



## Removal of anionic dyes (Reactive Black 5 and Congo Red) from aqueous solutions using Banana Peel Powder as an adsorbent



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### ARTICLE INFO

#### Keywords:

Adsorption  
Anionic dyes  
Isotherms  
Kinetics  
Temperature  
Thermodynamics

### ABSTRACT

The adsorption characteristics of Reactive Black 5 (RB5) and Congo Red (CR) onto Banana Peel Powder (BPP) from aqueous solution were investigated as a function of pH, contact time, initial dye concentration and temperature. The BPP was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) analysis. FTIR results revealed that hydroxyl (–OH), amine (–NH) and carboxyl (–C=O) functional groups present on the surface of BPP. The SEM results show that BPP has an irregular and porous surface morphology which is adequate for dye adsorption. The equilibrium data were analyzed using Langmuir and Freundlich isotherm models. Experimental results were best represented by the Langmuir isotherm model. The adjustments of models were confirmed by the Chi-square ( $\chi^2$ ) test and the correlation coefficients ( $R^2$ ). The maximum monolayer adsorption capacities of RB5 and CR on BPP calculated from Langmuir isotherm model were 49.2 and 164.6 mg/g at pH 3.0 and 298 K. Experimental data were also tested in terms of adsorption kinetics using pseudo-first-order and pseudo-second-order kinetic models. The results showed that the adsorption processes of both RB5 and CR followed well pseudo-second-order kinetic models. The calculated thermodynamic parameters  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  showed that the adsorption of RB5 and CR onto BPP was feasible, spontaneous and endothermic in the temperature range 298–318 K. The RB5 and CR were desorbed from BPP using 0.1 M NaOH. The recovery for both anionic dyes was found to be higher than 90%. Based on these it can be concluded that BPP can be used as an effective, low cost, and eco-friendly adsorbent for CR removal than RB5 from aqueous solution.

### 1. Introduction

Water pollution due to the release of various toxic chemicals from industrialization and urbanization is a global problem. Among the various notorious toxic chemicals, dyes, metals, organics and pharmaceuticals are highly concerned (Karthikeyan et al., 2012; Saleh and Gupta, 2011, 2012a, 2012b, 2012c, 2014; Mohammadi et al., 2011; Gupta et al., 2011a, 2011b, 2012a, 2012b, 2012c, 2013; Gupta and Nayak, 2012; Gupta and Saleh, 2013; Jain et al., 2003; Mittal et al., 2009a, 2009b, 2010a, 2010b; Khani et al., 2010; Saravanan et al., 2013a, 2013b, 2013c, 2013d, 2013e, 2013f, 2014a, 2014b, 2014c, 2015a, 2015b, 2015c, 2015d, 2016; Devaraj et al., 2016; Ahmaruzzaman and Gupta, 2011; Rajendran et al., 2016). The large quantities of colored effluent discharged from textile, leather, paper, plastic, cosmetics, food and mineral processing industries has become a significant environment problem (Chatterjee et al., 2011). The disposal of wastewater containing industrial dyes into rivers and lakes without proper treatment has caused many problems. Some dyes have

mutagenic, carcinogenic or teratogenic properties, in addition to colouring the body of water, because of which algae and phytoplankton in lakes and rivers are also adversely affected. Furthermore, the improper wastewater disposal leads to promotion of disturbances in gas solubility, causing damage to the tills of aquatic organisms and disrupting their spawning sites and refuges (Elisandra do Nascimento et al., 2015). Therefore, it is important to treat colored effluents for the removal of dyes. Dyes can be classified as anionic (acid, direct and reactive dyes), cationic (basic dyes) and nonionic (disperse dyes) dyes according to their dissociation in an aqueous solution. Azo dyes, (write cationic/anionic) generally possess one or more azo bonds (–N=N–), these are heavily utilized in the textile and several food industries.

