Regular Article

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Adsorption Capability of Cationic Dyes (Methylene Blue and Crystal Violet) onto Poly- γ -glutamic AcidFumihiko Ogata,^a Noriaki Nagai,^a and Naohito Kawasaki^{*,a,b}^aFaculty of Pharmacy, Kindai University; 3–4–1 Kowakae, Higashi-Osaka, Osaka 577–8502, Japan; and ^bAntiaging Center, Kindai University; 3–4–1 Kowakae, Higashi-Osaka, Osaka 577–8502, Japan.

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In this study, the adsorption capability of cationic dyes, which were methylene blue and crystal violet, by poly- γ -glutamic acid (PGA) in a single or binary solution system was investigated. The effect of the molecular weight of PGA, initial dye concentration, solution pH, and temperature on the adsorption of dyes was evaluated. The adsorption mechanism of dyes onto PGA was the interaction between –COOH group on the PGA surface and the polarity groups of dyes. These results indicated that PGA is useful for removal of dyes and cationic organic compounds from a single or binary solution system.

Key words poly- γ -glutamic acid; cationic dye; methylene blue; crystal violet

Dyes are widely used in various industries including the textile, paper, plastics, rubber, and coating industries, but discharge of dyes into water sources has raised global concerns over their detrimental impact on the environment.^{1–4)} Dyes present in liquid phase increase the toxicity and chemical oxygen demand (COD) and also affect the inherent light penetration.^{5–7)} The effect of dye toxicity may be transmitted to future generations through genetic mutations, birth defects, and inherited diseases.⁸⁾

Methylene blue (MB), on contact with skin, may cause discoloration, a feeling of cold, redness, or dryness. Ingestion of this dye may cause gastrointestinal irritation; discoloration of the oral mucosa; irritation of the lips, mouth, and throat; paleness of the complexion; lack of coordination; or drowsiness.⁹⁾ Moreover, crystal violet (CV) can cause bladder cancer in human and cancer of the digestive system in other animals.¹⁰⁾ Ingestion of CV at higher concentrations causes nausea, vomiting, and central nervous system depression.⁹⁾ Therefore, cationic dyes have to be removed from environmental water. There are various removal treatment processes for dye from wastewater, for example, physical separation, advanced chemical oxidation, and biological degradation. However, these methods are expensive to apply and may produce toxic by-products.^{11–17)} The adsorption method has many advantageous points in that it is economical, simply, and effective treatment for purification of wastewater.^{18–23)}

Particularly, biopolymer-based materials are interested in using as adsorbents because they are biodegradable and nontoxic. Several polysaccharide materials such as chitin, chitosan, and materials derived from plants have been used as adsorbents for removal of dyes.^{24–26)} In addition, natural polymers obtained from bacterial sources were also used as adsorbents.^{3,27)} Poly- γ -glutamic acid (PGA) was first discovered in 1973 by Ivanovic and colleagues in the form of a capsule in *Bacillus anthracis*.²⁸⁾ PGA is reported to be the major component in the viscous sticky mucilage of Natto, a health food in Japan.²⁹⁾ PGA is an anionic polypeptide synthesized by *Bacillus* species through a fermentation process and is composed of numerous repetitive glutamic acid units connected by an unusual γ -amide bond, leaving the side chain

α -carboxyl groups free for conjugation with a wide variety of compounds.¹⁾ However, except for a very few reports on the use of PGA for metal removal, its application as an adsorbent needs further investigation.^{2,3,27,30)} In addition, there are no reports on removal or adsorption of cationic dyes in binary solution systems; therefore, investigation of adsorption of MB and CV onto PGA is very useful both for water purification and to expand the application of PGA in industrial fields. In this study, the adsorption mechanism of cationic dyes onto PGA from a single or binary solution system is evaluated based on the molecular weight (MW) of PGA, initial dye concentration, solution pH, and temperature on adsorption.

Experimental

Materials MB, CV, and PGA (average MW: 200–500, 1500–2500 kDa) were purchased from Wako Pure Chemical Industries, Ltd. (Fig. 1 shows the structures of MB and CV). The morphologies and crystallinities of the PGA were studied using scanning electron microscopy (SEM, SU1510, Hitachi, Ltd., Japan). Pure water (15.0 m Ω cm, produced by Elix® Advantage 5, Millipore, France) was used for dissolving the dye.

