

## Waste coffee-grounds as potential biosorbents for removal of acid dye 44 from aqueous solution

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**Abstract**—Waste coffee-grounds (CG) with micro- and macropores are a potential biosorbent for the removal of organics or heavy metal ions from aqueous solutions. In several studies, CG was used as adsorbent for removal of heavy metal ions and organics (phenolic compounds). We investigated the potential application of CG as biosorbents for the removal of acid dye (Acid Red 44). To evaluate objectively the adsorption performance of the CG, conventional adsorbent (DA, Degussa alumina) was also tested and our previous reported data for mesoporous materials compared. In adsorption kinetics, experimental data followed the pseudo-second-order kinetic model and intraparticle diffusion was rate-controlled. The maximum uptake ( $Q_m$ ) capacity of CG proved half of DA, but its adsorption rate was fast (less than 1 h). Namely,  $Q_m$  of CG is 27.8 mg/g, and smaller than that of mesoporous adsorbents. However, coffee-ground biosorbent still possesses economical advantages compared to inorganic adsorbents.

Key words: Biosorbents, Coffee-ground Dye, Wastewater, Alumina, Waste-to-wealth

### INTRODUCTION

A typical example of adsorbents used for indoor air purification is charcoal, which generally adsorbs volatile organic compounds (VOCs). Such biomass-based adsorbents like charcoal are referred to as biosorbents. Rice husks, wheat shells, and tree leaves as biosorbents are also used to remove organic pollutants and heavy metal ions from wastewater [1]. Their adsorption capacity for phenolic compounds, dyes, and heavy metal ion is reported as 1-50, 10-100, and 10-50 mg/g, respectively. Its efficient capacity allows its use as conventional adsorbents. Another biosorbent besides biomass-based adsorbents cited in the literature can be found in daily life, namely, waste coffee-grounds (CG).

Coffee consumption in Korea is ranked as 11<sup>th</sup> in the world, with an average of 0.8 cups of coffee per day. Waste coffee-grounds after roasting and dripping *via* the drip brewing method are often used as a fragrance. For the dripping process, water penetrates into the coffee-ground and absorbs the liquid compounds and essence from the coffee, subsequently establishing the final, textural micro- or macropores within the coffee-grounds. Therefore, this porous material has the potential for use as a biosorbent to remove organic compounds from wastewater. For coffee-grounds, the potential application as an adsorbent has been reported for heavy metal ions [2-4], but few papers have been published. The adsorption capacity for  $Pb^{2+}$  and  $Cd^{2+}$  is approximately 20-160 and 10-40 mg/g, respectively, while that for methylene blue is 18 mg/g [5].

In general, an ideal adsorbent should have uniformly accessible pores, a high surface area, and chemical stability. To match these requirements, tailor-made adsorbents with uniform nanopores have

been suggested, such as mesoporous silica [6] and nanoporous alumina [7]. Their adsorption capacity is very high compared to conventional adsorbents, and they are widely used for removal of heavy metal ions and organic compounds. However, it is not as easy to commercialize as the conventional ones, due to high manufacturing costs. Although waste coffee-grounds have ill-defined pore structure and low surface area compared with mesoporous silica and activated carbon, it is economical to reuse waste (waste-to-wealth). Therefore, as a proof-of-concept test, we attempted to use waste coffee-grounds as adsorbents for removal of organic dye from wastewater.

The dyeing industry employs massive wastewater producing processes with various synthetic chemicals, accounting for 5% of the wastewater emission facilities, but 25% of the total pollution load in the water system. Moreover, dyes discharged through the dyeing process inhibit light penetration and do not easily decompose under biological treatment [8]. Therefore, adsorption and advanced oxidation processes are used to effectively treat dye contained in wastewater [9]. Acidic dyes are widely used in the manufacturing process of animal fibers like angora, wool, mohair, and silk, while basic dyes are extensively used in the dyeing of vegetable-tanned leather. Among those, we selected an acidic dye (Acid Red 44 with red color) as the target dye, with properties of accurate composition, water solubility, and non-toxicity. Adsorbents reported in the literature used to remove Acid Red 44 are mesoporous alumina and silica, with ca. 4,000 and 150 mg/g uptake capacities, respectively [10,11]. As mentioned before, although their performance is excellent, their high manufacturing cost is a drawback.

