

Original Research Article

Sulphate Minimization in Agricultural Drainage Water using Modified Rice Husk

ABSTRACT

Eutrophication, salinization, hypoxia, and toxic algae, among other environmental damages are costly consequences of agricultural drainage water (ADW), and therefore poses a threat to ecological biodiversity, food security and agriculture sustainability. This work aimed to assess the adsorption efficiency of rice husk (RH) modified by chemical and thermal treatments for sulphate minimization from ADW. RH obtained from a local rice mill was washed in distilled water, oven-dried at 105 °C for 24 h, milled and sieved into 0.3–1.18 mm particle sizes. The optimum condition for carbonization was determined by varying the temperature- 200, 300 and 400 °C and time- 1, 1.5, and 2 h respectively. The RH was activated by chemical (H_3PO_4 and $ZnCl_2$) and thermal treatment. Batch experiments were carried out varying temperature (40-60 °C), adsorption time (15–140 min) and adsorbent dose (1 and 2 g) in an ADW with known sulphate concentration, 30 mg/L. The carbonization yield at 400, 300 and 200 °C varies within 18.91- 27.48%, 27.39- 32.82 % and 81.94- 95.75% respectively. It was observed that the percentage of carbon converted into silica increases with burning time; hence, the optimum temperature of 350 °C for 2 h was used for carbonization. Also, sulphate adsorption rate increased with contact time and dosage suggesting that the process is controlled by surface and pore diffusion. Based on the temperature study, adsorption was favourable at lower temperatures. H_3PO_4 and $ZnCl_2$ treated adsorbents have similar removal efficiency; however, $ZnCl_2$ treated adsorbent has a higher efficiency due to its ability to enhance the stability and mesoporosity of carbonaceous material. Modified RH is a potential adsorbent that could be of noble use in ADW quality minimization. However, the huge gap between literature studies and field application needs to be bridged by good extension services and appropriate policy.

Keywords: Activated Carbon, Wastewater, Rice Husk, Agricultural Drainage Water

1. INTRODUCTION

The leaching runoff from agricultural and forest lands, and agricultural drainage water (ADW), is causing water quality problems in aquifers, lakes, wetlands and rivers [1]. ADW is the largest volume of agricultural wastewater. It contains valuable nutrients (nitrate and phosphate), excess salts and other toxicants [2]. Discharge of saline drainage water into natural water bodies reduces water quality, crop yields and soil microbial diversity. Also, the presence of nitrogen and phosphorus in ADW intensifies eutrophication events, leading to many problems downstream such as toxic algal blooms, depletion of dissolve oxygen and unpleasant smell and taste in water [3]. This water can be captured and reused via cycling or blending as irrigation water [4]. Treatment and reuse of ADW is essential to meet the rising demand for water in agriculture and prevent environmental damages such as soil salinization, eutrophication, and other environmental pollution [2].

However, ADW has high spatial and temporal variability and requires site-specific minimization of water quality [5]. Conventional techniques such as membrane filtration, coagulation, oxidation, ion exchange, reverse osmosis and precipitation may be required to reuse ADW for irrigation. However, such technologies are not widely adopted for ADW treatment due to expensive facilities, high maintenance costs, energy requirements and

secondary pollution [6]. Adsorption is a highly efficient method for the removal of various impurities/pollutants from wastewater [7]. Activated carbon is a well-known and proven adsorbent made from many carbonaceous sources such as coal, coke, peat and wood. However, the high initial cost of commercial activated carbon and the need for regeneration inhibits its large-scale application as an adsorbent [8]. In recent decades, agricultural waste biomass (palm shells, coconut shells, rice husk) is gaining importance as an inexpensive and renewable adsorbent [9].

Agricultural waste biomass is abundant and has low economic value. One of such is rice husks (RH), a hard protective covering separated from rice grains during milling. Rice husk contains 30%-50% organic carbon in form of cellulose, hemicellulose, and lignin; 15% of mineral ash which has more than 95% silica [10]. In its carbonated form, RH retains a cellular structure skeleton with high porosity and large surface area. RH is a proven adsorbent for removing ionic dyes, phenols, inorganic anions, pesticides and heavy metals such as cadmium, Copper (II) [11], [12]. Moreover, thermal and chemical pretreatment of RH enhances the adsorption kinetics and sorption capacity of RH via surface area, pore size, morphology, and functional group modification [9], [13].