Amount of MB and CV Adsorbed at Different Conditions The PGA (0.05 g) was added to 100 mg/L MB or CV (200 mL), and then was stirred at 100 rpm for 3 h at room temperature. After filtration through a 0.45- μ m membrane filter, the filtrate was analyzed using a spectrophotometer (UV-1200, Shimadzu Co., Ltd., Japan). The adsorption wavelengths used for MB and CV were λ =655 and 590 nm, respectively. The

Fig. 1. Structures of MB and CV

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Fig. 2. Structures of PGA

Fig. 3. SEM Images of PGA at Different Molecular Weight

Molecular weight of (a) and (b) is 1500–2500 and 200–500kDa, respectively.

Table 1. Characteristics of PGA

Requirement	Specification of PGA	
Appearance	White to pale white, Crystalline powder-powder	White to pale white, Crystalline powder-powder
Viscosity (5 g/L, 20°C) (Calculated on the dried basis)	Under investigation	20–65 mPa · S
Solubility in sodium hydroxide solution	To pass test	To pass test
Loss on drying at 60°C in vacuum	Under investigation	Max. 10.0%
Residue after ignition (as sulfate)	Under investigation	Max. 4.0%
Average molecular weight (kDa)	200–500	1500–2500000

Source: *Bacillus subtilis chungkookjang*.

Fig. 4. Effect of Contact Time on the Adsorption of MB or CV by PGA

Initial concentration: 100 mg/L; Temperature: ambient; Amount adsorbent: 0.05 g; Agitation speed: 100 rpm. ●: 1500–2500 kDa; □: 200–500 kDa.

amount of dye adsorbed was calculated using Eq. 1:

$$q = (C_0 - C_e)V / W \quad (1)$$

where q is the amount of dye adsorbed onto PGA (mg/g), C_0 is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), V is the solvent volume (L), and W is the mass of the adsorbent (g).

In addition, effect of initial dye concentration, solution pH, and temperature on the adsorption of MB and CV in single or binary solution system was measured by following conditions. PGA (average MW: 200–500 kDa, 0.05 g) was added to 10, 50, or 100 mg/L MB or (and) CV solutions (200 mL, and initial pH 3.0, 5.0, and 10.0), and then was stirred at 100 rpm for 2–3 h at 5, 25, and 50°C. The data are presented as the mean ± standard deviation (S.D.) of 3 experiments in this study. The coefficient of variation was less than 5%, indicating a good repeatability of experiments.

Results and Discussion

Properties of Adsorbent The structure and the chemical or physical properties of PGA are shown in Fig. 2 and Table 1, respectively. In this study, we selected two different types of PGA (MW is 200–500 or 1500–2500 kDa); both PGAs appear as white to pale white crystalline powder or powder. PGA is a homo-polyamide consisting of D- and L-glutamic acid monomers, which are interlinked by amide linkages formed between the α -amino and γ -carboxyl groups. It is an optically active biopolymer having a chiral center in each glutamic unit.^{23,28,31–33} Further, it is an extracellular polymer^{31,34–36} that is completely biodegradable and nontoxic to humans.³² PGA is synthesized by several microorganisms; however, for commercial proposes, *Bacillus* species (*B. licheniformis* and *B. subtilis*) are generally used to produce PGA.^{30,34–36} The PGA used in this study was synthesized by *Bacillus subtilis chungkookjang*, and the D:L ratio is 7:3. We examined SEM imag-

Fig. 5. Effect of Initial Dye Concentration on the Adsorption of MB or CV by PGA

Temperature: ambient; Amount adsorbent: 0.05 g; Agitation speed: 100 rpm. ◇: 10 mg/L; □: 50 mg/L; ●: 100 mg/L.

