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Adsorptive Removal of Reactive Dyes in Wastewater Using APTES-modified Spent Coffee Grounds

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In this study, spent coffee grounds (SCG) were treated using sodium hypochlorite (NaClO) to remove organics. The NaClO-treated SCG was modified with 3-aminopropyltriethoxysilane (APTES) to improve its adsorption performance. To understand the characteristics of the prepared adsorbents, samples were characterized by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The pH edge, kinetic, and isotherm experiments were conducted to evaluate the adsorption performance of APTES-SCG for Reactive Black 5 (RB5), Reactive Orange 16 (RO16), and Reactive Yellow 2 (RY2). The pH edge experiments were carried out in the pH range of 2-12 at an initial dye concentration of 100 mg/L. The results showed that the dye uptakes on APTES-SCG increased with decreasing pH value. The adsorption experiments for kinetics confirmed that the equilibrium time was reached within 30 min at pH 2. The adsorption isotherm experiments were performed at initial dye concentrations of 30 to 300 mg/L, and the experimental data were well-fitted by the Langmuir model. The dye-loaded APTES-SCG was desorbed using 0.01 M NaOH solution and repeated adsorption-desorption experiments showed that APTES-SCG could be reused at least 3 times.

1. Introduction

Coffee, brewed from roasted beans, is a highly consumed beverage globally. Typically, every 1 kg of soluble coffee results in 2 kg of wet coffee waste (Tsai, 2017). In 2016, the International Coffee Organization published an estimate revealing that the worldwide consumption of coffee surpassed 9.3 billion kg (McNutt and He, 2019). The increasing popularity of coffee is expected due to its association with reduced risks of heart disease and specific cancers (Atabani et al, 2019).The coffee industry generates significant quantities of waste that are frequently disregarded and not utilized, causing concern. The extraction of specific compounds during coffee bean brewing produces substantial quantities of spent coffee grounds (SCG), resulting in significant waste generated by the coffee industry. SCG refers to the leftover grounds after the extraction of desired compounds. Coffee contains a variety of compounds, including caffeine, phenols, organic acids, and heavy metals, which are environmentally harmful elements. Unlike other organic wastes, the presence of these harmful elements in coffee makes its disposal challenging. Specifically, caffeine is toxic to humans and can also have detrimental effects on aquatic life if it leaks into the water environment. Phenols, on the other hand, are potent oxygenators that can cause environmental impacts and hinder the decomposition of materials (Li et al, 2014). SCG are often sent to landfills instead of being utilized as compost, leading to resource wastage and potential greenhouse gas emissions. To address these issues, proper management and innovative recycling methods for coffee waste are essential to minimize its environmental impact. This waste management approach has negative economic and environmental implications, highlighting the need for innovative methods to deal with SCG.

SCG are residual organic powder left after the extraction of coffee beans using high temperature and pressure steam. Carbon materials extracted from these biowastes are eco-friendly, inexpensive, and abundant, making them ideal for use as adsorbents for water treatment (Lavecchia et al., 2016). However, studies show that using raw SCG as adsorbents can lead to increased phytotoxicity or low adsorption capacity (Ferraz and Yuan, 2020). While preparing SCG in the form of biochar by high-temperature (500-800 °C) treatment can enhance its

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adsorption performance, the energy required for heat treatment is significant (Zhang et al., 2020). Pre-treatment and modification studies are necessary to effectively use coffee grounds as an adsorbent.

In this study, SCG was pre-treated with sodium hypochlorite solution (NaClO), a relatively inexpensive and widely used chemical, and after a simple pre-treatment, the surface of coffee grounds was functionalized using 3-aminopropyltriethoxysilane (APTES). The prepared adsorbent (APTES-SCG) was characterized using FTIR and SEM. RB5, Reactive Black 5 (RB5), Reactive Orange 16 (RO16), and Reactive Yellow 2 (RY2) were used as representatives to test the adsorption performance of APTES-SCG for reactive dyes. The adsorption performance of APTES-SCG was evaluated by pH edge, isotherm, and kinetic experiments. Reusability experiments were also carried out to estimate the reusability of APTES-SCG adsorbent in wastewater treatment.

2. Materials and methods

2.1 Materials

The SCG samples were obtained from a Starbucks branch located in Tongyeong, South Korea. Daejung Chemicals & Metals Co., Ltd., based in Siheung, Korea, provided the NaClO (5 %) and APTES (99 %). For the experimental purposes, RB5, RO16, and RY2 were acquired from Sigma-Aldrich Korea Ltd. These dyes were used as representative substances to study adsorption. All other chemicals utilized, such as ethanol, NaOH, and HCl, were of analytical grade.