Sulphate is a major ion in natural waters, soluble and highly mobile. Among other sources, mineral dissolution (gypsum), atmospheric deposition and application of sulphur bearing synthetic fertilisers such as ammonium and potassium sulphate, superphosphate and complex fertilisers are common sources of sulphate in soil [14]. Sulphate is essential for plant growth and plays an important role in many plant processes. Nevertheless, the use of water with considerable high sulphate will result in a long-term sulphur accumulation in deeper soil layers and will ultimately impact rivers and shallow aquifers [15], [16]

The present work focuses on the development of low-cost adsorbents from rice husk modified by chemical and thermal treatments for the effective removal of excess sulphate from ADW. The effect of contact time, dosage and temperature on the adsorption process were investigated using the batch technique.

2. MATERIAL AND METHODS

2.1 The Study Area

The Agricultural drainage samples used in this study were collected from the project site of the Lower Niger River Basin Development Authority (LNRBDA) at Oke-Oyi, latitudes 8°35'N and longitudes 4°43'E. The community is located in Kwara State, Nigeria. Oke-Oyi has a tropical climate with distinct wet and dry seasons, high humidity and temperature (20 °C to 34 °C) around the year [17]. The terrain is 360m high above the sea level and gently slopes (>10%) towards the Southwest and Northwest direction, the area is drained in the east by River Oshin [18]. The area has intermittent water sources, and medium to high productive soil; hence, a viable area for irrigation [19]. Crops grown include maize, rice, vegetables, guinea corn and millet.

2.2 Materials

Rice husk (5 kg) was obtained from the mill at Arada local market, Ogbomoso. Phosphoric Acid (H₃PO₄) and Zinc Chloride (ZnCl₂) were purchased from Bond Chemicals and distilled water was obtained from Chemical Engineering Laboratory, LAUTECH, Ogbomoso. The Agricultural drainage was gotten from the Oke-Oyi irrigation project site of LNRBDA. The equipment used includes Electric Oven (Saisho, S 936, Temperature 250 °C, Time 60 min), Rotary Shaker (HZ 300, Max 300 rpm, 960 min), Muffle furnace (Gallenkamph, Size 2), Digital Weighing balance (DT 502A, Max 500g, d = 0.01g), UV Spectrophotometer (Model

No U V752 (D), Axiom Medical Ltd, UK), Crusher, pH meter, Burette, Centrifuge, Laboratory Mortar and Pestle.

2.3 Adsorbent Preparation

The Rice husk obtained from the rice mill was washed multiple times in distilled water to remove dust and soluble impurities. Then, it was oven-dried at 105°C for 24 h. The dried RH were milled and sieved into different particle sizes; 0.3, 0.42, 0.5, 0.71 and 1.18 mm for optimum carbon yield and lesser ash content.

2.4 Thermal and Chemical Modification of the Adsorbent

Thermal treatment was carried out by burning RH using ceramic crucibles in a Muffle furnace at 200, 300 and 400°C for 1, 1.5, and 2 h respectively. The different temperature and burning times were selected to determine the burning time that develops the optimum adsorption performance.

Activated carbons were prepared from the RH by chemical activation with H_3PO_4 and ZnCl_2 as summarized in Fig. 1. **Carbonization of Rice Husk**

. The milled rice was carbonized inside a muffled furnace at 350 °C for 2 hours. The carbonized RH (CRH) was allowed to cool inside the furnace and weighed in a crucible. Phosphoric acid (0.001 M) was prepared from a stock solution of 0.007 M. The CRH was mixed with 0.001M of H_3PO_4 for 24 hours at 150 rpm; 1 gram of CRH to 4 mL H_3PO_4 . The H_3PO_4 treated CRH was filtered and washed with distilled water till a stable pH was attained. The CRH was oven-dried at 110°C for 4 hours and ground with laboratory mortar and pestle to reduce the particle size thereby increasing the surface area. The CRH was stored in anti-moisture plastic bottles and the same process was repeated for 0.1 M of Zinc-chloride (ZnCl_2).

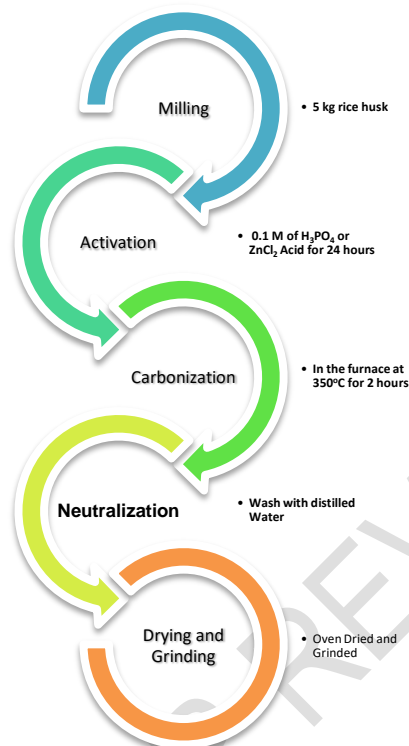


Fig. 1. Carbonization of Rice Husk

2.5 Water Sample Collection

ADW was collected from LNRBDA medium-scale irrigation site. The Agricultural drainage was collected in a 12 litres High-Density Polythene container previously acid-washed and cleaned with distilled water, 1 litre of the water sample collected was sent to the lower LNRBDA laboratory for analysis. The nitrate, bicarbonate, chloride, pH, temperature, electrical conductivity, sodium and sulphate concentration of the water were determined in three replicates.

