



## Rice Husk Ash as a Great Potential Adsorbent in Multi-Purpose Adsorption of Various Pollutants: A Review

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### Abstract

Rice husk ashes are waste materials from the burner and found easily in rice production countries including Vietnam. However, the main application of this material in these countries is as a filler for the land used in agricultural production and the minor part applied in construction. Recently, the rice husk ash and their surface modified styles were interested in adsorption experiments conducted in laboratory scale for the removal of various types of pollutants such as heavy metal ions, nutrient ions, organic compounds. The question is that these sorbents are effectively deployed in the full or large scale. The contents of this article work towards the collection of synthesized methods for the adsorbents production from these natural sources, adsorption characteristics such as the specific surface area, adsorption capacity and the adsorption mechanisms. The results have also shown that the Si-O-H which exists on the surface of rice husk ashes plays an important role or support for the ability of adsorption process of these adsorbents. In particular, the aspects of continuous adsorption are thoroughly exploited as a basis for the conclusion of the application capability of these materials in the actual conditions.

**Keywords:** Rice husk ash; surface modification; ions adsorption; organic compounds; adsorption mechanisms; column adsorption; multi-purpose adsorption

### 1. Introduction

The current wastewater treatment is not only a big problem in urban and industrial areas but also a mission that urges to be solved effectively, seriously, and inexpensively in many rural areas. For example, environmental pollution from animal husbandry is one of the tough problems in many localities. The farm wastes generated from these activities are mainly treated by the biogas reactor which is known as an anaerobic digester. The treated wastewater from

biogas systems still contains the high contaminated components such as nitrogen and phosphorus. These factors seriously cause eutrophication and destroy ecosystems [1, 2]. For wastewaters containing many organic, ions and ionic compounds, the treatment process is combined in several steps sequentially. These unit works include both physicochemical and biological methods. In particular, the adsorption method is used as an advanced, less costly, and effective method to thoroughly treat the remaining pollutant components that exist in the primary effluent that has been previously treated. In addition, the

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adsorption method is known as a common application method with simple operation, reuse of adsorbent material, and ability to treat many contaminated components under eco-friendly conditions [3].

Traditional effective adsorbents should be replaced by other materials which are inexpensive and can be well applied in the large-scale systems. Activated carbon (AC) is considered as a traditional adsorbent material that has microporous structure, large surface area, and high porosity [4]. Most research on the adsorption ability of AC in which adsorbates are usually organic compounds, heavy metal ions, and small amounts of non-polar compounds in the liquid phase shows the physical adsorption nature of this material [5-7]. Besides, the adsorption capacity of AC is much lower than other adsorbents improved by surface modification methods (**Table 1**). In the case of nitrate adsorption, this capacity of AC is significantly lower than chitosan, SBA-15 silica, and rice husk ash with 20.9, 25.4, and 39.9 times, respectively. Other limitations also mentioned are the high cost or scarce resources used in the production of high-quality activated carbon. These reasons have been carefully considered and consequently, the search for cheap adsorbents and high adsorbent capacity to replace conventional adsorbents is the main goal in recent studies [4]. Since then, adsorbent materials derived from agricultural by-products or wastes such as bagasse, coconut fiber, rice husk, and rice husk ash are obviously attracting the attention of researchers [8-10].

Rice husk ash (RHA, Fig. 1), which would be obtained after burning rice husk (RH, Fig. 2), appears to be an abundant raw material and a more promising material due to its high adsorption capacity. The survey shows that each ton of paddy rice would correspond to 200 kg of rice husk (RH) and 40 kg of RHA [11]. Rice husk is a protective layer covering over the rice grain. After the milling process, this coating layer is separated and becomes a solid waste [12]. The containing of RH requires a large amount of space while the composting process of this low-nutritional value material is not quick and feasible, so the daily handling of large quantities of RH at rice milling plants is often difficult [13]. In the past, the waste rice husk was discharged directly into soils, rivers, lakes, and the environment, so this environmental pollution must be seriously concerned and properly managed. In recent times, this material is

