-order (a–c) and pseudo-second-order (d–f) kinetics for adsorptions of CR by unmodified and modified GS at different CR concentrations (0.1, 0.5, 1, 3, 6 and 10 g/L).

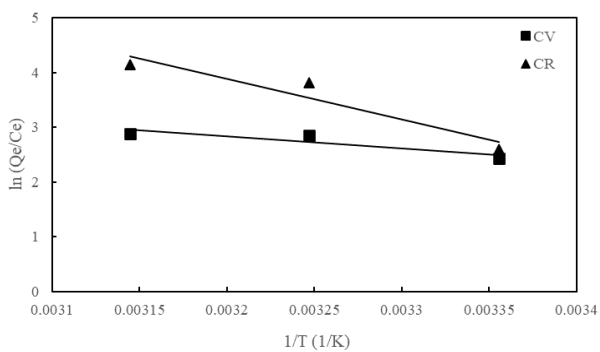


Fig. 10. Plot of $\ln(Q_e/C_e)$ vs. $1/T$ for the adsorption of CV by sodium hydroxide modified GS and the adsorption of CR by citric acid modified GS.

Table 4
Isotherm parameters of the adsorption of CV by sodium hydroxide modified GS and the adsorption of CR by citric acid modified GS at 308.15 K

Dye	Langmuir			
	Q_{max} (mg/g)	K_L (L/mg)	R_L	R^2
CV	63.69	0.02439	0.1202	0.8997
CR	998.3	0.00074	0.1190	0.8929

at 308.15 K for CV and CR, respectively. The adsorption processes fitted well with pseudo-second-order kinetic model. Thermodynamic parameters indicated that the adsorption processes were spontaneous and endothermic. In general,

this work introduced a new approach towards the utilization of GS and revealed the high potential of agricultural by-products for application to wastewater treatment considering their favorable adsorption properties and low cost.

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