In this work, the adsorption characteristics of an acidic dye for waste coffee-grounds were investigated to confirm that waste coffee-grounds are possible to use as a biosorbent. Degussa alumina was selected as the adsorbent of comparison, which is referred to as the artificial adsorbent.

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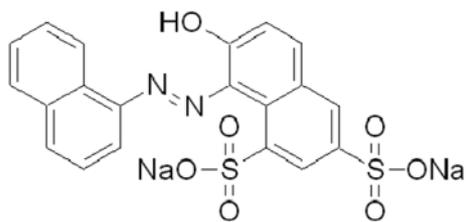


Fig. 1. Chemical structure of acid red 44.

## EXPERIMENTAL

### 1. Materials

Acid Red 44 ( $C_{20}H_{12}N_2Na_2O_7S_2$ ) was purchased from Sigma-Aldrich, and a working solution with concentration of 1.0–100 mg/L was prepared in deionized water. As shown in Fig. 1, Acid Red 44 possesses two  $SO_3^-$  and one OH functional groups; thus the adsorbent with the positive charge will be combined with the  $SO_3^-$  groups *via* charge matching. Its molecular size is assumed to be approximately 5 Å (radius) × 15 Å (length) [11]. Coffee-grounds were obtained from Caffé MAURO and were composed of 10% Arabica and 90% Robusta beans. Conventional alumina, as a comparison adsorbent, was purchased from Degussa Company, with an average pore size and surface area of 40 nm and 103 m<sup>2</sup>/g, respectively [7]. Herein, the coffee-grounds and Degussa alumina will, respectively, be referred to as CG and DA.

### 2. Biosorbent Preparation

Waste coffee-grounds, after roasting and dripping, were washed over 10 times with deionized water, ethanol, and NaOH to remove the brown color and residual organics. They were then dried at 100 °C for 10 h. This washing procedure proved helpful in reducing color leaching with the organics during the isotherm experimental. The Degussa alumina was also dried in a convection oven using the same

procedure.

### 3. Analysis of Acid Red 44

The dye concentration in aqueous solution was measured using absorption in a UV/Vis spectrophotometer (UV-1800, Shimadzu) at a characteristic wavelength. The maximum absorbance of the dye was 513 nm. To analyze the surface charge of the adsorbents at various pH values, the zeta potential of the dried biosorbent was analyzed with electrophoretic light scattering spectroscopy (ELS-Z, Photal Otsuka Electronics).

### 4. Isotherms and Kinetics Studies

To determine the optimum pH for the maximum uptake of the acidic dye, several buffer solutions between pH 1 and 11 were used as stock solutions. After establishing the optimum pH, isotherms and kinetics studies were worked with at that point, which were adjusted using HCl and NaOH solutions.

The equilibrium concentrations for the Acid Red 44 were controlled at 1–100 mg/L of dye. Approximately 0.1 g of dried adsorbents (coffee-grounds and Degussa alumina) was added to 100 mL of a solution prepared at a predetermined dye concentration using deionized water, followed by shaking at room temperature for 12 h. The samples were separated by filtration, and the adsorption capacities calculated from the difference between the initial and final concentrations. To ascertain the dependence of the initial concentration ( $C_o$ ) of the dye upon adsorbent, the adsorption ratios for different  $C_o$  (25, 35, 45, 75, 100 mg/L) were tested over elapsed time. Several isotherms, Freundlich, Langmuir, and Dubinin-Radushkevich, were examined to establish the most appropriate correlation with the equilibrium curves. The maximum uptake capacity was calculated by using the Langmuir equation.