also being used in the burning process to provide heat for brick kilns and agricultural dryers [14]. Besides, the chemical composition of RHA, which is well and conveniently applied in adsorption field, has been mentioned in many previous studies [15]. In general, the components of rice husk ash often include silica (72-98%), carbon (20-50%), and some metallic impurities [16, 17]. These values often vary slightly depending on factors such as the genes of rice, geographical conditions, irrigation methods, fertilizer, climate, fertility, and harvesting time. The recovery ratio of RHA is around 22% and the content of carbon and SiO<sub>2</sub> is changed insignificantly after the RH burning at 800 °C. This evidence shows that RHA has a very particular structure, high specific surface area, high heat resistance, and good mechanical strength due to its characteristic components consisting of silicon



**Fig. 1.** Rice husk ash



**Fig. 2.** Rice husk

oxide and carbon [18-20]. In addition, the physicochemical adsorption of nutrient ions such as nitrate and phosphate [21, 22], the competitive adsorption of heavy metal ions [23-25], and simultaneous adsorption organic compounds [26-28]

on RHA has been successfully experimented.

Based on the above advantages, RHA can be well applied for adsorbing many contaminants and considered to be used as an alternative to activated carbon. Moreover, the current practical demand for wastewater treatment is the simultaneous removal of pollutants that exist in the effluent. And, the exploration of the adsorption mechanism should focus on the ability to simultaneously remove many contaminants. Therefore, this article aims to investigate surface-modified methods, adsorption mechanisms of heavy metal ions, nutrient ions, organic compounds on RHA in multi-purpose adsorption, batch and column mode adsorption.

## 2. The manufacturing of adsorbent materials by surface modification methods

The methods of changing the surface characteristics of the materials used are very common and specific depending on the nature of the original material [29]. The adsorption enhancement and the selectivity of adsorption are subtly concerned. The physical and chemical processing stages are often applied to produce adsorbents with superior features. In most cases, the surface area and porosity of the adsorbents are increased after heat treatment. This physical method also helps to remove impurities on the surface of the material, and thus increases the adsorption capacity. Nevertheless, the adsorption of ions such as nitrate and phosphate could occur on the surface of adsorbents where are treated by chemical methods. This type of adsorption is explained based on electrostatic attraction and ion exchange theory. Electrostatic bonding is formed by an electrostatic force that occurs when positively charged surface of adsorbent is close to the anions, or as the functional groups of adsorbent have a higher affinity for these anions. The method which likewise is used to activate the positive charge of the material surface by acid embedding, also known as protonation, is a common, simple, and inexpensive method for removing pollutants [30]. The typical products created by the surface activation process are activated rice husk ash (ARHA) and protonated crosslinked chitosan beads (PCB). This method facilitates an increase in the amount of positive charge contributing to the stronger

**Table 1** The nature of adsorption in multi-purpose adsorbents for nutrient anions

adhesion of the negatively charged anions through electrostatic attraction. In fact, after grafting with amine groups, the surface of the material requires to be protonated to convert into positively charged ammonium functional groups for anion adsorption. A typical application for this combination is the nitrate ions adsorption on silica carriers that have been attached to protonized mono-, di- and tri-amine groups [31]. Similarly, rice husk ash and some materials made from agricultural products were used as an effective carrier for the amine functional group [21, 32]. Active centers for anion adsorption are formed after this functional group binds to heavy metal ions or protons. A large number of amine groups are attached, and the dispersion of these groups contributes to increased access and binding of anions to these functional groups as well as to optimize adsorption efficiency [33]. The increase of amine groups contributing to the increase of adsorption capacity is clearly reflected in the nitrate adsorption on SBA-15 which is shown in **Table 1**. This explanation is consistent with the results of previous research on adsorption efficiency of these anions that are less affected by the surface area and pore volume of adsorbents which have not been surface modified. The evidence for this phenomenon is that the adsorption efficiency of anions on the surface-treated silica is higher than that of raw silica [34]. Raw silica has a high pore volume and high surface area, and these parameters of denatured silica are smaller due to the occupation of amine organic groups on the inner surface of the pores. Furthermore, the BET surface area of adsorbent materials that were created by applying the silica dissolution method increased 4.47 times more than the original material [35]. In addition, silica material characteristics are also important in adsorption performance. For example, SBA-15 with MCM-41 gives significant differences in adsorption efficiency of nutrient anions (**Table 1**), and the nitrate adsorption capacity on triamine-bearing ARHA is much higher than that of triammonium functionalized SBA-15 silica.