Several conventional methods are available for color removal from wastewater, such as membrane separation (Ciardelli et al., 2000), chemical oxidation (Swaminathan et al., 2003), electrocoagulation (Alinsafi et al., 2004), adsorption (Mall et al., 2005) and coagulation and flocculation (Panswed and Wongchaisuwat, 1986). Most of these methods have certain limitations in their applications, for example,

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very harsh reaction conditions, high cost and secondary pollution. From the viewpoint of sustainable development and comprehensive utilization of resources, adsorption has a promising prospect and a wide range of applications due to its high removal efficiency, low cost, mild operating conditions, no secondary pollution and good performance over other conventional treatment processes in the removal of dyes from waste water.

Many sorbents based on low-cost agricultural by-products had been used for dye sorption from wastewater, which included mandarin peels (Pavan et al., 2007), wood apple shell (Jain and Jayaram, 2010), green coconut fibers (Cristovao et al., 2011), grape fruit peels (Saeed et al., 2010), peanut hull (Gong et al., 2005), peat (Allen et al., 2004) rice husk (Han et al., 2008) wood sawdust (Jain and Sikarwar, 2008), peanut husk (Sadaf and Bhatti, 2014), pine sawdust (Ozacar and Sengil, 2005), banana peel and green coconut mesocarp (Nascimento et al., 2015), electrocoagulation/banana peel (Carvalho et al., 2015), Banana peel-activated carbon (Ma et al., 2015) and orange peel (Arami et al., 2005). As one of the most consumed fruits in the world, banana is a very common fruit. Banana peel is the main residue, corresponding to 30–40% (w/w), and has been mainly used in composting, animal feeding and the production of proteins, methane, ethanol, pectin and enzymes (Silva et al., 2013). Cellulose, pectin, chlorophyll, and other low molecular weight species are its main constituents. Various chemical groups exist on the banana peel surface, including carboxyl, hydroxyl and amide groups, which have been extensively proven to play a critical role in the adsorption processes (e.g. enhancing sorption capacity and shortening stable time) (Mohammed and Chong, 2014). Banana peel contains lipids (1.7%), proteins (0.9%), crude fiber (31%) and carbohydrates (59%). The various minerals present are potassium (78.10 mg/g), manganese (76.20 mg/g), sodium (24.30 mg/g), calcium (19.20 mg/g) and iron (0.61 mg/g). Preliminary investigations show that several tones of banana peels are produced daily in market places and household garbage, creating an environmental nuisance and disposal problem. Reuse of banana peel as adsorbent is an interesting way to solve this problem. It is an abandoned, readily available, low-cost and cheap, environment friendly bio-material. Considering the above criteria, banana peel was chosen as an adsorbent for the removal of anionic dyes from aqueous solutions.

RB5 and CR are the well known anionic azo dyes which are soluble in water. The sulfonic acid groups present in them made them to exist in anionic nature. Therefore one can expect the same type of adsorption for the two dyes on an adsorbent or CR showing more adsorption than RB5 on BPP. This investigation gave us the real or experimental adsorption trend of the two dyes on BPP. The objective of the present work is to investigate the adsorption potential of BPP as an alternative adsorbent material for RB5 and CR removal from aqueous solution. The study includes an evaluation of the effects of various process parameters such as pH, contact time, initial dye concentration and temperature. The adsorption kinetic data was tested by pseudo-first-order and pseudo-second-order kinetic models. The equilibrium data were analyzed using Langmuir and Freundlich isotherm models. The results at different temperatures are used to evaluate thermodynamic parameters. In addition, Scanning Electron Microscopy (SEM) was used to identify the morphological structure of BPP and Fourier Transform Infrared (FTIR) spectroscopy was employed to elucidate the adsorption mechanism.

