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# Comparison of a homemade cocoa shell activated carbon with commercial activated carbon for the removal of reactive violet 5 dye from aqueous solutions

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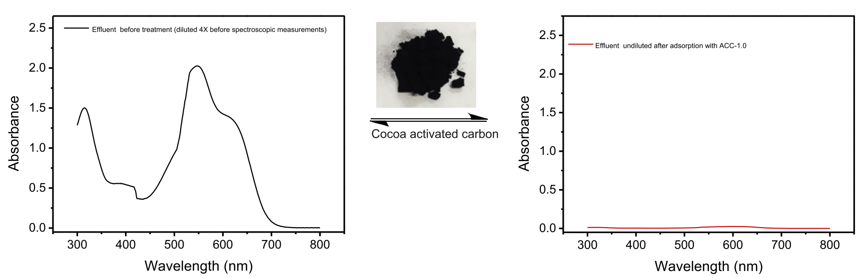
## HIGHLIGHTS

- Acidified cocoa activated carbon (ACC-1.0) was prepared and characterised.
- Adsorption of RV-5 dye was studied using ACC-1.0 and CAC.
- Adsorption maximum values were 603.3 mg $g^{-1}$ (ACC-1.0) and 517.1 mg $g^{-1}$ (CAC).
- General order kinetic model suitably described the adsorption processes.
- ACC-1.0 effectively decolourised simulated industrial effluents.

## GRAPHICAL ABSTRACT

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## ABSTRACT

A novel homemade furnace setup for preparation of chemically activated carbon was proposed in a quest for industrial wastewater treatment. Cocoa shell was initially mixed with inorganic components (red mud + lime + KOH + $Al(NO_3)_3$ + $Na_2SO_4$) and water to form a paste. The paste was placed in a mould cylinder, dried at a room temperature, and then the material was placed in a stainless steel reactor and heated up to 1073 K under inert atmosphere. Three carbon adsorbents with inorganic: organic ratio of 1.0 (CC-1.0), 1.5 (CC-1.5) and 2.0 (CC-2.0) were prepared. The adsorbents were acidified with a 6 mol $L^{-1}$ HCl under reflux (24 h) to obtain corresponding ACC-1.0, ACC-1.5 and ACC-2.0. The chemical activation process was completed by leaching the inorganic components from the carbonaceous matrix through acidification. ACC-1.0 exhibited highest sorption capacity compared with the other two adsorbents. CC-1.0 and ACC-1.0 were characterised using FTIR, SEM, $N_2$ adsorption/desorption curves and X-ray diffraction. A well-known commercially activated carbon (CAC) was used to compare the sorption capacity of ACC-1.0. The ACC-1.0 and CAC adsorbents were used for adsorption of reactive violet 5 (RV-5) textile dye from aqueous solutions. The equilibrium times of 45 and 150 min were observed for ACC-1.0 and CAC, respectively, at optimum pH 2.0. General order kinetic model best described the adsorption process than pseudo first-order and pseudo-second order kinetic models. Liu isotherm model gave the best fit of

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the equilibrium data at all experimental temperatures. The maximum amounts of RV-5 dye adsorbed at 298 K were 603.3 (ACC-1.0) and 517.1 mg $g^{-1}$ (CAC). The adsorbents were tested on two simulated dye-house effluents. ACC-1.0 is effectively capable of decolourising industrial textile effluents.



## 1. Introduction

Synthetic dyes are used by nearly all the textile industries as colourants. These industries use reactive dyes, which constitute about 30% of dyes used in the textile industries [1,2]. Coloured wastewater emanates from textile industries because dyes (10–60%) are lost during dyeing process [3]. The effluent from textile industries is hazardous to the living organisms; it lowers the rate of photosynthesis of aqueous flora by impeding light penetration [4–6]. Some of these dyes are toxic, mutagenic and cancer inducing [7–9], which invariably have negative impacts on the environment [4,10]. Reactive dyes are characterised with complex aromatic molecular structure, which makes it difficult to treat the effluents containing reactive dyes [11,12]. Reactive dyes are, therefore, stable and non-biodegradable [13]. As a result of imposition strict regulations [3], effluents emanating from the fabric industries must be treated before being discharged into the environment [14,15]. This has led to quest for nature friendly techniques for removal of dyes from wastewater [16,17].

To remove synthetic dyes from wastewaters, adsorption is a useful one technology [17,18]. Adsorption is now a predominant technique for effluent treatment because of its simplicity, effectiveness and availability of low cost adsorbents [19–24]. It is a process that transfers pollutants from the effluent to a solid phase thereby reducing the bioavailability of toxic species to living organisms [25]. The treated effluent can be regarded not harmful and then discharged into the environment [25,26]. For industrial processes that requires water of low or moderate purity, the treated water could also be used. Adsorbents can be regenerated after adsorption process, stored and reused [25,26].