Table 2. Kinetic Parameters for MB and CV Adsorption onto PGA

Samples		$q_{e, \text{exp}}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
			$q_{e, \text{cal}}$ (mg/g)	k_1 (1/h)	r	$q_{e, \text{cal}}$ (mg/g)	k_2 (g/mg/h)	r
PGA (1500–2500 kDa)	MB	362.8	49.8	3.20×10^{-2}	0.925	365.6	1.97×10^{-3}	0.999
	CV	527.6	169.2	3.52×10^{-2}	0.986	538.1	5.66×10^{-4}	0.999
PGA (200–500 kDa)	MB	349.6	57.8	3.20×10^{-2}	0.913	352.4	2.27×10^{-3}	0.999
	CV	557.4	154.4	3.13×10^{-2}	0.986	566.6	5.11×10^{-4}	0.999

es of the PGA (Fig. 3), which showed nonspherical structures. SEM images of PGA have never been reported, therefore the results obtained in this study provide useful information.

Effect of Contact Time on the Adsorption of MB and CV by PGA Figure 4 shows the effect of contact time on the adsorption of MB or CV by PGA. MB and CV required approximately 60 and 120 min, respectively, to reach equilibrium. The MW was not affected by the amount of dye adsorbed in this experimental condition. MB was adsorbed more rapidly by PGA than CV was. Inbaraj *et al.* reported the adsorption capabilities of basic brown 1, Auramine O, Rhodamine B, Safranin O, MB, and malachite green by the natural or modified biopolymer PGA.^{1–3,37} Their results showed that the time required to reach equilibrium is 5–60 min. Therefore, we could confirm similar trends in this study.

The rate constant of adsorption is determined from the pseudo-first-order equation of Lagergren and Svenska³⁸:

$$\ln(q_e - q_t) = \ln(q_e - k_1 t) \quad (2)$$

where q_e and q_t (mg/g) are the amounts of adsorbate at equilibrium and at any time t (h), respectively, and k_1 (1/h) is the adsorption rate constant. On the other hand, a pseudo-second-order equation based on equilibrium adsorption is expressed as³⁹

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (3)$$

where k_2 (g/mg/h) is the pseudo-second-order rate constant for the adsorption process.

The corresponding parameters and correlation coefficients are listed in Table 2. Although the correlation coefficient values in the pseudo-first-order model are higher than 0.913,

the experimental $q_{e, \text{exp}}$ values do not agree with the calculated ones. The values of $q_{e, \text{exp}}$ for PGA were much closer to the values of $q_{e, \text{cal}}$ in the pseudo-second-order model than to those in the pseudo-first-order model. The correlation coefficients for the pseudo-second-order model are greater than 0.999, indicating the applicability of this kinetic equation and the second-order nature of the adsorption process of dyes on PGA. The success of the pseudo-second-order model in fitting the experimental data suggests that the dyes are chemisorbed on PGA.^{40–42}

Effect of Initial Dye Concentration on Adsorption of MB or CV by PGA Figure 5 shows the effect of the initial dye concentration on adsorption of MB or CV by PGA. The adsorption rate of MB and CV increases with decreasing initial concentration. The residual percentages of MB or CV at 10, 50, and 100 mg/L after 120 min were 0, 0, and 3.2% or 1.9, 3.9, and 5.4%, respectively; these results suggest that PGA treatment was very useful for removing dyes from aqueous solution. In addition, we confirmed the changes in the MB or CV solution (Fig. 6).

Effect of pH on Adsorption of MB or CV by PGA The pH value of the solution is an important factor that determines the adsorption of solutes when sorption occurs principally through the chemisorption mechanism. Figure 7 shows the effect of pH on adsorption of MB or CV by PGA. The amount of dye adsorbed onto PGA increased with increasing solution pH. It is evident that for an initial concentration of 100 mg/L, the dye adsorption rose by 71.8, 91.3, and 96.8% for MB and by 79.4, 97.5, and 98.2% for CV at initial pH values of 3.0, 5.0, and 10.0, respectively. This result is explained as follows:

Fig. 6. Photographs of MB and CV Adsorption by PGA

Fig. 7. Effect of pH on the Adsorption of MB or CV by PGA

Initial concentration: 100 mg/L; Temperature: ambient; Amount adsorbent: 0.05 g; Agitation speed: 100 rpm. ●: pH 3.0; □: pH 5.0; ◇: pH 10.0.

