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# Adsorption thermodynamics and kinetics of ranitidine hydrochloride onto superheated steam activated carbon derived from mung bean husk

Sandip Mondal[a], Keka Sinha[a], Kaustav Aikat[a], Gopinath Halder[b,*]

[a] *Department of Biotechnology, National Institute of Technology, Durgapur 713209, India*
[b] *Department of Chemical Engineering, National Institute of Technology, Durgapur 713209, India*

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ABSTRACT

Pharmaceutical compound possessing eco-toxicological effects in the aqueous system have been a growing concern over the few decades. The present work investigates the use of low cost mung bean husk (MBH), an agricultural waste, for the preparation of superheated steam activated carbon towards removal of ranitidine hydrochloride (RH) from synthetic wastewater. The adsorbent was examined as a function of dosage (0.010–1 g), pH (2–12), agitation (40–120 rpm) and temperature (303–318 K) for the optimization of operational parameters. The experimental equilibrium data were evaluated by non linear Langmuir, Freundlich, Sips and Redlich–Peterson models. The Sips model was found to express high level of agreement with experimental data. The maximum sorption of 100 ppm RH onto MBH derived steam activated carbon (MBH-SAC) was estimated to be 99.16% at 298 K. The kinetic study conducted at four temperatures indicates that the adsorption process follows the fractionary order kinetics. A negative value ($-11.307\ \mathrm{kJ\,mol^{-1}}$) of enthalpy change ($\Delta H^\circ$) suggests that the adsorption process was exothermic. Gibbs free energy ($\Delta G^\circ$) confirms that the reaction of the adsorption process was spontaneous and feasible in nature. The results suggest that MBH-AC can be used as an efficient and low cost adsorbent for the removal of RH from aqueous solution.

## Introduction

The detection and removal of pharmaceutical compounds present in the aqueous system are of a great concern and a matter of potential research because of their toxicological impacts on the aquatic environment [1,2]. There are tons of pharmaceutical compounds (PC) produced annually all over the world. The common pathway of PC into the environment is through unaltered excretion of urine and faeces, household disposal, sewage treatment plant, metabolic post consumption, diagnostic compound, etc. Pharmaceutical compound in the aquatic system leads to eco-toxicological impact and bioaccumulation for the aquatic and terrestrial ecosystem [3,4]. The presence of very minute (nano gram) quantities of the PC or their derivatives is therefore, highly undesirable for the aquatic system [3,5].

Ranitidine hydrochloride (RH), histamine $H_2$ receptor antagonist is used to decrease acid production from parietal cells of the stomach. RH is one of the most prescribed drugs in the world. It reaches into the environment from different sources and ranitidine may undergo biotic and abiotic transformation yielding environmental metabolites. RH itself does not have any acute toxicity in the aquatic environment at its highest concentration tested ($100\ \mathrm{mg\,L^{-1}}$). However, photo-degraded forms of the drugs are potentially hazardous for all organisms tested [6]. After solar simulator irradiation in ranitidine water two types of photo-transformation product were found; compound 1 ($C_{12}H_{21}N_3O_2S$) and compound 2 ($C_{12}H_{21}N_3O_4S$). Ranitidine along with the photo-degraded product inhibits growth population of rotifers and crustacean on their chronic dosage. The compound 1 shows most genotoxic and mutagenic effects [6]. Hence, the treatment of such waste becomes an urgent necessity for the protection of aquatic environment.

From the point of view of the hazardous effect of the PC on the environment and human health, it is essential to remove them from wastewater before being discharged into the environment. Conventional wastewater treatments are not well equipped to eliminate and or to degrade most of these compounds [7,8]. Out of several other techniques, adsorption is observed to be one of the

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[*] Corresponding author. Tel.: +91 9434788189; fax: +91 3432754078.
*E-mail address:* gopinathhaldar@gmail.com (G. Halder).

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**Nomenclatures**

| | |
|---|---|
| $a_{RP}$ | Redlich–Peterson constants $(\mathrm{mg\,dm^{-3}})^{-g}$ |
| $C$ | Constant related with the thickness of boundary layer $(\mathrm{mg\,g^{-1}})$ |
| $C_i$ | Initial pharmaceutical concentration $(\mathrm{mg\,L^{-1}})$ |
| $C_e$ | Equilibrium pharmaceutical concentration $(\mathrm{mg\,L^{-1}})$ |
| $D_q$ | Differential of $q$ |
| $g$ | Dimensionless exponent of Redlich–Peterson equation |
| $k_{Av}$ | Avrami kinetic constant $(\mathrm{h^{-1}})$ |
| $k_f$ | Pseudo-first order rate constant $(\mathrm{h^{-1}})$ |
| $K_F$ | Freundlich equilibrium constant $(\mathrm{mg\,g^{-1}}(\mathrm{mg\,dm^{-3}})^{-1/n_F})$ |
| $K_{id}$ | Intra-particle diffusion rate constant $(\mathrm{mg\,g^{-1}\,h^{-0.5}})$ |
| $K_L$ | Langmuir equilibrium constant $(\mathrm{dm^3\,mg^{-1}})$ |
| $K_{RP}$ | Redlich–Peterson equilibrium constant $(\mathrm{dm^3\,g^{-1}})$ |
| $K_s$ | Sips equilibrium constant $(\mathrm{mg\,dm^{-3}})^{-1/n_s}$ |
| $k_s$ | Pseudo-second order rate constant $(\mathrm{g\,mg^{-1}\,h^{-1}})$ |
| $m$ | Mass of adsorbent (g) |
| $n_{AV}$ | Fractionary reaction order (Avrami) which can be related, to the adsorption mechanism |
| $n_F$ | Dimensionless exponent of the Freundlich equation |
| $n_S$ | Dimensionless exponent of the Sips equation |
| $q$ | Amount adsorbed of the dryg by the adsorbent $(\mathrm{mg\,g^{-1}})$ |
| $q_e$ | Amount adsorbate adsorbed at the equilibrium $(\mathrm{mg\,g^{-1}})$ |
| $Q_{max}$ | Maximum adsorption capacity of the adsorbent $(\mathrm{mg\,g^{-1}})$ |
| $q_t$ | Amount of adsorbate adsorbed at time $(\mathrm{mg\,g^{-1}})$ |
| $t$ | Time of contact (h) |
| $V$ | Volume of dye solution put in contact with the adsorbent $(\mathrm{dm^3})$ |