2.2 Fabrication of APTES-modified SCG and hydrolyzed dyes solution

To effectively remove contaminants, the SCG was immersed in a 5 % NaClO solution for 1 h, targeting the elimination of any organic substances that may have been present on the surface. Afterwards, it was rinsed multiple times with distilled water and freeze-dried for 24 h. To create APTES-modified SCG (APTES-SCG), 2 g of SCG and 4 mL of APTES were combined with 200 mL of 30 % ethanol and stirred at 25 °C for 24 h. The resulting APTES-SCG was filtered, washed with ethanol several times, and freeze-dried (Kang et al., 2023). The hydrolyzed reactive dyes were prepared using a previously reported method (Osman et al., 2006). For dye hydrolysis, 2 g/L of dye solution was dissolved in 0.1 M NaOH. To ensure complete hydrolysis, the alkaline dye solution was incubated in an 80 °C water bath for 4 h. After incubation, the pH of the solution was adjusted to pH 7. The hydrolyzed reactive dye solutions were appropriately diluted before being used in sorption experiments.

2.3 Analytical methods

The IR spectra of SCG and APTES-SCG were investigated using a FT-IR spectrometer in the range of 4,000–400 cm^{-1} (Nicolet IS50, Thermo Fisher, USA). The surfaces of SCG and APTES-SCG were imaged using SEM (JSM-6010, Jeol, Japan).

2.4 Adsorption experiments

After undergoing hydrolysis, all dye solutions were utilized for adsorption experiments. Comparative experiments were conducted using SCG, NaClO-SCG, and APTES-SCG with all dyes at an initial concentration of 300 mg/L, pH 2, and a duration of 24 hours. Adsorption isotherm experiments were conducted using initial dye concentrations ranging from 30 to 300 mg/L. The obtained isotherm experimental data were analysed using the Langmuir and Freundlich isotherm models. In each conical tube (50 mL), 0.03 g of APTES-SCG and 30 mL of dye solutions were combined and subjected to shaking under 25 °C at 160 rpm. The effects of pH (ranging from 2 to 12) and contact time (ranging from 0 to 180 min) on the adsorption of dyes by APTES-SCG were assessed at an initial dye concentration of 100 mg/L. The dye concentrations were determined at specific wavelengths (404 nm for RY2, 597 nm for RB5, and 494 nm for RO16) using an UV–Vis spectroscopy (X-ma 3000pc, Human, Korea) following dilution (ranging from 11 to 101 times). The dye uptake q (mg/g) was then calculated using Eq(1).

$$q = \frac{V_i C_i - V_f C_f}{m} \quad (1)$$

where V_i and V_f (L) are the initial and final volumes of the solution. C_i and C_f (mg/L) are the initial and final dye concentrations. m (g) is the dry weight of the adsorbent.

2.5 Reusability experiments

During the adsorption process, a combination of 0.03 g of APTES-SCG and 30 mL of a dye solution with an initial concentration of 100 mg/L was allowed to interact for 4 h at room temperature. Subsequently, the dye-laden adsorbent was rinsed with 0.01 M HCl, and a desorption cycle was conducted using a 0.1 M NaOH solution to extract the dye from the adsorbent. To assess the reusability of APTES-SCG, the experiment was repeated for three successive cycles. The dye concentration was measured using a UV-Vis spectrophotometer after dilution (ranging from 11 to 101 times). The desorption efficiency was then calculated using Eq(2).

$$Desorption\ efficiency\ (\%) = \frac{Desorbed\ dye\ amount\ (mg)}{Initailly\ adsorbed\ dye\ uptake\ (mg)} \times 100 \qquad (2)$$

3. Results and discussion

3.1 Characterization of SCG and APTES-SCG

The SCG material and its modified counterpart were characterized by FT-IR analysis (Figure 1a). The peaks of APTES-SCG were explained by different bands associated with NH_2 and Si–O bonds. The NH_2 asymmetric and symmetric stretching showed a shift after APTES coating, with changes observed at 3,347 shifting to 3,361 cm^{-1} (Majoul et al, 2015). The amine function group (NH_2) was observed at 1,643 and it was shifted to 1,636 cm^{-1} and the Si–O–Si bond was observed at 1,057 which was shifted to 1,056 cm^{-1} (Majoul et al., 2015). The stretching vibration of Si–C resulting from the propylsilane group was assigned to new bands observed at 807 and 580 cm^{-1} (Sepehr et al., 2014).