at low pH values, excessive hydrogen ions in the solution may compete with the dye cations for the active sites (COO^-) of PGA; hence, a reduction in dye adsorption was observed. In addition, the reported pK_a value (4.29) of glutamic acid in the protein pK_a database,⁴³⁾ which is due mainly to the ionizable group $-\text{COOH}$, suggests that a dye solution at pH values above this pK_a value would cause the $-\text{COOH}$ group in PGA to become completely deprotonated, facilitating maximum exchange of dye cations. Sorption through ion exchange is favored at high pH values, especially when the sorption rate is controlled mainly by ion exchange rather than by complexation.^{1-3,37,44-46)}

Effect of Temperature on Adsorption of MB or CV by

PGA The effect of temperature on adsorption of MB or CV by PGA is shown in Fig. 8. The amount of dye adsorbed onto PGA clearly increased with increasing temperature. The temperature is a major factor influencing the adsorption process. Dye adsorption by PGA was monitored at three temperatures (5, 25, 50°C). The thermodynamic parameters [standard free energy change (ΔG), enthalpy (ΔH), entropy (ΔS)] were calculated; ΔG was obtained using the following equation:

$$\Delta G = -RT \ln K \quad (4)$$

According to the van't Hoff equation, the equilibrium constant K can be obtained by finding the slope of the plot of $\ln(q_e/C_e)$ against C_e at different temperatures and extrapolating

Fig. 8. Effect of Temperature on the Adsorption of MB or CV by PGA

Initial concentration: 100 mg/L; Amount adsorbent: 0.05 g; Agitation speed: 100 rpm. $\diamond$: 5°C; $\square$: 25°C; $\bullet$: 50°C.

Table 3. Thermodynamic Parameters for the Adsorption of Dyes onto PGA

Samples	ΔH (kJ/mol)	ΔS (J/mol K)	ΔG (kJ/mol) at temperature		
			5°C	25°C	50°C
MB	0.5	39.9	-10.7	-11.1	-12.5
CV	15.3	90.5	-9.8	-11.7	-13.9

indicate that MB or CV adsorption was spontaneous.⁴⁸⁾ The positive values of ΔS (39.9 and 90.5 J/mol K for MB and CV, respectively) indicate that the randomness at the interface between the solid and the solution increased during adsorption. Moreover, the positive ΔH values confirmed the endothermic nature of the adsorption process, which is also demonstrated by the enhancement of dye adsorption at higher temperatures.⁴⁹⁾

Amount of MB and CV Adsorbed onto PGA in Single or Binary Solution System

The amount of MB and CV adsorbed by PGA in a single or binary solution is shown in Fig. 9. PGA showed adsorption capability for MB and CV in a binary solution. The amount of dye adsorbed in a single solution was greater than that adsorbed in a binary solution, indicating that MB and CV competed with each other for PGA adsorption sites. In addition, the removal percentages of MB and CV were 19.7 and 13.9% smaller, respectively, in a binary solution system. We confirmed the changes in the dyes in solution by the shifts in the wavelength (Fig. 10). Previous studies had not reported removal or adsorption of dyes onto PGA in binary or ternary solution systems. However, considering application in industrial fields, it is very important to evaluate the removal or adsorption of dyes from complex solution systems. The data obtained in this study are very useful for purification of dye effluent. Both the pseudo-first-order and pseudo-second-order models were applied to the data in Fig. 9. The corresponding parameters and correlation coefficients are listed in Table 4. The correlation coefficients of the pseudo-second-order kinetic model (MB: 0.980, CV: 0.992) are greater than those of the pseudo-first-order kinetic model (MB: 0.792, CV: 0.781) for adsorption of MB and CV onto PGA. This suggests that the rate-limiting step may be chemisorption and that the rate equation follows the pseudo-second-order model.⁴³⁾ The experimental values of the uptake were close to the uptake values obtained by the pseudo-second-order kinetic model. Similar trends were previously observed in Fig. 4 and Table 2.