Activated carbons possess pore structures that enhance high adsorption. This characteristic feature makes activated carbons one of the materials employed for removal of organic compounds from wastewaters [27–30]. Ability of activated carbons to remove pollutants from aqueous solutions depends on the nature of organic material used for the preparation of the activated carbon [27,28] and experimental conditions in the activation processes [28,29]. Among the reagents widely used for chemical activation of activated carbons are $H_3PO_4$, $ZnCl_2$, KOH, NaOH, $H_2SO_4$, and $K_2CO_3$ [28–30]. In a chemical activation process, the raw materials and inorganic activating agents are mixed in aqueous medium. The resulting material is subsequently dried in an oven and carbonised (673–1073 K). Inorganic material (activating agent) can be excluded using water or solutions of acid. However, this procedure did not provide a homogeneous distribution of the inorganics in all the organic carbonaceous materials because of the problems related with the drying of impregnated organic material [28–30].

Cocoa shell is a residue that corresponds to 80% of the dry weight of all cocoa fruit [31]. The annual production of cocoa in Brazil is about 250,000 ton/year that would correspond to approximately 200,000 ton cocoa shell per year. Therefore, the Brazilian industry of chocolate generate large quantities of cocoa shell, most of which are discarded in aquifers and soil environments. The decomposition of these residues leads generating various chemicals and microorganisms that can contaminate the environment in an uncontrolled manner. Therefore it is necessary to find a use for this waste in order to avoid environmental problems, with sustainable solution.

To the best of our knowledge, this is the first paper that reports the chemical activation of an activated carbon using a mixture of inorganic components (28.6% red mud, 28.6% lime, 14.3% KOH, 14.3% $Al(NO_3)_3$ and 14.2% $Na_2SO_4$) and powdered cocoa shell with inorganic: organic proportions of 1.0, 1.5 and 2.0. In the preparation, water was added to allow formation of a paste. The paste was dried at room temperature for 24 h and thereafter placed in a stainless steel reactor, where it was heated up to 1073 K under inert atmosphere. The carbonised materials (CC1.0, CC-1.5, CC-2.0) were acidified with a 6.0 mol $L^{-1}$ of HCl under reflux to obtain chemically activated cocoa shell carbons (ACC1.0, ACC-1.5, ACC-2.0). Preliminary experiments in this study revealed that ACC-1.0 has best adsorption capacity for reactive violet 5 (RV-5) textile dye from aqueous solutions than ACC-1.5 and ACC-2.0. Commercially available activated carbon (CAC), an established adsorbent for removal of toxic species from aqueous solutions, was used to verify the sorption capacity of ACC-1.0. ACC-1.0 and CAC were utilised for the adsorption of RV-5 dye from aqueous solutions. Influence of pH of dye solutions, time and temperature on adsorption capacity were investigated. The adsorbents were used for treatment of different simulated dye-house effluents.

## 2. Materials and methods

### 2.1. Solutions and reagents

Deionised water was utilised for preparation of solutions. The textile dye, C.I. Reactive violet 5 dye (RV-5, C.I. 18097; CAS: 12226-38-9; $C_{20}H_{16}N_3O_{15}S_4Na_3$, 735.58 g $mol^{-1}$, $\lambda_{max}$ = 545 nm see Supplementary Fig. 1) at 85% purity, was purchased from Sigma-Aldrich (St. Louis, M.O., USA) and was used without purification. The RV-5 dye contains one sulphato-ethyl-sulphone and two sulphonate groups. The functional groups of the dye are negatively charged. Their $pK_a$s are lower than zero [32]. RV-5 dye was used in this study, because it is largely employed in the Brazilian industries for dye clothing.

A stock solution (5.00 g $L^{-1}$) of RV-5 dye was prepared by weighing a calculated amount of the dye and dissolving in deionised water. The stock solution was diluted to obtain various working solutions. The pH of the solutions was adjusted using the Schott Lab 850 set pH meter with a 0.10 mol $L^{-1}$ NaOH and/or a 0.10 mol $L^{-1}$ HCl.

### 2.2. Adsorbents

Commercial activated carbon (CAC) supplied by Merck (325–400 mesh) was used to compare the sorption performance of cocoa shell activated carbon used in this work.

The activated carbon adsorbent was prepared using the following procedures (Fig. 1): a 70.0 g of powdered cocoa shell, a 70.0 g of inorganic components (28.6% red mud, 28.6% lime, 14.3% KOH, 14.3% $Al(NO_3)_3$ and 14.2% $Na_2SO_4$) and 50.0 mL of water were thoroughly mixed to obtain a homogeneous paste. The resulting paste was placed in a 4.8 by 14.0 cm mould cylinder (253.34 $cm^3$), wet-shaped and dried at room temperature for 24 h. The dried cylinder (without the mould) was subsequently placed in a stainless steel reactor (Fig. 1). The reactor allowed uniform gas distribution and homogeneous gas exchange rate (argon at 100 mL $min^{-1}$) to