2.6 Sulphate Adsorption Percentage (SAP)

The concentration of sulphate in the sampled water, 30 mg/l, exceeds the FAO guideline value. High concentration of sulphate in water increase the number of soluble salts in irrigation water resulting in soil salinity. Salinity derived from sulphate requires more effort to remove than that of other soluble salts. Equation (1) was used to calculate the sulphate removal efficiency.

$$SAP = \frac{C_i - C_o}{C_i} \times 100\% \dots \dots \dots (1)$$

where C_i and C_o are the initial and equilibrium sulphate concentration in mg/L.

2.7 Adsorption Experiment

A batch adsorption study was carried out by the addition of the adsorbent into the ADW at a specified time interval. The concentration of the sulphate used for the study is 30 mg/L which serves as the stock solution. Activated carbon adsorbent was added to each sample containing sulphate ions and stirred by a Rotary Shaker (HZ 300) at 200 rpm for 60 minutes. The RHA was removed from the solution filtering with Whatman filter paper. Then the residual sulphate ion in the solution was measured at a wavelength of 230 nm using a UV Spectrophotometer. The experiments were carried out at various temperatures of 40, 50 and 60 °C; Adsorbent dosage 1 and 2g and contact time 15 to 140 mins.

The sulphate adsorption percentage (SAP) is calculated for each sample using equation (1). SAP was plotted against concentration to establish a linear relationship between both parameters, **Error! Reference source not found.** The slope (0.006) and the intercept (0.15) of the plot were inputted into the general equation of a straight line.

$$y=mx+c..... (2)$$

$$SAP=0.66(Concentration)+0.1505..... (3)$$

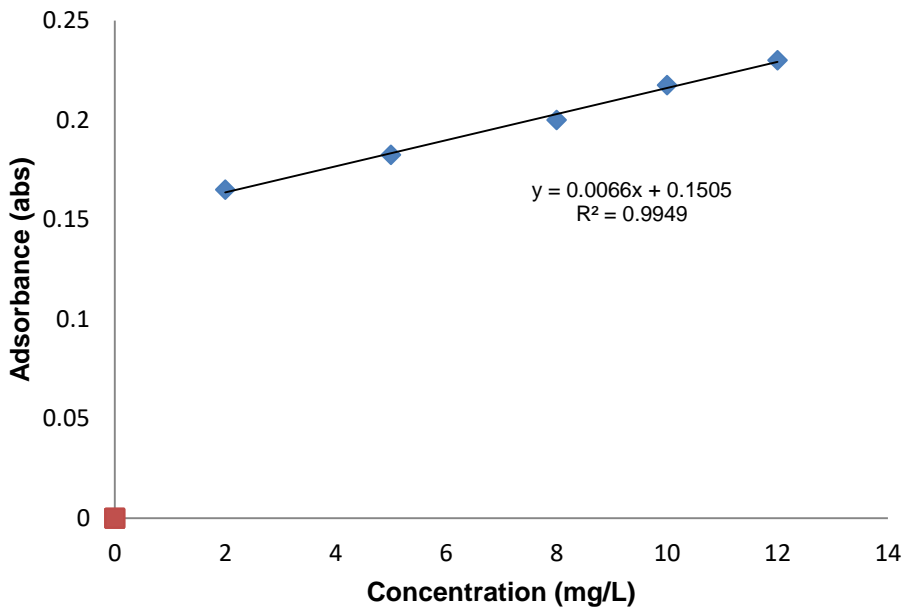


Fig. 2. Standard Curve for Sulphate Concentration Determination

3. RESULTS AND DISCUSSION

3.1 Quality of Sample Water

The results of the analyses of the Agricultural drainage compared to the FAO guidelines were presented in Table 1. All parameters were within FAO guideline permissible level with the exemption of sulphate and nitrogen.

Table 1. Physico-Chemical Analysis of Untreated Agricultural drainage sample compared to FAO Guidelines.