Another method similar to surface protonation is the metal or metal oxides impregnation method. The presence of positively charged metal ions on the surface of the material will be enhanced after the material has been fabricated by this method. The anions will be trapped by positively charged metal ions

Adsorbent	Adsorbate	Surface modification method	Adsorption mechanism	Adsorption capacity (mg/g)	Reference
PAC	Nitrate	Protonation in acidic pH	Electrostatic attraction	4.1	[36]
GAC	Nitrate	Non-surface modification	Electrostatic attraction	1.7	[37]
ZCGAC	Nitrate	Metal ion impregnation	Electrostatic attraction	10.2	[37]
Tri-ARHA	Nitrate	Grafting amine groups	Ion exchange	163.4	[21]
Mono-SBA-15	Nitrate	Grafting amine groups	Ion exchange	49.6	[38]
Di-SBA-15	Nitrate	Grafting amine groups	Ion exchange	71.9	[38]
Tri-SBA-15	Nitrate	Grafting amine groups	Ion exchange	85.6	[38]
Mono-MCM-41	Nitrate	Grafting amine groups	Ion exchange	31.7	[39]
Di-MCM-41	Nitrate	Grafting amine groups	Ion exchange	38.6	[39]
Tri-MCM-41	Nitrate	Grafting amine groups	Ion exchange	38.8	[39]
nCCB	Nitrate	Amino protonation with sodium bisulfate solution	Electrostatic interactions	90.7	[40]
ECCB	Nitrate	Amino protonation with sodium bisulfate solution	Electrostatic interactions	104.0	[40]
HCB	Nitrate	Amino protonation in acidic pH	Electrostatic interactions	92.1	[41]
GC- Fe <sup>3+</sup>	Nitrate	Amino protonation with ammonia solution	Electrostatic interactions	8.35	[42]
PCB	Nitrate	Amino protonation with HCl solution	Electrostatic interactions	113.1	[43]

CCCB	Nitrate	Grafting groups chloroacetic and NaOH	carboxyl with acid	Electrostatic interactions	90.6	[43]
ZI-ACN	Phosphate	Metal impregnation	ion	Ligands exchange and electrostatic interactions	26.3	[44]
Am-MCM-41-RH	Phosphate	Grafting groups	ammonium	Ion exchange	21.0	[45]
ARHA	Phosphate	Protonation HCl solution	with	Electrostatic interactions	1.6	[22]
Mono-SBA-15	Phosphate	Grafting groups	amine	Ion exchange	68.4	[38]
Di-SBA-15	Phosphate	Grafting groups	amine	Ion exchange	77.9	[38]
Tri-SBA-15	Phosphate	Grafting groups	amine	Ion exchange	111.2	[38]
PCB	Phosphate	Amino with HCl solution	protonation	Electrostatic interactions	58.5	[43]
CCCB	Phosphate	Grafting groups chloroacetic and NaOH	carboxyl with acid	Electrostatic interactions	48.8	[43]

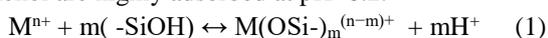
that exist on the adsorbent surface. The appearance of gravity and the ligand exchange mechanism play a major role in this adsorption [29].

