

Application of Modified Persimmon Tannin Gels in the Removal of Dyes from Aqueous Solution

L. O. AHMAD^{1*}, D. A. MURGUIA FLORES², H. OKUMURA³, Y. KANEKI², M. HONDA², M. SUDA²,
and K-K. KUNIMOTO²

¹Department of Chemistry, Universitas Halu Oleo, Kendari, Sulawesi Tenggara, Indonesia 93232

²Graduate School of Natural Science & Technology, Kanazawa University, Kakuma-machi,
Kanazawa 920-1192, Japan

³Department of Materials Engineering, Nagaoka National College of Technology, Nishikataki-machi,
Nagaoka 940-8532, Japan

*la.ode.ahmad@gmail.com <http://www.uho.ac.id>

Abstract: - Persimmon tannins (PTs) were modified using formaldehyde and amine compound. The formaldehyde-modified (F) PT gel was prepared through cross-linking PT with various concentrations of formaldehyde under acidic conditions. The amine-modified (A) PT gel was brought out by reacting PT with formaldehyde and ammonium chloride in combination. Their adsorption of methylene blue (MB) and remazol brilliant orange 3R (RBO) in aqueous solution was considered. The gels were characterized using Fourier transform-infrared spectrometry. In the FPT gel, the intensity of the aromatic C-H bending vibration at 1030 cm^{-1} decreased with increasing formaldehyde concentration, indicating that formaldehyde crosslinking occurs in the aromatic rings. In contrast, in the APT gel, shoulders were newly observed around 3200 cm^{-1} and 1070 cm^{-1} , which can be respectively assigned to N-H and C-N stretching of the aminomethyl group. Batch adsorption studies were directed to investigate the adsorb ratio of the gels to dyes. The FPT gel is proven to be an effective material for adsorbing basic/cationic dyes, while the APT gel effectively absorbs acidic/anionic dyes from aqueous solution.

Key-Words: - adsorption, dye, gel, methylene blue, persimmon tannin, remazol brilliant orange 3R

1 Introduction

Organic dyes are widely used in various industries such as textiles, cosmetics, foods, printing and plastics. Industrial dyestuff effluents are a major source of environmental pollution because of their strong color, hazard to human health, high chemical oxygen demand and low biodegradability. Thus, the removal of dye is critical during wastewater treatment.

Many techniques have been built up for removing dyes from aquatic environments, including biological, chemical and physical methods. Adsorption techniques are advantageous because of their low price and ease. While various activated carbon substrates are characterized by excellent adsorption properties, they are generally cost-prohibitive. Therefore, researchers are concentrating on alternative low-cost adsorbents with high adsorption properties [1].

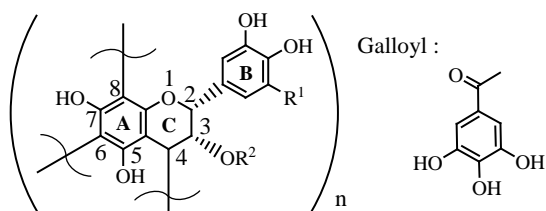
Natural materials are potential low-cost and eco-friendly adsorbents [2]. Tannins represent a promising class of adsorbents. Tannins are

polyphenolic compounds widely distributed in many plant species, where they serve as a defense mechanism against predators. They form complexes and precipitates with macromolecules such as proteins, lipids, polysaccharides, and heavy metals [3] [4] [5].

Tannins are water-soluble compounds, which limits their practical application as adsorbents in aqueous systems. Hence, tannin gelation by crosslinking, or immobilization of tannins in water-insoluble matrices, are methods used to overcome this issue [6]. Various methods have been reported for tannin gelation; most involve formaldehyde or other aldehydes in basic or acidic media [7] [8] [9]. Other researchers have reported acidic gelation [10] and autoxidation processes [11].

Young persimmon fruits (*Diospyros kaki* L.) contain abundant persimmon tannins (PTs), which are chemically classified as condensed tannins (proanthocyanidins). Low molecular weight soluble PTs are thought to be responsible for the astringency of persimmon fruit. The primary structure of PT

consists of two types of flavan-3-ols, catechin (CA) and gallocatechin (GC), and their gallated forms, CA-3-O-gallate (CG) and GC-3-O-gallate (GCG), with carbon-carbon interflavan linkages at the C-4 position of one unit and the C-8 (or C-6) position of the other. The stereochemistry of the flavan-3-ol unit of PT is predominantly 2,3-cis, which corresponds to an epi-type catechin, as depicted in Fig. 1 [12].



$R^1 = \text{H or OH}$, $R^2 = \text{H or galloyl}$

Fig. 1 Proposed chemical structure of PT [13]

We previously showed the removal of caffeine, a typical purine base, from a green tea infusion using a PT gel. The gel was prepared by an autoxidation process of a soluble PT solution [13]. The gel showed selective adsorption of basic compounds; however, considerable preparation time was required. This study extends our previous work by reporting on the preparation of a PT gel formed with formaldehyde under acidic conditions. The adsorption properties of the gel of dyes such as methylene blue (MB), a basic/cationic dye, were investigated. Furthermore, we looked into the adsorption properties of the PT gel for an acidic/anionic dye, such as remazol brilliant orange 3R (RBO), using the aminomethylation reaction [14] (Wang et al. 2013).