A kinetics study was carried out at different intervals of time according to the above procedure to determine the rate of dye removal by CG and DA. The rate constants were calculated using the conventional rate expression, such as a pseudo-second-order equation,

Table 1. Isotherms and kinetics equations used in this work

|                                  | Equations                           | Remarks  |
|----------------------------------|-------------------------------------|--|
| Isotherms                        |                                     |  |
| Freundlich                       | $Q_e = K_F C_e^n$                   | $C_e$ : equilibrium concentration on the solution<br>$Q_e$ : equilibrium concentration on the adsorbent<br>$K_F$ : Freundlich adsorption capacity<br>$n$ : Freundlich exponent |
| Langmuir                         | $Q_e = Q_m K_L C_e / (1 + K_L C_e)$ | $K_L$ : Langmuir adsorption capacity<br>$Q_m$ : maximum adsorption capacity  |
| Dubinin-Radushkevich             | $Q_e = Q_s \exp(-B \varepsilon^2)$  | $Q_s$ : constant of Dubinin-Radushkevich<br>$B$ : constant correlated with sorption energy<br>$\varepsilon$ : constant correlated with $C_e$                                   |
| Kinetics                         |                                     |  |
| Pseudo-second-order rate         | $t/Q_t = 1/(k_{ad} Q_e^2) + t/Q_e$  | $Q_t$ : adsorption capacity of adsorbent at time $t$<br>$k_{ad}$ : rate constant of adsorption<br>$t$ : time   |
| Intraparticle diffusion rates    | $Q_t = k_{id} t^{1/2}$              | $k_{id}$ : rate constant of intraparticle diffusion  |
| Thermodynamics                   |                                     |  |
| Equilibrium constant (K)         | $K = C_{ad,e} / C_e$                | $C_{ad,e}$ : equilibrium concentration on the adsorbent  |
| Gibbs free energy ( $\Delta G$ ) | $\Delta G = -RT \ln(K)$             | $T$ : temperature<br>$R$ : gas constant  |

as suggested by Ho [12]. The rate constant for intraparticle diffusion ( $k_{if}$ ) was calculated by the Weber-Morris equation [13]. In addition, a thermodynamic study was conducted at three isotherm points (25, 35, 45 °C) to determine the Gibbs free energy ( $\Delta G$ ) for adsorption. Equations correlated with isotherms and kinetics studies are summarized in Table 1.

## RESULTS AND DISCUSSION

The surface charge (zeta potential) of the CG and DA adsorbents in the aqueous solutions was analyzed with the ELS-zeta. The target adsorbate (Acid Red 44) possessed negative functional groups ( $\text{SO}_3^-$ ), and thus, the surface of the adsorbents should be represented with a positive charge. The pH value at the point of zero charge ( $\text{pH}_{\text{pzc}}$ ), at which the surface charge becomes neutral and the effect of ionic strength on the surface  $\text{H}^+$  exchange diminishes, was 6.0 and 8.5 for CG and DA, respectively. Because CG and DA were charged positively under  $\text{pH}_{\text{pzc}}$ , they can be used as adsorbents for dyes for low-pH solutions. In SEM image (not shown here), CG showed irregular pore structure with ca. 50-100  $\mu\text{m}$ , and  $\text{N}_2$  adsorption/desorption result showed 0.1162  $\text{m}^2/\text{g}$  of surface area.