### 3. The role of RHA in multipurpose adsorption

RHA was applied early in the field of Hg (II) adsorption in 1995 [46]. The report showed that this material is suitable for Hg (II) adsorption and well fitted the Langmuir isotherm model. By 2006, in a metal ions adsorption study, the FTIR result significantly expressed that the presence of polar groups (e.g., -OH, -C-OH, Si-O-Si, and Si-H) on the surface of the adsorbent represents the ability to perform a metal cation exchange [47]. Moreover, the presence of silanol groups (-SiOH) on the RHA surface is the main component in the ion exchange

mechanism of RHA and optimal pH value in the range of 6 to 8 was suitable for the formation of a weakly acidic silica surface which contributes to the occurrence of the metal ion exchange reaction as shown in eq. 1. The negligible influence of carbon content and the significant impact of functional groups of RHA on the adsorption of heavy metal ion have been mentioned recently [48]. Under acid pH solution value (3.8), Fe<sup>2+</sup> adsorption capacity corresponds to 16% and 0.93% of the carbon composition of RHA are 6.74 and 7.22 mg/g, respectively. In the solution pH range of less than 6.0, many reports indicated that RHA has very good heavy metal ion adsorption properties. Specifically, Naiya *et al.* [49] noted the condition for optimal adsorption of Pb (II) ions at pH 5 with an equilibrium adsorption capacity of 91.74 mg/g (**Table 2**). Besides, Youssef *et al.* [50] created a composite derived from rice husk ash combined with

aluminum oxide to selectively adsorb uranium with an absorption capacity of 85 mg/g at low pH range. Moreover, the ability and uptake-rate of Zn (II) ions on RHA is higher and faster than that of the Se(IV) adsorption recorded by El-Said *et al.* [51]. The adsorption equilibrium of Zn (II) and Se (IV) was achieved and these values were 9.59 and 2.01 mg/g, respectively. On the other hand, the diffusion of dye molecules into the pores of adsorbent was found to be the mechanism of Brilliant Green adsorption on RHA [52]. This statement is consistent with the previous study that RHA was discovered as a mesoporous material with the BET surface area of 36.44 m<sup>2</sup>/g [47]. However, the adsorption mechanism of Indigo Carmine dye on RHA was inferred by Lakshmi *et al.* [53] when the pH solution is compared with the pH recorded at the point of zero charge (PZC). Experimental results of these authors have shown high and stable adsorption efficiency in the pH range from 4.0 to 9.0, and the optimum pH value is 5.4. According to previous studies, the surface of RHA would be positively charged in dye solution with a pH of less than 8.3 because pHPZC of RHA was 8.3. Therefore, an electrostatic attraction is understood as an adsorption mechanism between RHA and anionic dye. Similar to the above observations, the interesting thing is that the Si-O bond of silica and ionization of phenol have been detached as agents supporting the successful phenol adsorption on RHA [54]. The electrostatic adsorption mechanism occurs between this ionic structure and this organic compound. Similarly possessing ionization capabilities like phenol, pyridine (Py) is converted into PyH<sup>+</sup> when the pH solution is less than 5.2 [55]. In fact, both of these existing forms of Py and phenol are highly adsorbed at pH~6.2.



Besides cations like heavy metal ions, anions such as nitrate, phosphate, and fluoride in the liquid phase are also effectively removed by RHA. The activation of RHA by HCl solution was applied by Mor *et al.* [22] with the phosphate removal efficiency of 89% at pH 6 corresponding to the adsorption capacity of 0.736 mg/g. The Langmuir model and the pseudo second kinematic model were found to be best suited to describe phosphate adsorption on this material. Thermodynamic parameters show that phosphate adsorption on this material is exothermic and spontaneous. Ganvir and Das [56] showed the adsorption efficiency of fluoride on RHA denatured by

a surface coating of aluminum hydroxide. The fluoride adsorption capacity reaches 15.08 mg/g, and experimental data follow the Freundlich isothermal model. Furthermore, with another useful improvement, a new zeolite made up of stirring between NaA-zeolite previously synthesized from RHA with colloidal hydrated alumina, well applied recently in the adsorption of fluoride with 104.2 mg/g of adsorption capacity [57].

Broader applicability of rice husk ash will be achieved after the material is chemically modified to increase the functional groups mounted. For instance, in the chemical modification process conducted in 2015, the material properties have changed significantly such as increasing specific surface area, reducing pHPZC value, and increasing -COOH groups on the surface of RHA [58]. These changes contribute greatly to increase the adsorption capacity and ability to adsorb more components. The specific transformations were noted that the specific surface area is increased from 0.52 to 2.81 m<sup>2</sup>/g, the value of pHPZC is decreased from 8.3 to 6.5, and the increased amount of -COOH is 0.104 meq/g, respectively.