## 2. Materials and methods

### 2.1. Preparation of adsorbent

Bananas were purchased from a local market, Seoul, Korea. The Banana Peels were thoroughly washed with distilled water to remove surface dirt and adhering impurities, cut into small pieces, crushed and sieved in a mesh size 150  $\mu\text{m}$  size by standard sieves. The Banana Peel Powder dried in an air oven at 105  $^{\circ}\text{C}$  for 2 h until a constant weight

was reached. After complete drying, the Banana Peel Powder was stored in air tied bottles for experimental uses.

### 2.2. Preparation of dye solution

Stock solutions (1000 mg/L) of dyes were prepared in deionized and double distilled water and diluted to get the desired concentration of dyes. Calibration curves for dyes were prepared by measuring the absorbance of different concentrations of the dyes.

### 2.3. Chemicals and equipment

All chemical used in this work, were of analytical reagent grade and were used without further purification. RB5 ( $\approx 55\%$  dye content, M.W. = 991.80) and CR ( $\geq 35\%$  dye content, M.W. = 991.82) were purchased from Sigma-Aldrich Korea Ltd. (Seoul, Korea). The structure of dyes is shown in Table S1. Double deionized water (Milli-Q Millipore 18.2  $\text{M}\Omega\text{cm}^{-1}$  conductivity) was used for all dilutions. A pH meter (pH-240 L, NEOMET, Korea) was used for pH measurements. The pH meter was calibrated using standard buffer solutions of pH 4.0, 7.0 and 10.0. Fourier Transform Infrared Spectrometer (BIO-RAD, FTS-135, USA) was used for the IR spectral studies ( $4000\text{--}400\text{cm}^{-1}$ ) of adsorbent. For IR spectral studies, 1 mg of sample was mixed and ground with 100 mg of KBr and made into pellet. The background absorbance was measured by using pure KBr pellet. Scanning Electron Microscopy (JEOL, JSM-7600F, Japan) was used to study the morphological features of the adsorbent. The dye concentrations in the samples were analyzed using UV/Vis spectrophotometer (Optizen Pop, Korea). The wavelength was selected so as to obtain maximum absorbance for each dyestuff and the  $\lambda_{\text{max}}$  values are 597 nm and 497 nm for RB5 and CR, respectively.

### 2.4. Batch experimental procedure

Batch experiments were carried out in 50 mL falcon tubes at 25  $^{\circ}\text{C}$  to evaluate various parameters such as pH, contact time, initial dye concentration and temperature. The pH edge experiments were performed by mixing 30 mL solution of RB5 and CR concentration (300 mg/L) and 0.03 g of adsorbent in 50 mL of falcon tubes. The pH values of the solutions were adjusted in the range of 3–10 using 0.1 M HCl and 0.1 M NaOH solutions. All tubes were agitated in a shaker at 180 rpm and 25  $^{\circ}\text{C}$  for 24 h. After reaching equilibrium, the adsorbent was separated by means of centrifugation at 3000 rpm for 3 min. The remaining dye concentration was appropriately diluted with distilled water and analyzed using UV/Vis spectrophotometer.

The dye uptake ( $q$ ) was calculated from the difference between the concentrations of RB5 and CR before and after sorption using the Eq. (1):

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

In this equation,  $C_i$  and  $C_f$  are the initial and final dye concentrations in the solution (mg/L),  $V_i$  and  $V_f$  are the initial and final (initial plus added HCl or NaOH solutions) solution volumes, and  $M$  is the mass of sorbent (g).

Adsorption isotherms of RB5 and CR were evaluated at different temperatures (298, 308 and 318 K) to measure the maximum sorption capacities of BPP. The initial concentration of RB5 and CR was varied from 50 to 300 mg/L, which resulted in different final dye concentrations after sorption equilibrium. Adsorption kinetic experiments were carried out using different RB5 and CR concentrations such as 50, 100 and 150 mg/L. The experimental procedure was the same as described in the pH edge experiments, except that the samples were collected at different time intervals to determine the attainment of sorption equilibrium. Other remaining procedures were the same as those used in the pH edge experiments.

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