To determine the optimum pH for complete dye removal, an equilibrium test was carried out at ten different pH levels from 1 to 10. As shown in Fig. 2, it is clear that the adsorption capacities of CG and DA correlated with the initial pH. The maximum uptake for CG was obtained at a very low pH, while that for DA was pH 4, which was consistent with our previous report of arsenate ( $\text{HAsO}_4^{2-}$ ) adsorption by alumina [7]. The CG did not act as adsorbent above pH 4. Utomo and co-worker used NaOH solution to leach the organics from commercial ground coffee [2]. Therefore, at a high pH range, the adsorbed organic dye was also leached out. Furthermore, metal oxide (alumina) is soluble in acidic and strongly alkaline solutions. This feature correlated with curve shapes of the upper maximum, as shown in the DA data of Fig. 2. Thus, it is evident that the target species with negatively charged Acid Red 44 could be effectively adsorbed by CG and DA adsorbents at pH values of 1 and 4, respectively. At a high pH range, adsorption does not occur

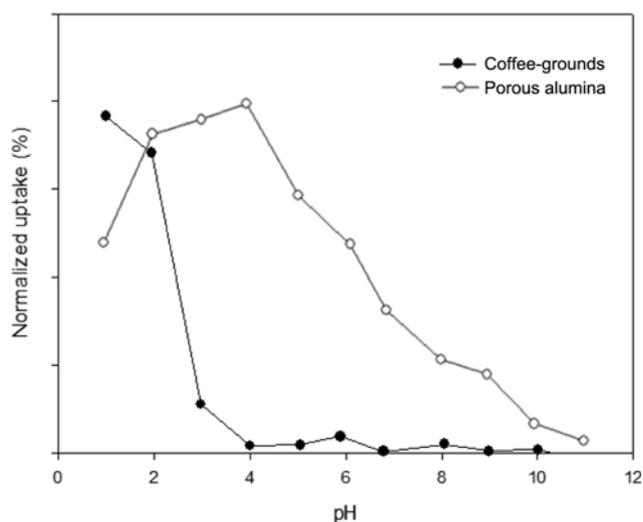


Fig. 2. Dye uptake at various initial pH values to maximize uptake.

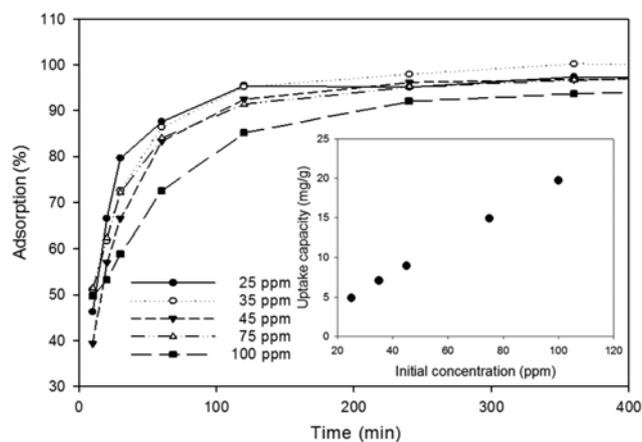


Fig. 3. Dye adsorption by CG as a function of initial concentration (25-100 ppm) of dye.

and can be thus used for a desorption procedure.

The effect of contact time on the dye by CG is shown in Fig. 3, as a function of the initial dye concentration ( $C_o$ ). As the initial concentration of the dye increased, the uptake capacity by the CG adsorbent increased linearly (inset of Fig. 3). Although the uptake capacity calculated by the Langmuir equation (Table 1) is linear with  $C_o$ , the adsorption rate was slower with  $C_o$ . This similar behavior can be also found in the literature for methylene blue adsorption onto coffee husks [14], whereby this phenomenon was explained with a two-step adsorption mechanism: the first stage at the adsorbent surface (faster); the second (slower) within the adsorbent pores. Thus, the Acid Red 44 molecules are adsorbed mainly on the surface of the CG adsorbent at lower concentrations.