The synthesis of adsorbent materials that RHA relates to as a basic component has been gradually formed in recent times. Hazardous pollutants with organic ingredients such as crude oil, dyes, phenols, humic acids, pyridine, and  $\alpha$ -picoline have been successfully adsorbed on adsorbents synthesized from RHA (**Table 3**). Oseke *et al.* [59] have made adsorbents by physically combining the powdered chitosan and the RHA synthesized from sulfuric acid-pretreated RH. The chitosan-RHA composite was applied to remove crude oil from the effluent. This composite adsorption capacity is 20660 mg/g which corresponds to a weight ratio of chitosan/silica of 0.9, a volume ratio of crude oil/water of 0.25, and 5 min of contact time. Physical adsorption nature has been discovered in this case. Moreover, in the study of Vaz *et al.* [60] and Liou, et al [61], the adsorption capacity of Methylene Blue (MB) on chitosan-g-poly(acrylic acid)/RHA hydrogel composites (CHT-g-PAAC/RHA) and GO/SBA-15/RHA were 1952.0 mg/g and 632.9 mg/g, respectively. Although RHA contributes only 5% (w/w) or a small portion in the composition of this composite compound, the adsorption capacity increases to 107.3 times (1952.0/18.2) or 34.8 times (632.9/18.2) that of Chowdhury's result. In the structure of this composite

compound, RHA acted as the silica source. The hydrogel formation by the presence of chitosan, acetic acid, acrylic acid, and sodium persulfate was done first. The product, called CHT-g-PAAC/RHA, was later formed by adding RHA to the reaction steps. Similar to MB, Crystal Violet (CV) is also known as a toxic dye that has been more effectively adsorbed on the nZSM-5 zeolite that RHA is used in the synthesis of this material [62]. The adsorbent preparation steps performed include the extraction of silica from acid-treated RHA and Teflon autoclaving of the mixture of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O. The adsorption capacity of CV on nZSM-5-zeolite is higher than that of adsorption on magnetically modified activated carbon, crosslinked poly tartaric acid treated rice husk ash specifically 1.9 times (125.4/67.1), 1.3 times (125.4/93.5), respectively.

The orientation of multi-purpose adsorption of RHA in the near future is the simultaneous adsorption of the same or different type of adsorbate and the strength of this trend highly depends on the flexible application of various adsorption mechanisms. The same heavy metal ions (Cd(II) and Zn(II)) and the same adsorbent (RHA) were used shortly in a single and binary cation adsorption study in which the adsorbate solution prepared with pH 6.0 [25]. The adsorption antagonistic relationship was found after conducting adsorption analysis. Furthermore, the

**Table 2** Capacity of adsorbing inorganic components of rice husk ash and surface-modified rice husk ash

Adsorbent	Adsorbate	Adsorption capacity (mg/g)	Reference
RHA	Pb (II)	91.7	[49]
RHA	Zn (II)	9.6	[51]
RHA	Se (IV)	2.0	[51]
RHA	Cd (II)	3.04	[25]
RHA	Zn (II)	5.88	[25]
RHA	Hg (II)	40.0	[46]
RHA	Fe (II)	7.22	[48]
RHA-AC	Uranium	85.0	[50]
RHA-AH	Flouride	15.1	[56]
RHA-NaA-Al(OH) <sub>2</sub>	Flouride	104.2	[57]

**Table 3** Results of adsorption of organic compounds of rice husk, rice husk ash and modified rice husk ash

Adsorbent	Adsorbates	Adsorption capacity	Reference
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competitive adsorption of organic substances in binary mixtures on the same adsorption site of RHA was outlined by Thakur *et al.* [26]. This interpretation was done based on the high compatibility of the extended Langmuir multi-component isotherm model [26, 63]. The mutual effects that occur between phenol–resorcinol, catechol–phenol, and catechol–resorcinol on total quantities of adsorptions were recorded as antagonistic.