The SEM image shows the surface morphology of SCG and APTES-SCG. The surface of SCG exhibits irregularities such as small holes and protrusions. After NaClO treatment and APTES coating, the SEM image of APTES-SCG showed regular-sized voids on the particle surface compared to the SEM image of pre-treated SCG. This is attributed to the oxidation and removal of organic matter on the particle surface by NaClO, resulting in a cleaner particle surface. The formation of regular-sized voids can potentially improve the adsorption performance of APTES-SCG by providing a larger adsorption site.

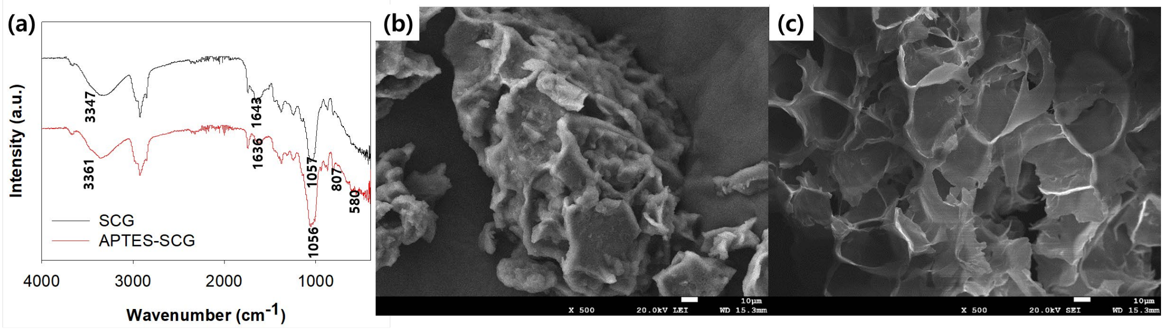

Figure 1: (a) FT-IR analysis results of the SCG and APTES-SCG and (b) SEM image of the SCG and (c) APTES-SCG (magnification: ×100)

3.2 Comparative dyes adsorption capacity of SCG, NaClO-SCG, and APTES-SCG at pH 2

The adsorption capacity of APTES-SCG for dyes was significantly increased at pH 2 when amine groups were concentrated on the adsorbent surface (Figure 2).

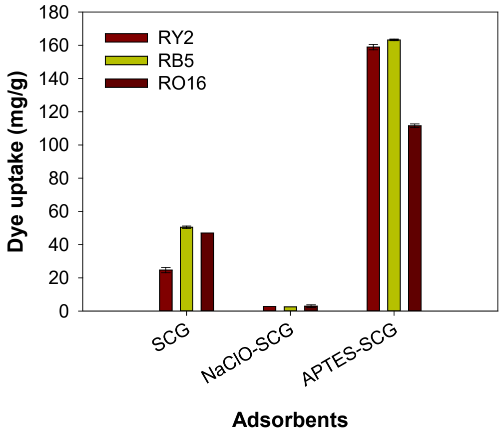

Figure 2: Comparison of dye uptakes in SCG, NaClO-SCG, and APTES-SCG.

At pH 2, APTES-SCG demonstrated a remarkable increase in dye uptake capacity, ranging from111.60 to163.28 mg/g, in comparison to SCG (24.67-50.43 mg/g) and NaClO- treated SCG (NaClO-SCG) (2.58-2.94 mg/g). It is supposed that the decreased dye adsorption capacity observed in NaClO-SCG can be attributed to the removal of the functional groups of organic matter, which is known to contribute to the adsorption of dyes. The difference in the amount of dye adsorption between SCG and APTES-SCG was between 2.37-6.44 times, suggesting that the presence or absence of APTES significantly affected the amount of dye adsorption.It can be concluded that the presence of a functional group is essential for achieving high levels of dye adsorption in SCG-based adsorbents.

3.3 Dye adsorption capacities by APTES-SCG under different pHs.

The pH of the solution is a crucial factor that affects both the adsorption process and adsorption capacity, as the surface of the adsorbent and the dye molecules become charged when the pH of the solution changes (Figure 3a). The dye adsorption capacities of APTES-SCG were found to be pH-dependent, with higher adsorption capacities observed for RY2, RB5, and RO16 under lower pH conditions. The adsorption capacities dramatically decreased as the pH increased from near neutral (pH 6) to alkaline (pH 12) conditions. When the solution pH was 2, the adsorption capacities of APTES-SCG for RY2, RB5, and RO16 were 96.74, 84.56, and 42.19 mg/g for RY2, RB5, and RO16. When the pH increased to 6, the dye uptake for RY2, RB5, and RO16 we significantly decreased to 24.08, 8.52, and 8.68 mg/g. As the pH further increased to 12, the dye uptakes were decreased to 0 mg/g. These results are likely due to changes in the surface charge of APTES-SCG under different pHs, which have also been reported in previous studies on amine-modified adsorbents (Wamba et al, 2018). Also, the desorption process could take place at elevated pH levels.