To optimize the design of a sorption system for the removal of acidic dye from effluents, it is important to establish the most appropriate correlation for the equilibrium curves. Several isotherms (Langmuir, Freundlich, Dubinin-Radushkevich) were examined and its parameters summarized in Table 2. Langmuir isotherms are plotted in Fig. 4. The respective correlation coefficient ( $R^2$ ) of the Freundlich isotherms for CG and DA are 0.930 and 0.949, while those of the Langmuir isotherms are 0.995 and 0.996, respectively. In addition, the Freundlich exponent ( $n$ ) lies generally in the range of 0.2

Table 2. Freundlich, Langmuir, and Dubinin-Radushkevich isotherm constants for Acid Red 44 adsorption by CG and DA

| Isotherms                    | CG     | DA     |
|------------------------------|--------|--------|
| Freundlich                   |        |        |
| $K_F$ ( $\text{mg g}^{-1}$ ) | 10.433 | 37.788 |
| $n$                          | 0.379  | 0.124  |
| $R^2$                        | 0.930  | 0.949  |
| Langmuir                     |        |        |
| $Q_m$ ( $\text{mg g}^{-1}$ ) | 27.778 | 55.556 |
| $K_L$ ( $\text{L mg}^{-1}$ ) | 1.306  | 0.389  |
| $R^2$                        | 0.995  | 0.996  |
| Dubinin-Radushkevich         |        |        |
| $E$ ( $\text{kJ mol}^{-1}$ ) | 9.473  | 17.125 |
| $R^2$                        | 0.957  | 0.967  |

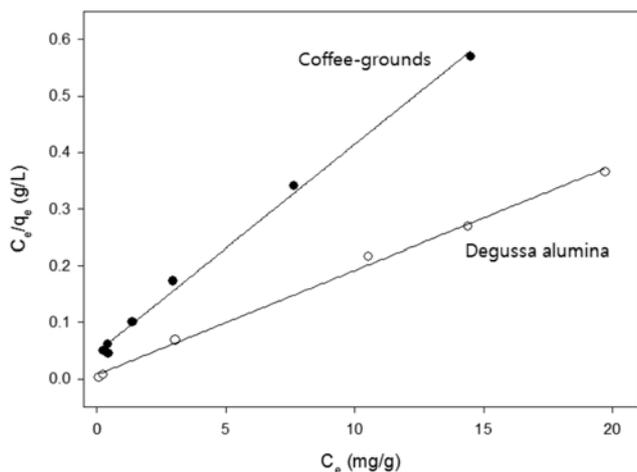


Fig. 4. Langmuir isotherms of dye by CG and DA at the same temperature.

to 1, and thus the correlation of DA using the Freundlich isotherm bears no physical meaning ( $n=0.124$  for DA). A basic assumption in the Langmuir theory is that chemisorption occurs at specific homogeneous sites within the adsorbent, while the Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface [15]. Because the Langmuir equation represents a better fit of the experimental data than the Freundlich equation, interaction between Acid Red 44 molecules and adsorbents (CG and DA) is by chemisorption, not physisorption.

The maximum uptake capacities ( $Q_m$ ) of CG are 27.8 mg/g, and that of DA is two times larger. Some experiments for the removal of Acid Red 44 using inorganic adsorbents have been reported: bimodal mesoporous alumina (4,200 mg/g) [10]; PDDA/SBA-15 (154 mg/g); PDDA/conventional silica (48 mg/g) [11]. Although the  $Q_m$  of CG is smaller than those data, coffee-ground biosorbent still possesses economical advantages compared to inorganic adsorbents.

When transferred to the surface of the solid from infinity within the solution, the mean free energy ( $E$ ) of sorption per molecule of