Along with adsorption, desorption is also appreciated and mentioned in the studies because the recovery of adsorbent should be conducted to reduce the operating costs. In fact, RHA's sources are readily available, abundant, and inexpensive, so the recovery of this adsorbent is less recommended [55]. Despite the presence of these strengths, the elution of adsorbate from RHA was done, and the desorption efficiencies are not so high. The maximum desorption efficiency of Cd(II), Zn(II), Se(IV), Uranium, Methylene Blue, and Congo Red is 26.44%, 27.28%, 10.67%, 99.99%, 6.00%, and 40.00% respectively [18, 25, 50, 51]. And, in accordance with the above results, the chemicals used in the elution process of Cd(II), Zn(II), and Se(IV) are HNO<sub>3</sub> (0.1 N) and CH<sub>3</sub>COOH (0.1 N). Besides, acetone (50%) and HNO<sub>3</sub> (0.5 mol/L) were applied for the desorption of dyes and Uranium, respectively.

		(mg/g)	
RHA	Methylene Blue	18.15	[18]
RHA	Indigo Carmine	33.5	[53]
RHA	Brilliant Green	25.1	[52]
RHA	Congo Red	7.05	[18]
RHA	Phenol	0.9	[54]
ARHA	Phenol	27.6	[8]
RHA-NH <sub>2</sub>	Humic acid	8.2	[64]
RHA	Pyridine	11.7	[55]
RHA	$\alpha$ -picoline	15.5	[65]
RHA	pesticides	0.078 – 0.166	[27]
Chitosan-RHA composite	Crude oil	20660.0	[59]
CHT-g-PAAC/RHA	Methylene Blue	1952.0	[60]
GO/SBA-15/RHA	Methylene Blue	632.9	[61]

#### 4. Column mode adsorption for multi-purpose adsorption

Batch adsorption mode still has many limitations in implementing the design for larger scale adsorption systems in practice [66-69]. These limitations include the small volume of the adsorbate, the driving force of adsorption generated by the fluid flow is not included. A probe of batch adsorption is the premise for the implementation of column mode adsorption at a laboratory scale. The morphology, characteristics, and nature of the adsorption process and adsorbent materials are carefully considered and surveyed in the batch model. Besides, the inspection on the effectiveness of the adsorption system contains a very large volume of liquid flow in a limited volume of adsorbent on the continuous operation, with the presence of a driving force for adsorption is of more concern. These conditions contribute to the explanation that the column adsorption capacity is usually greater than the batch adsorption capacity [70].

The breakthrough, exhaustion phenomenon, and the theory of Mass Transfer Zone (MTZ) have been sequentially explored to assess the adsorption capacity and the influence by characteristics of adsorbent in column-mode adsorption. Here, the adsorption capacity is greatly influenced by the flowrate which is noted as closely related to dispersion and diffusion. In

addition, the properties of adsorbent are found to be part of the function that describes the length of MTZ. The adsorbate concentration will decrease to the minimum value after the liquid flow of these adsorbates passes through a layer of space in the column where the depth corresponds to the MTZ. The movement of MTZ in a top-down direction corresponds to the direction of flow. The saturation state of adsorption is first obtained from the upper layers and the MTZ is then slowly moved inside the bed of adsorbent until the breakthrough appears. Normally, breakthrough and exhaustion occur at a time when the concentration of adsorbate in the effluent is equal to 5 and 95 percent of the initial concentration, respectively. Eq.1 shows the calculation of the height of the MTZ ( $H_{MTZ}$ ) based on the height of the adsorbent bed ( $Z$ ), throughput volume to breakthrough ( $V_B$ ) and throughput volume to exhaustion ( $V_E$ ). When the hydraulic loading rate is too large or the value of  $V_B$  is too small,  $H_{MTZ}$  is much larger than  $Z$ , which will cause incomplete adsorption.

$$H_{MTZ} = Z \left[ \frac{V_E - V_B}{V_E - 0.5(V_E - V_B)} \right] \quad (1)$$

The scale-up of the real adsorption system was conducted more conveniently and accurately through the application of experimental models specifically applied to the fix-bed adsorption process [71]. These models described as mathematical formulas that are commonly applied to this adsorption column type are