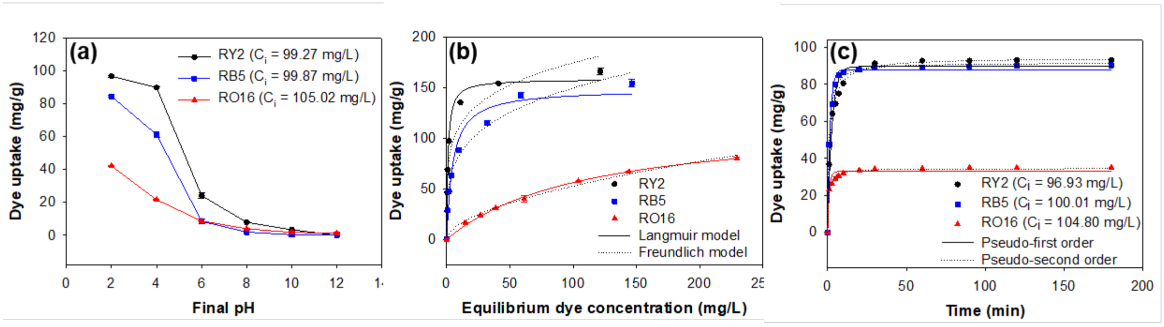

Figure 3 (a) Effect of pH on dyes adsorption amount by APTES-SCG, (b) Adsorption isotherm of dyes on APTES-SCG at pH 2, and (c) Adsorption kinetics of dyes on APTES-SCG at pH 2.

3.4 Isotherm studies

Figure 3b illustrates the adsorption isotherms of dyes onto APTES-SCG and the experimental data were analyzed using the Langmuir and Freundlich models to gain a better understanding of the adsorption performance. The Langmuir model equation (Eq(3)) and the Freundlich model equation (Eq(4)) were used to fit the isotherm data.

Langmuir model: $$q_e = \frac{q_{max} K_L C_e}{1+K_L C_e} \qquad (3)$$

Freundlich model: $$q_e = K_F C_e^{1/n} \qquad (4)$$

The adsorption behavior of the dyes was characterized using several parameters in the equations. These parameters include q_e (mg/g), C_e (mg/L), q_{max} (mg/g), b_L (L/mg), K_F (mg/g), and $1/n$, which represents the adsorption intensity. The adsorption intensity can be classified as either effective ($0 < 1/n < 1$) or cooperative ($1/n > 1$). The Langmuir and Freundlich parameters were listed in Table 1. The values of the coefficient of determination (R^2) ranged from 0.914 to 0.997 as derived from the linear regression of the Langmuir and the Freundlich models, respectively. The Langmuir model estimated q_{max} values for APTES-SCG as 158.49 mg/g for RY2, 148.68 mg/g for RB5, and 118.32 mg/g for RO16. The Langmuir constant (b_L) reflects the affinity between the sorbate (dye) and the adsorbent (APTES-SCG). Therefore, the higher b_L values obtained for RY2 than for RB5 and RO16 suggest that APTES-SCG has a higher adsorption affinity for dyes with more sulfonate groups (Wang et al., 2020). The favorable sorption of dyes by APTES-SCG was indicated by the values of 1/n in the Freundlich model, which were found to be 0.19, 0.25, and 0.55.

Table 1: Isotherm parameters for the adsorption of dyes onto APTES-SCG

	Langmuir model			Freundlich model		
Dye	q_{max} (mg/g)	b_L (L/mg)	R^2	$1/n$	K_F (L/g)	R^2
RY2	158.49	0.975	0.990	0.193	71.851	0.914
RB5	148.68	0.209	0.980	0.254	46.600	0.957
RO16	118.32	0.009	0.997	0.550	4.194	0.993

3.5 Kinetic studies

The adsorption kinetics of dyes onto APTES-SCG were investigated by conducting experiments with an initial dye concentration of 100 mg/L at pH 2. The experimental data were analyzed using two kinetic models: the pseudo-first-order and pseudo-second-order models, and the kinetic parameters were determined (Table 2 and Figure 3c).