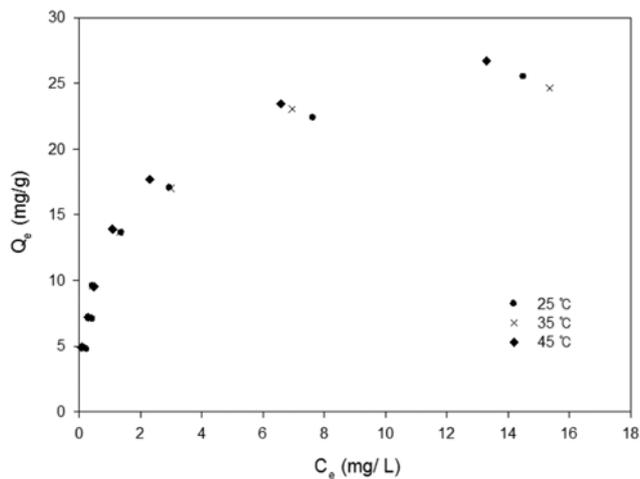


Fig. 5. Adsorption isotherms of dye by CG at difference temperatures (25, 35, 45 °C).

Table 3. Langmuir isotherm constants for dye adsorption by CG at different temperature

| Isotherms                                       | 25 °C  | 35 °C  | 45 °C  |
|---|--------|--------|--------|
| $Q_m$ (mg g <sup>-1</sup> )                     | 27.778 | 26.738 | 28.090 |
| $K_L$ (L mg <sup>-1</sup> )                     | 1.306  | 0.904  | 0.958  |
| $R^2$   | 0.995  | 0.992  | 0.995  |
| $\Delta G$ (kJ mol <sup>-1</sup> ) <sup>a</sup> | -1.397 | -1.212 | -1.848 |

<sup>a</sup> $\Delta G$  value of DA at 25 °C is -7.973 kJ mol<sup>-1</sup>

the sorbate can be calculated with the correlated constant ( $B$ ) of the Dubinin-Radushkevich (D-R) equation. In the D-R equation,  $\epsilon$  and  $E$  can be computed using the following equations:

$$\epsilon = RT \ln \left[ 1 + \frac{1}{C_e} \right] \text{ and } E = \frac{1}{\sqrt{2B}}$$

The sorption energy of the dye for CG (9.5 kJ/mol) is two times lower than for DA. It is noteworthy that the lower the sorption energy of the dye with the adsorbent, the lower the uptake capacity.

To determine the Gibbs free energy for adsorption, three different adsorption tests for CG were carried out at 25, 35, and 45 °C. Uptake capacities *versus* equilibrium concentration were plotted in Fig. 5, and the Langmuir isotherm constants summarized in Table 3. The maximum uptake capacity with temperature was slightly different within the range of 26.7 to 28.1 mg/g. Furthermore,  $\Delta G$  for CG is in the range of -1.2 to -1.8 kJ/mol, and four times smaller than that for DA at 25 °C (-7.9 kJ/mol). These results indicate that Acid Red 44 adsorption with a more negative value is more easily adsorbed onto the solid adsorbents. It is also consistent with the above adsorption analysis for the maximum uptake.

The kinetics of sorption that describe the solute uptake rate governing the residence time of the sorption reaction is one of the important characteristics that define sorption efficiency. Hence, the kinetics of the dye removal was carried out and the initial sorption rate ( $h$ ) and intraparticle diffusion rate ( $k_{it}$ ) calculated. The adsorption of the dye to CG was found to be time-dependent, and its rate slower compared to DA (Fig. 6). Half of the initial concentration of dye was removed at 20 min for CG with adsorption slowing con-

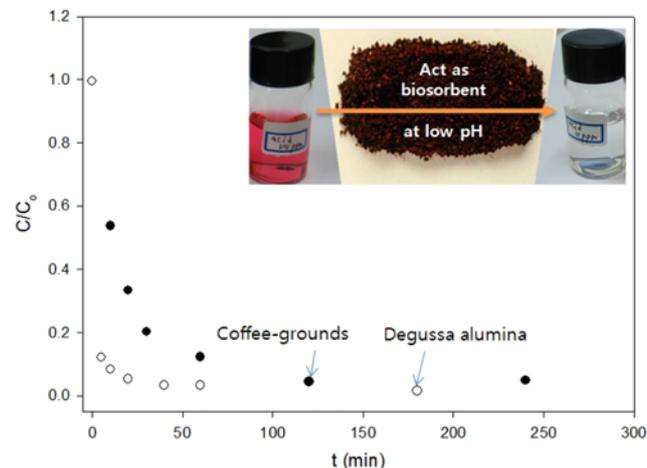


Fig. 6. Adsorption kinetic data for coffee-grounds and Degussa alumina.