Bohart and Adams, Thomas, and Yoon – Nelson [68]. The Bohart and Adams model (showed in eq. 2) describes the intimacy between the duration time of the adsorption process in the adsorbent layer and the specific bed depth of this adsorbent. This model assumes that the force generated from the internal diffusion and the mass transfer resistance from the outside are both negligible. On the other hand, axial dispersion does not occur according to the theory of the Thomas model (described in eq. 3). This model is applied when the adsorption equilibrium and the rate driving force follow Langmuir isotherm and reversible second-order reaction kinetics. The Yool Nelson model (written in eq. 4) applied when the rate of adsorption decreases at each molecule is proportional to the adsorbed and penetrating ability of the adsorbate.

$$t = \frac{N_0}{C_0 U} Z - \frac{1}{C_0 k_{AB}} \ln \left( \frac{C_0}{C_b} - 1 \right) \quad (2)$$

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp((q_0 m - C_0 \nu t) k_{Th} / \nu)} \quad (3)$$

$$\ln \left( \frac{C_t}{C_0 - C_t} \right) = k_{YN} t - \tau k_{YN} \quad (4)$$

$$q_0 = \frac{N_0}{\rho_A} \quad (5)$$

Not only limited to the short column-model in the laboratory, the enlargement at the full scale has also been generalized by Crittenden *et al.* [72] with simulated experimental ratios which are determined in Eq. 6. Parameters recorded in this equation include empty bed contact time (EBCT), the diameter of particle (d, mm), operating time (t, min) obtained after the adsorption with a volume of liquid phase treated (V), superficial velocity (v, m/h) in short column (SC) and long column (LC), respectively. The duration of time recorded after the liquid phase of adsorbate is in full contact with the solid phase of adsorbent is defined as EBCT. Eq. 8 shows the relationship between EBCT, the volume of adsorbent in the contactor ( $V_A$ , L) and volumetric flow rate (Q, L/h). Besides, the amount of adsorbent ( $m_A$ , g) to be used in the period corresponding to the EBCT is determined by Eq. 9, in which  $\rho_A$  is the density of adsorbent ( $\text{kg/m}^3$ ). The number of bed volumes (BV) is determined by operating time and EBCT (Eq. 11) [67].

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[ \frac{d_{SC}}{d_{LC}} \right]^{2-x} = \frac{t_{SC}}{t_{LC}} \quad (6)$$

$$\frac{v_{SC}}{v_{LC}} = \frac{d_{LC}}{d_{SC}} \quad (7)$$

$$EBCT = \frac{V_A}{Q} \quad (8)$$

$$m_A = EBCT \times Q \times \rho_A \quad (9)$$

$$V = Q \times t \quad (10)$$

$$BV = \frac{t}{EBCT} = \frac{V}{V_A} \quad (11)$$

Eq. 6 and 8 showed the importance of EBCT in the scale-up of column adsorption. Moreover, to determine EBCT, the parameters including  $q_0$  and Z (or  $V_A$ ) that are determined in the mathematical models of the adsorption column test (eq. 2 – 5) need to be compatible with Q,  $C_0$  and the properties of adsorbent. Therefore, the important parameters relating to the design of continuous adsorption models that should be considered are the influent adsorbate concentration, flow rate as well as the volume of liquid phase, bed depth of adsorbent, EBCT and adsorption capacity.

A helpful explanation was given from Sarici-Özdemir [67] and Saadat *et al.* [73] about the effect of EBCT, driving force, and adsorbate concentration on adsorption efficiency. EBCT must be controlled in accordance with the contact time which occurs between adsorbate and functional groups of the adsorbent. The low value of EBCT will cause incomplete interaction between adsorbate molecules and functional groups. Besides, the cause of high driving force is a high difference in the concentration of adsorbate. Meanwhile, the decreasing of column adsorption capacity in the presence of a high driving force has been demonstrated by Han *et al.* [74]. Besides, the performance of fix-bed adsorption is also collected through the volume of uptaken adsorbate (eq. 10). The values of V obtained respectively with the duration time of adsorption maintained until the occurrence of exhaustion phenomenon. The larger value of V indicates the longer operation time of the column adsorption system.