Greek letters

| | |
|---|---|
| $\alpha$ | Initial adsorption rate $(\mathrm{mg\,g^{-1}\,h^{-1}})$ of the Elovich equation |
| $\beta$ | Elovich constant related to the extent of surface coverage and also to the activation energy involved in chemisorptions $(\mathrm{g\,mg^{-1}})$ |

most promising technologies due to its convenience and low cost [9,10]. Till date adsorption phenomena has been applied to remove PC through natural material like clays [11,12], soil [13], silica [14] etc.

Agricultural waste materials which are easily available, low cost, produced worldwide and most importantly transforming them into remediation purpose are of great interest nowadays. Different types of agricultural waste are used for remediation like sugarcane biomass, peanut husk, etc. [15–17]. In this regard, utilization of agricultural waste of mung bean husk as an adsorbent is the first attempt for removal of RH from aqueous media.

Mung bean, the seeds of *Vigna radiate* is native from the Indian subcontinent, and it is one of the most important grain legumes in South Asia [18]. Mung bean is an annual crop, cultivated mostly in rotation with cereals. About 90% of world's mung bean is produced in Asia, and India is the top producer of this crop [19]. In India, it is among the most important pulse crop depending upon its contribution in national production. MBH is cultivated in 4.2 million hector area with the annual capacity of 1.3 million tonnes production in 2008 [20]. The large amount of husk, an agro byproduct that is produced during milling of mung bean by legume seed splitting process, has been used as an adsorbent for RH removal. The conversion of a waste material into a useful commodity towards the removal of a potential contaminant seems to be an attractive way in economic as well as environmental point of view.

The main objective of the present study is to evaluate the efficacy of MBH-SAC as low cost adsorbent for the removal of RH from contaminated waste water. Various operational parameters like pH, agitation, time and temperature was optimized in the PC removal process by thoroughly characterized activated carbon prepared from the mung bean husk. The adsorption kinetic model, equilibrium isotherm and thermodynamic parameters related to this process were also performed and analysed.

## Experimental

### *Materials*

Analytical reagent grade chemicals were used in this study. The ranitidine hydrochloride ($C_{13}H_{22}N_4O_3S{\cdot}HCl$) was purchased from Sigma–Aldrich (St. Louis, MO, USA). The purity of the compound was >99%, and molecular weight is 350.87 $(\mathrm{g\,mol^{-1}})$. Reagent was doubly washed with distilled water and used for the preparation of the drug solution.

### *Preparation of activated carbon from mung husk and their characterization*

The mung bean husk used for preparation of activated carbon was obtained from a local market in Durgapur, India. The MBH was washed several times with distilled water followed by drying to obtain the desired precursor. In the first step, the material was carbonized gradually with the heating rate of 55 °C/15 min at 550 °C for 1 h in a cylindrical shelled stainless steel furnace chamber. In the second step, the temperature was raised to 650 °C, and steam was introduced into the furnace chamber at a pressure of 1.5–2.0 $\mathrm{kg\,cm^{-2}}$ for 1 h for activation of carbon. The activated product was then cooled to room temperature and then used for the study. Similar type of method for preparation of activated carbon was also done from coconut shell [21,22].

The precursor of the activated carbon has been appropriately characterized before pyrolysis for analysing fixed carbon, moisture content, volatile matter and ash content.

The Brunauer–Emmett–Teller (BET) surface area analyser (Quantachrome NOVA 2200C, USA) was used to measure the surface area, the total pore volume and the pore size distribution of the prepared activated carbon at 77 K by means of $N_2$ adsorption. $N_2$ adsorption was performed due to the fact that $N_2$ is adsorbed on the surface of variable sizes of micro-pores [23]. Prior to BET experiment, the carbon was degassed at 300 °C under vacuum for 3 h.

FTIR (PerkinElmer RXI, USA) analyser was used to understand the presence of surface group on the adsorbent surface and to identify the groups responsible for pharmaceutical adsorption. Scanning electron microscopy (SEM) analysis was carried out for investigating the surface textures and the development of porosity using SEM analyser (Hitachi S-3000N, Japan). X-ray diffraction patterns of the adsorbent were collected on a PANalytical X'pert pro model diffractometer.

### *Preparation of adsorbate solutions*

A stock solution of 400 $\mathrm{mg\,L^{-1}}$ was prepared by dissolving accurately weighed out quantity of RH doubly washed with distilled water. During the experiment, different concentrations of RH were made by the dilution method from stock solution. The solution of pH was adjusted by using 0.1 N NaOH and 0.1 N HCl.