Effect of pH on Adsorption of MB or CV by PGA in Binary Solution System

Figure 11 shows the effect of pH on adsorption of MB or CV by PGA in a binary solution system. The amount of dye adsorbed was in the order pH

Fig. 9. Amount of MB and CV Adsorbed by PGA in Single or Binary Solution System

Initial concentration: 100 mg/L; Temperature: ambient; Amount adsorbent: 0.05 g; Agitation speed: 100 rpm. $\diamond$: MB (single); $\blacktriangle$: CV (single); $\square$: MB (binary); $\bullet$: CV (binary).

to zero C_e . R is the gas constant [=8.31 J/(mol K)]. The values of ΔH and ΔS were determined from the slope and intercept of a plot of $\ln K$ versus $1/T$.⁴⁷⁾

The thermodynamic parameters for adsorption of dyes are shown in Table 3. The ΔG value decreased when the temperature was increased from 5 to 50°C, suggesting an increase in the reaction spontaneity. The negative values of ΔG (-10.7 to -12.5 and -9.8 to -13.9 kJ/mol for MB and CV, respectively)

Fig. 10. Shifts of Wavelength of MB or CV Adsorption by PGA in Binary Solution System

Table 4. Kinetic Parameters for MB and CV Adsorption onto PGA

Samples	$q_{e, \text{exp}}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
		$q_{e, \text{cal}}$ (mg/g)	K_1 (1/h)	r	$q_{e, \text{cal}}$ (mg/g)	K_2 (g/mg/h)	r
MB	321.0	126.9	4.30×10^{-3}	0.792	306.8	3.13×10^{-4}	0.980
CV	418.3	122.7	5.60×10^{-3}	0.781	407.9	3.78×10^{-4}	0.992

Fig. 11. Effect of pH on the Adsorption of MB or CV by PGA in Binary Solution System

Initial concentration: 100 mg/L; Temperature: ambient; Amount adsorbent: 0.05 g; Agitation speed: 100 rpm. ●: pH 3.0; □: pH 5.0; ◇: pH 10.0.

Table 5. Comparison of MB and CV Adsorption Capacities of Various Adsorbents

Adsorbents	Adsorption capacity (mg/g)		Reference
	MB	CV	
PGA	349.6	557.4	This study
Uncalcined RB	325.9	783.8	50)
RB1000	172.5	401.3	50)
ZnO-NRs-AC	89.3	93.5	51)
Rice husk activated carbon	343.5	—	52)
AG-NPs-AC	71.4	—	53)
Banana waste	243.9	—	54)
Palm kernel fiber	—	78.9	55)
Tomato plant root	—	94.3	56)

3.0 < pH 5.0 < pH 10.0. In addition, the amount adsorbed in a single solution was greater than that adsorbed in a binary solution (Fig. 7). The data obtained in this study showed that one adsorption mechanism is related to the $-\text{COOH}$ group in PGA, and another is competition between the dyes for PGA adsorption sites.

Comparison of Adsorption Capacities for MB and CV
Table 5 summarizes the reported adsorption capacities of various MB and CV adsorbents in the literature.^{50–56)} The data show that PGA has higher adsorption capacities than many of the other reported adsorbents for MB and CV. Therefore, it can be concluded that PGA is an efficient adsorbent for removal of MB and CV from aqueous solution.

Conclusion

In this study, the adsorption capability of PGA for cationic dyes (MB, CV) was investigated. PGA shows the ability to adsorb MB and CV in a single or binary solution. MB and CV required approximately 60 and 120 min, respectively, to reach equilibrium. The adsorption data were fitted to the pseudo-second-order kinetic model (correlation coefficient: 0.999) and the pseudo-first-order kinetic model (correlation coefficient: 0.913–0.986). The amount of dye adsorbed increased with increasing solution pH and temperatures. The adsorption mechanism of cationic dyes was related to active sites (COO^-) on the PGA surface. From the thermodynamic parameters, the negative values of ΔG (-10.7 to -12.5 , -9.8 to -13.9 kJ/mol for MB, CV, respectively) indicate that the MB or CV adsorption process was spontaneous. Moreover, the amount adsorbed in a single solution was greater than that adsorbed in a binary solution, indicating that the dyes competed with each other for adsorption sites on the PGA surface. The removal percentages of MB and CV were 19.7 and 13.9% smaller, respectively, in a binary solution system. The adsorption capability of PGA for the dyes was greater than that of previously reported adsorbents. Taken together, these results indicate that the adsorbent PGA can be used as an efficient sorbent for removal of dyes, e.g., MB and CV, and has potential applications in environmental and related industrial areas.

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Conflict of Interest The authors declare no conflict of interest.

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