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# Intensive insight into the enhanced utilization of rice husk ash: Abatement of rice mill wastewater and recovery of silica as a value added product

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### ABSTRACT

The present study deals with the preparation of adsorbents from rice husk ash for the efficient treatment of rice mill wastewater. By chemical modification, two different adsorbents were prepared—adsorbent (ADS) was synthesised from raw RHA that contain silica and another adsorbent (ADC) was prepared from leftover RHA which remained after silica extraction. The maximum chemical oxygen demand (COD) removal was observed at adsorbent dose 10 g/L, pH 5 and 120 min. Freundlich isotherm model was fitted to the equilibrium adsorption data and pseudo second order model was found most appropriate to characterize the kinetic data for ADS and ADC. Negative values of change in Gibbs free energy indicated the feasibility and spontaneity of the adsorption process. The enthalpy and entropy change for adsorption of rice mill wastewater ADS were 32.88 kJ/mol and 0.161 kJ/molK, whereas for ADC the results were 39.51 kJ/mol and 0.213 kJ/molK, respectively.

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# 1. Introduction

In the last two decades, to meet the demand of rice as principle food for the increasing population, the major portion of rice production is carried out in modern rice mills. Rice husk is the by-product obtained from the milling, which is generally used as fuel in the paddy milling to save energy, thus turning the process resource efficient as it has a calorific value of 13.6 MJ/kg (Armestoa et al., 2002). With the combustion of rice husk at high temperature (573 K), the burnt rice husk generates rice husk ash (RHA) which is mainly considered as waste and disposed at landfill site leading to air and water pollution. Parboiling is the widely employed method for pre-cleaning and soaking of paddy to produce the improved quality of rice (Ituen and Ukpakha, 2011; Oli et al., 2014), constituting a water-intensive industrial step. In modern rice mills, high amount of harmful solid and liquid wastes are being generated, finally released in the form of wastewater (15 L/kg of rice produced) and RHA (0.22 kg/kg of rice produced). Thus, generation of huge

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http://dx.doi.org/10.1016/j.ecoleng.2016.02.034 0925-8574/© 2016 Elsevier B.V. All rights reserved. volumes of wastewater (1.0–1.2 L/kg of paddy) contains an excessive load of organic and inorganic pollutants (Rajesh et al., 1999). Therefore, increased efforts have been paid in recent years in the efficient treatment of rice mill wastewater (Kumar et al., 2015).

Abundantly available waste RHA has been widely used as raw material for the preparation of silica gel and powder (Kumar et al., 2016), improved quality of cement and concrete, adsorbents for the organic dyes, metal ions and heavy metals from aqueous solutions (Kamnath and Proctor, 1998). Rice mill wastewater (the other waste), whose proper disposal is a challenging issue for an industry considering the cost, complexity and the limited efficiency of the conventional processes. Rice mill wastewater is generally treated by different physicochemical processes such as coagulation (Kumar et al., 2008), oxidation (Gogate and Pandit, 2004) and biological treatment methods (Behera et al., 2010). Besides these processes, there is an increasing interest in preparing activated carbon, which can be used as an adsorbent to remove organic contaminants from different effluents. Adsorption is one of the most useful treatment processes of being cheaper, fast, efficient and eco-friendly (Pizarro et al., 2015).

The current study made a detailed exploration of the plausible effective (Fig. 1), eco-benign route for the treatment of rice mill wastewater by means of two distinctly prepared adsorbents





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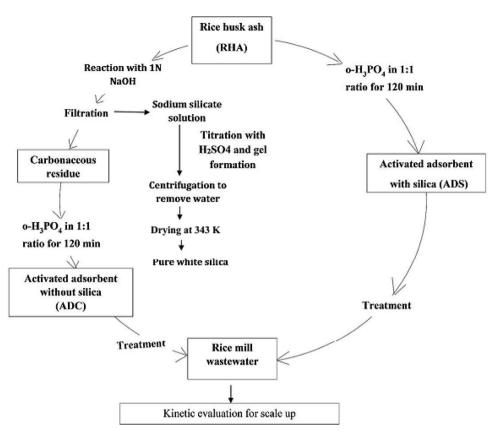


Fig. 1. A simplified route for enhanced utilization of rice husk ash (RHA) for the efficient abatement for rice mill wastewater.

from RHA—adsorbent (ADS) synthesised from raw RHA which naturally contain silica along with carbon and other adsorbent (ADC) was prepared from leftover RHA which remained after silica extraction. Simultaneously, the extracted silica from RHA was thoroughly characterized by scanning electron microscope (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectrometer (FTIR).

To the best of our knowledge, study pertaining to the preparation of such two different adsorbents (with and without silica) was not addressed earlier. Moreover, the comparative analysis and applicability of these adsorbents from RHA in the treatment of rice mill wastewater were not investigated. The mechanism of adsorption, characterization of the adsorbent, kinetics along with equilibrium and thermodynamic parameters were determined and impacts of governing parameters on adsorption of contaminants from rice mill wastewater were carried out to determine the best efficient adsorbent.

# 2. Materials and methods

## 2.1. Rice husk ash and rice mill wastewater

Rice husk ash (RHA) and rice mill wastewater were collected from Laxmi Shree rice mill of Burdwan, West Bengal, India. In the present work, 20 L of rice mill effluent was collected from the rice mill for the entire experimental work, followed by addition of sodium azide (5 mg/L) to inhibit the biological activity (Gulkaya et al., 2006). The effluent was transported to the lab in an ice box and immediately stored at 277 K after its arrival in order to avoid changes in the physico-chemical features of rice mill effluent. In this rice mill, rice husk is burnt in a furnace at about 973–1373 K to produce steam for parboiled rice production. This results in the generation of rice husk ash by combustion process. RHA is mainly composed of silica and carbon. RHA was washed with distilled water and subsequently dried. Then RHA was ground to prepare finer particles (smaller than  $90 \,\mu$ m). The initial characteristics of rice mill wastewater were pH 5.5; chemical oxygen demand (COD) = 3388 mg/L; colour = yellowish; odour = obnoxious; lignin = 284 mg/L; phenol = 32 mg/L.

### 2.2. Extraction of silica

RHA was washed repeatedly with 1 N solution of  $H_2SO_4$  till dirt and minerals were removed. Washed RHA was then heated at 363 K with 1 N NaOH leading to the formation of sodium silicate solution (Kalapathy et al., 2000). Subsequently, the left over filtrate was continuously titrated with  $H_2SO_4$  till the neutral pH was attained. Afterwards it was centrifuged for extracting the silica gel from the liquor. The silica gel was dried at 343 K for 48 h and finally crushed to prepare powdered silica.

The silica extraction was done using the following reaction (Soltani et al., 2015; Lu and Hsieh, 2012)

$SiO_2(ash) + 2NaOH \rightarrow Na_2SiO_3 + H_2O$	(1)
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$$Na_2SiO_3 + H_2SO_4 \rightarrow SiO_2 + Na_2SO_4 + H_2O$$
(2)

### 2.3. Preparation of adsorbents

After silica extraction, the left solid RHA residue was used for the preparation of adsorbent. For this, solid RHA residue was washed with distilled water and dried to get carbonaceous RHA. It was then ground to prepare finer particles (smaller than 90  $\mu$ m). Afterward, adsorbent ADC was prepared by activation with o-H<sub>3</sub>PO<sub>4</sub> in 1:1 ratio followed by carbonization at 623 K for 120 min. Then it was washed with ammoniacal water till the pH was 7 followed by air drying at room temperature.

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