**Table 4. Parameters of Pseudo-second-order rate and intraparticle diffusion rates for Acid Red 44 adsorption by CG and DA**

| Kinetics  | CG    | DA     |
|---|-------|--------|
| Pseudo-second-order rate                        |       |        |
| $h$ ( $\text{mg g}^{-1} \text{min}^{-1}$ )      | 3.558 | 37.037 |
| $R^2$   | 0.999 | 0.999  |
| Intraparticle diffusion rates                   |       |        |
| $k_{id}$ ( $\text{mg g}^{-1} \text{h}^{-1/2}$ ) | 177.6 | 461.6  |
| $R^2$   | 0.942 | 0.938  |

siderably as the reaction approached equilibrium.

To quantify the changes in sorption over time, we used the pseudo-second-order equation (Table 1) to describe the adsorption of dye [12]. In the pseudo-second-order equation, the  $k_{ad}Q_e^2$  value is known as the initial sorption rate ( $h$ ). As represented in Table 4, the initial sorption rate was 3.6 mg/g min. Naturally, those rates for the CG were smaller than that of DA.

The initial steep-sloped portion, 0 to 30 min, in Fig. 6 is attributed to surface adsorption and gradual adsorption, where the intraparticle diffusion is rate-controlled and its rate obtained from the slope of the steep-sloped portion. The dye molecule was initially adsorbed by the exterior surface of the CG and DA, as mentioned in the literature [2]. When the adsorption at the exterior surface reached the saturation level, the dye molecules began to enter the pores and were adsorbed by the interior surfaces of the particles [7]. The intraparticle diffusion rate ( $k_{id}$ ) for CG was 177 mg/g h<sup>1/2</sup> and that for DA was three times larger. Although all of adsorption rates for the CG were smaller than DA, almost all the acidic dye was eliminated from the aqueous solution within one hour.

### CONCLUSIONS

We investigated the potential application of waste coffee-grounds as biosorbent for the removal of an acidic dye (Acid Red 44) from the aqueous phase. To evaluate objectively the adsorption performance of CG Degussa alumina was selected as the conventional adsorbent. Although all of its initial sorption ( $3.558 \text{ mg g}^{-1} \text{min}^{-1}$ ) and intraparticle diffusion ( $177.6 \text{ mg g}^{-1} \text{h}^{-1/2}$ ) rate for the CG were smaller than that of DA, the adsorption procedure was complete in under one hour and proved faster than that reported in the literature [10,11]. In addition, the maximum uptake capacity ( $27.78 \text{ mg/g}$ ) of the CG was only two times smaller than DA and conventional silica [11]. In our previous study for similar adsorption testing using several inorganic adsorbents, we found the following correlation of adsorption performance with physical properties (pore and surface area): meso-

porous materials with uniform pore and large surface area showed 150-4,000 mg/g of Acid Red 44; conventional silica and alumina with non-uniform pore and larger surface area compared to CG with an approximate capacity of 50 mg/g. Namely, a regular pore structure and large surface area are the most critical factors towards obtaining high-performance adsorbents. However, the most critical merit for waste coffee-grounds is its low cost and accessibility from daily life, and thus, it is very economical as a concept of waste-to-wealth. Therefore, waste coffee-grounds can possibly be used as biosorbent for the removal of organic compounds, including Acid Red 44, from the aqueous phase. As shown within the inset in Fig. 6, waste coffee-grounds can be used as biosorbents in daily life after color leaching and pH control through addition of vinegar as acetic acid.

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