Pseudo-first-order model: $q_t = q_1\left(1 - exp(-k_1 t)\right)$ (5)

Pseudo-second-order model: $q_t = \frac{q_2^2 k_2 t}{1+q_2 k_2 t}$ (6)

In these equations, q_1 and q_2 (mg/g) represent the amount of dyes adsorbed at equilibrium, q_t (mg/g) is the amount of dyes adsorbed at a given time, t, and k_1 (L/min) and k_2 (g/(mg·min)) are the rate constants for the pseudo-first-order and pseudo-second-order models, respectively.

The adsorption equilibrium of APTES-SCG for RY2, RB5 and RO16 was reached within 30 min. The R^2 values of the pseudo-second order model for RY2, RB5, and RO16 were higher compared to those of the pseudo-first order model. In addition, the q_2 values of APTES-SCG were closer to the experimental values (93.07, 90.34, and 35.18 mg/g for RY2, RB5 and RO16, respectively). The pseudo-second-order model was fit for explaining the adsorption of reactive dyes onto APTES-SCG.

Table 2: Kinetic parameters for the adsorption of dyes onto APTES-SCG

	Pseudo-first-order model			Pseudo-second-order model		
Dye	q_1 (mg/g)	k_1 (L/min)	R^2	q_2 (mg/g)	k_2 (g/mg min)	R^2
RY2	89.67	0.368	0.964	94.46	0.0066	0.998
RB5	87.94	0.630	0.985	91.72	0.0126	0.996
RO16	32.92	0.995	0.929	34.54	0.0445	0.984

3.6 Desorption and reusability studies

The reusability of adsorbents is a crucial property for promising candidates. The ability to recycle an exhausted adsorbent can extend its replacement cycles and provide financial benefits.

The results presented in Figure 4 indicate that the APTES-SCG adsorbents showed desorption efficiencies ranging from 96.31 to 98.80 % for RY2, 95.37 to 97.39 % for RB5, and 84.10 to 89.08 % for RO16 over three cycles of reusability tests using a 0.1 M NaOH solution. The adsorbents maintained high adsorption capacities of 98.15 % for RY2, 98.28% for RB5, and 88.49 % for RO16 over the three cycles of reusability tests. These results confirmed that the APTES-SCG has excellent reusability.

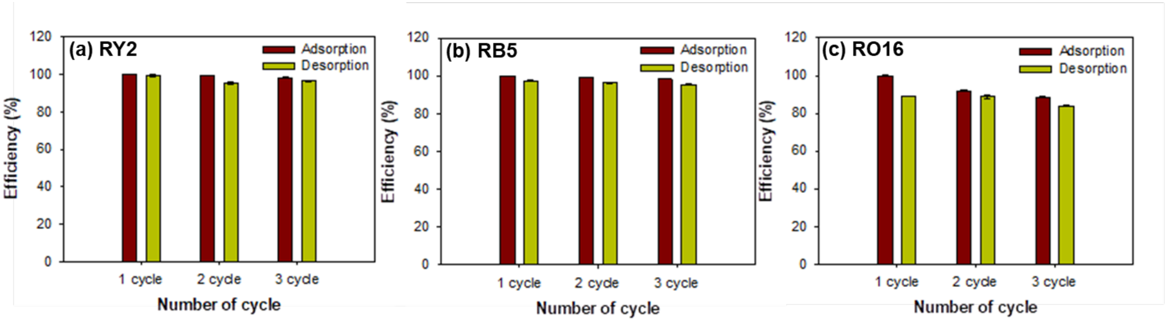

Figure 4: Repeated adsorption and desorption cycles for (a) RY2, (b) RY5 and (c) RO16

4. Conclusions

The APTES-SCG adsorbent demonstrated excellent adsorption abilities for anionic reactive dyes at acidic pH conditions (2-4) due to the positive surface charge maintained by the APTES functional group, which facilitates electrostatic interaction with the dyes. The Langmuir model revealed adsorption capacities of 158.49 mg/g (RY2), 148.68 mg/g (RB5), and 118.32 mg/g (RO16) at pH 2. APTES-SCG is a promising adsorbent due to its effectiveness in adsorbing reactive dyes and the straightforward pore structure fabrication process involving NaClO treatment. While the study only investigated dye-containing solutions, future research should examine the adsorbent's selectivity for potential pollutants or water system components in real-world conditions.

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