2 Materials and Methods

2.1 Materials

MB and RBO were obtained from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan and DyStar Singapore Pte. Ltd., respectively. Chemical structures are shown in Fig. 2. Soluble PT (*kakishibu*) was a kind gift from Kakitafu Co., Ltd. (Osaka, Japan). Formaldehyde (37%) was obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Ammonium chloride was purchased from Nacalai Tesque, Inc. (Kyoto, Japan). All other chemicals used were commercial products of analytical reagent grade. Ultra-pure water (Arium

611UV system; Sartorius, Göttingen, Germany) was used throughout this study.

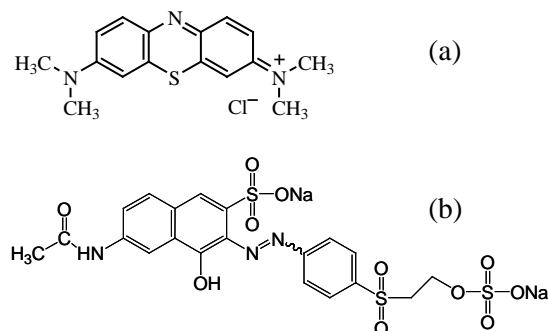


Fig. 2 Chemical structure of (a) MB and (b) RBO

2.2 Gel preparation

2.2.1. Preparation of formaldehyde-modified PT gel

A 5% PT solution (20 mL) was gelled by cross-linking with various volumes of a 37% formaldehyde solution (0.02-20 mL) at room temperature. The mixture was diluted to 40 mL with ultra-pure water, and 0.4 mL of HCl solution was then summed. The solution was stirred at 250 rpm for 2 hours, then went away overnight at room temperature. The obtained gel was crushed and washed with ultra-pure water until the supernatant was clear. The gel was stored in a brown bottle in a wet state, and was termed formaldehyde-modified persimmon tannin (FPT) gel. The same batch of FPT gel was used for all adsorption experiments.

2.2.2. Preparation of amine-modified PT gel

Formaldehyde solution (37%) and ammonium chloride were mixed at 1 mL and 660 mg or 0.01 mL and 6.6 mg, respectively. The mixtures were diluted to 10 mL with ultra-pure water. The mixtures were stirred at 250 rpm for 1 hour, and 10 mL of 5% PT solution was then summed. The mixture was stirred at 250 rpm for 24 hours at room temperature. The obtained gel was crushed and washed with ultra-pure water until the supernatant was clear. The gel was stored in a brown bottle in a wet state, and named amine-modified persimmon tannin (APT) gel. The same batch of APT gel was used for all adsorption experiments.

2.3 Characterization of gels

Infrared (IR) spectra of dried FPT and APT gels were recorded using a Horiba FT-720 Fourier

transform infrared (FT-IR) spectrometer (Horiba, Kyoto, Japan). FT-IR measurements were recorded using KBr discs, and spectra from 20 scans at 4 cm^{-1} resolution were averaged.

2.4 Adsorption experiments

The batch method was applied to assess the adsorption behavior of the FPT gel. Experiments were carried out in 20 mL screw cap tubes containing 0.05 g of FPT gel dosage per 20 mL solution, an initial dye concentration of 75-175 mg/L, and pH neutral. The mixture was stirred at 250 rpm at $30\text{ }^{\circ}\text{C}$. The contact time ranged between 0 and 90 minutes. Afterwards, the mixture was centrifuged at 10,000 rpm, and the absorbance of the supernatant was recorded by a Shimadzu UV-2500 spectrophotometer (Shimadzu Corp., Kyoto, Japan) using 10 mm path length quartz cuvettes.

The same experimental set up was carried out to obtain the adsorption behavior of the APT gel for RBO. Nevertheless, the initial dye concentration ranged between 100 and 200 mg/L.

All experiments were done in duplicate. The adsorbed ratio (%) was calculated from:

$$\text{Adsorbed ratio} = ((C_0 - C_t)/C_0) \times 100 \quad (1)$$

where C_0 and C_t are the initial and at time t dye concentrations in solution (mg/L), respectively.

3 Results and Discussion

3.1 Characterization of gels

Figure 3 compares the IR spectra of freeze-dried PT with those of FPT gels prepared with various formaldehyde concentrations. Several IR bands characteristic of polyphenols can be distinguished. The hydrogen-bonded O-H stretching vibration of the phenolic group is seen as a broad intense band at ca. 3300 cm^{-1} . The C=O stretching vibration of the galloyl group is observed at ca. 1700 cm^{-1} . Aromatic C=C stretching modes dominate the $1400\text{-}1600\text{ cm}^{-1}$ region. The mixed C-O stretching and O-H bending vibrations are observed at $1150\text{-}1350\text{ cm}^{-1}$. The aromatic C-H bending vibration at 1030 cm^{-1} (denoted by an arrow) in the spectrum of freeze-dried PT exhibits a decreasing intensity in the spectra of FPT gels with increasing formaldehyde content in the gels. This finding suggests that cross-

linking with formaldehyde occurs at the aromatic rings.