Table 4 presents the condition of short column mode experiments used RHA as an adsorbent. These experiments were operated with relatively low flowrate (5 – 30 mL/min). In addition, the lower flow

rate is used, the higher volume of treated water is obtained. In the same condition, when the much lower initial concentration of adsorbate is controlled, the much higher value of  $V$  is treated. For example, the value of  $V$  reached 6800 mL and 300 mL when the initial concentrations of Mn (II) and Hg (II) were 10 mg/L and 500 mg/L, respectively. Besides, as the same value of  $V_A$  (12.5 cm<sup>3</sup>), when the values of EBCT increases to 1.98 times (1.25/0.63), the value of  $t$  and

$V$  are increased by 2.59 times (623.3/240.2) and 1.30 times (6233/4804), respectively. Furthermore, in column adsorption of Mn (II) and Cr (VI), with the same value of flowrate (10 mL/min), the higher value of initial concentration contributes to the larger value of  $q_0$  at the same duration time (~ 600 min). Therefore, these results are very useful for the scale-up of the adsorption system.

**Table 4** The operating parameters in the column adsorption using RHA as adsorbent

Adsorbate	Operation condition											Reference
	$C_0$	$Q$	$d$	$Z$	$A$	$V_A$	EBCT	$t$	$V$	$q_0$	$N_0$	
Hg(II)	500	30	2.4	65.0	4.5	292.5	9.75	10.0	300	58.40	-	[46]
Mn (II)	10	10	3.0	22.5	7.1	159.8	15.98	678.0	6800	2.97	14.37	[75]
Cr(VI)	30	10	1.8	5.0	2.5	12.5	1.25	623.3	6233	29.81	68.27	[76]
Cu(II)	30	20	1.8	5.0	2.5	12.5	0.63	240.2	4804	22.87	55.96	[76]
2,4-D	100	7	1.2	13.0	1.1	14.3	2.04	135.8	951	6.79	2.83	[77]
pesticides	0.05	5	2	45	3.1	139.5	27.9	2000	10000	-	-	[27]
MB	20	10	0.8	20.0	0.5	10.0	1.00	65.7	657	10.75	0.44	[71]

$C_0$  (mg L<sup>-1</sup>),  $Q$  (mL min<sup>-1</sup>),  $d$  (cm),  $Z$  (cm),  $A$  (cm<sup>2</sup>),  $V_A$  (cm<sup>3</sup>), EBCT (min),  $t$  (min),  $V$  (mL),  $q_0$  (mg g<sup>-1</sup>),  $N_0$  (g L<sup>-1</sup>)

## 5. Conclusions

Studies have shown that the adsorption capacity of rice husk ash and the sorbents synthesized from RHA fluctuates quite broadly depending on the material modification methods. Moreover, their adsorption behaviors are good for the removal of various pollutants in aqueous phase like other traditional materials. And, high adsorption efficiency, abundant, and low-cost silica source are the specific advantages of these adsorbents which will enhance the demand for exploitation and wide application in the protection of water resources. On the other hand, the prominence of multi-purpose adsorption mechanism has been confirmed. Besides evaluating adsorption characteristics from batch adsorption models, the simultaneous implementation of column adsorption experiments is essential to record the operational parameters for the scale-up in the real adsorption system. The orientation of applying adsorbents in the column model with the advantage of a small volume of adsorbents is an effective and interesting solution to obtain design parameters for adsorbent equipment in

the industry. The widespread adoption of column-mode adsorption with a small volume of these adsorbents in the lab-scale is an effective and interesting approach to obtain main design parameters including the initial concentration of adsorbate, flow rate, the height of the adsorbent bed, empty bed contact time, and adsorption capacity must be clearly defined in adsorption column mode prior to deploying the scale-up.

## 6. Conflicts of interest

There are no conflicts to declare.

## 7. Acknowledgments

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