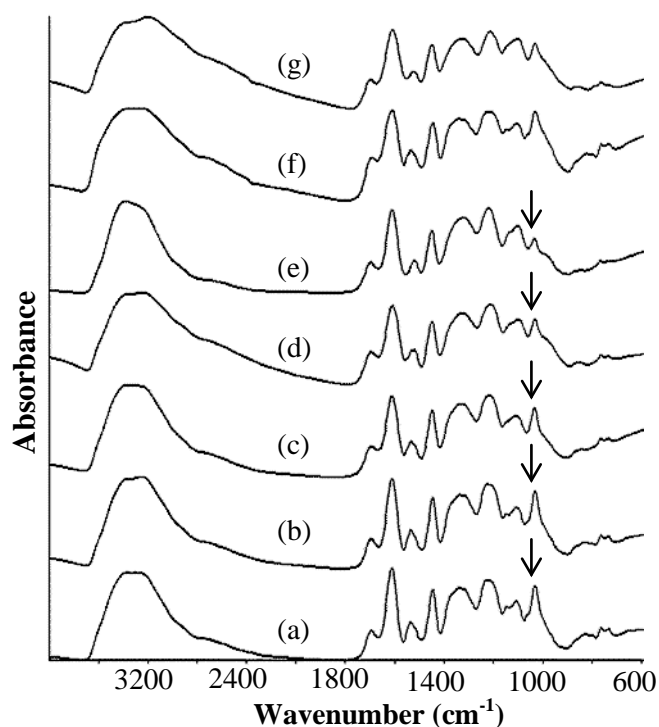


Fig. 3 IR spectra of (a) freeze-dried PT, (b)-(e) FPT gels prepared from 0.02, 0.2, 2.0 and 20% concentration formaldehyde solutions, respectively, (f) APT gels prepared from 0.02% formaldehyde solution and 6.6 mg ammonium chloride and (g) APT gels prepared from 2.0% formaldehyde solution and 0.66 g ammonium chloride

Figure 3 also shows the IR spectra of APT gels ((f)-(g)). In the APT gel spectra, shoulders are newly observed around 2300 cm^{-1} and 1070 cm^{-1} , which are assigned to N-H stretching and C-N stretching bands, respectively. This notice suggests the existence of an aminomethyl group in the APT gels. The intensities of the shoulders increase in the APT gels with increasing ammonium chloride content. This finding also supports the proposed aminomethylation in the APT gels. Decrease in the intensity of the aromatic C-H bending vibration at 1030 cm^{-1} is also observed in the APT gel spectra, suggesting cross-linking at the aromatics rings similar to the FPT gels.

3.2 Comparison of the adsorption capacity of FPT and APT gels

The observed adsorbed ratio of MB is higher for the FPT gel than the APT gel (Table 1). MB showed a

larger adsorbed ratio for the FPT gel than RBO. This is because the positive charges of MB can interact with the electronegative phenolic OH moieties of the FPT gel, while the anionic dye RBO repulses these moieties. In contrast, the adsorption of RBO is higher in the APT gel than in the FPT gel (Table 1). Electrostatic attraction occurs between the APT gel and RBO, while MB is repulsed by the APT gel. Thus, the aminomethylation of the PT gel enhanced its adsorption of acidic dyes. These results indicated that the FPT gel is an effective adsorbent for cationic dyes, whereas the APT gel effectively adsorbs anionic dyes.

Table 1 Adsorbed ratio for different PT gel to MB and RBO (Initial dye concentration: 100 mg/L; contact time: 60 min; temperature: 30 °C; volume of dye solution: 20 mL; pH: neutral; gel dosage: 0.05 g)

Gel	Adsorbed ratio (%) to	
	MB	RBO
FPT	58.4	3.3
APT	2.3	96.6

We also examined the effect of formaldehyde concentration on FPT gel adsorption of MB. An inverse relationship between formaldehyde concentration and MB adsorption was observed. As the concentration of formaldehyde increases, there is a concomitant growth in the act of cross-linkages formed, which contributes to a reduction in the nucleophilicity of the phenolic rings, consequently reducing MB adsorption to the gelatin. This finding is supported by the FT-IR spectra shown in Fig. 3 ((b)-(e)).

For the APT gel, the degree of aminomethylation in the PT gel increases with increasing ammonium chloride concentration. These results are also consistent with the FTIR analysis, as shown in Fig. 3 ((f)-(g)). Therefore, the higher the ammonium chloride concentration, the greater the APT gel adsorption of RBO.

4 Conclusion

PT was cross-linked with formaldehyde under acidic conditions, and the obtained FPT gel was employed in adsorption experiments of MB in aqueous solution. Also, PT was amine-modified and employed to adsorb RBO in aqueous solution. The interaction between adsorbent and adsorbate occurred via hydrogen bonding with a weak

attractive force. The FPT gel represents an effective adsorbent for basic/cationic dyes, whereas the APT gel can effectively adsorb acidic/anionic dyes from aqueous solution.

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