S/N	Water Parameter	Symbol	Units	Analytical Results	Permissible Range (FAO)
<u>Salt Content</u>					
1	Electrical Conductivity	EC	ds/m	0.036	0–3
2	Total Dissolved Solids	TDS	mg/l	33.9	0–2000
<u>Cations and Anions</u>					
3	Chloride	Cl ⁻	mg/l	1.19	0–1062.5
4	Sodium	Na ⁺	mg/l	748	0–919.6
5	Sulphate	SO ₄ ⁻	mg/l	30	0–20
6	Bicarbonate	HCO ₃ ⁻	mg/l	0.15	0–6102
<u>Nutrients</u>					
7	Nitrate – Nitrogen	NO ₃ ⁻ - N	mg/l	41.5	0–10
<u>Miscellaneous</u>					
8	Acid/Basicity	pH	mg/l	9.94	6.50–8.40

3.2 Modification of Rice Husk

Modification of RH via combustion potentially yields 20% of mineral ash with more than 95% silica content. The cellulose–lignin matrix burns away but the ash retains the skeleton of the cellular structure with porous and very fine particles. However, the porosity and functional groups of the produced ash vary with combustion temperature and time [20]. In practice, combustion yield between 17-33% have micropores pore structure, at higher burn off existing pores walls are eroded resulting in wider pores [21]. The results of the combustion at 200°C, 300°C and 400°C and at 1 hour, 1.5 hours and 2 hours are given in **Error! Reference source not found.** The plot indicates that the percentage yield at 200°C is above 80% at all time intervals; hence the temperature and time were not sufficient for carbonization. However, the yield at 300°C (27.39-32.82%) and 400°C (18.91-27.48%) fell between the desired range. Therefore, the average temperature (350°C) was selected as the optimum condition for carbonization. Also, as the burning time increases (1-2 hours), the yield percentage increases at all temperatures. This implies more carbon was converted into silica as the burning time increased. However, at a higher burning duration, there will be a gradual decrease in pore sizes as more micropores will be converted to large mesopores and macropores [9], [11]. Hence, the thermal treatment of RH has an optimum yield at 350°C burning temperature for 2 hours.

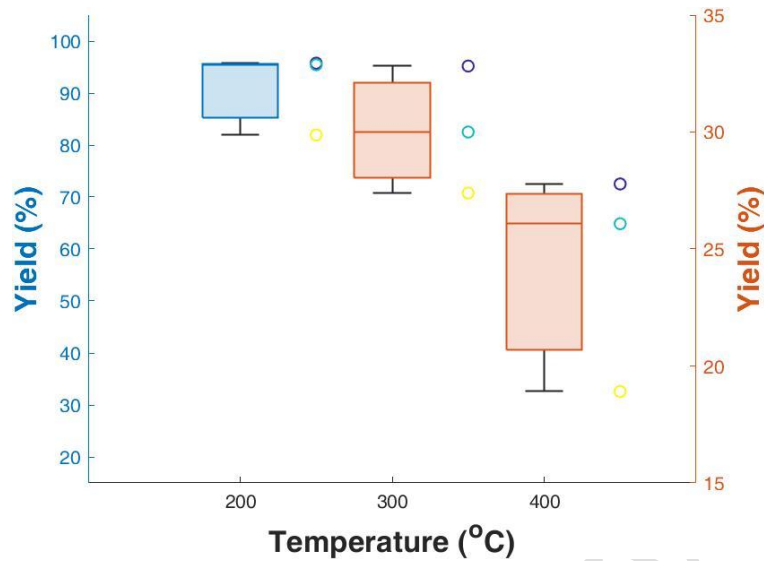


Fig. 3. Percentage Yield of Carbonized Rice Husk

3.3 Variation on Contact Time

The effect of contact time on the uptake of sulphate ions onto CRH was studied and is shown in Figure 4. The rate of sulphate adsorption increased sharply in the first 50 minutes, then the increase of adsorption rate tended to be gradual between 50 and 100 minutes. After a sharp rise, the adsorption rate eventually reached its peak at 140 min for all temperatures 78.28, 75.76 and 73.23 % respectively. Many active sites on the adsorbent surface are empty at the initial stage of the adsorption resulting in rapid initial adsorption. After lapse of time, the remaining vacant surface sites can be occupied difficultly due to repulsive forces between the solute molecules on the adsorbent surface and the bulk phase. Hence, the removal efficiency will increase with the contact time until the surface of the adsorbent active sites is saturated. This phenomenon has also been observed by [22], [23]. The results indicated that the efficiency of the activated carbon in removing sulphate content in Agricultural drainage is greatly influenced by contact time, as the contact time increases the removal efficiency increases.

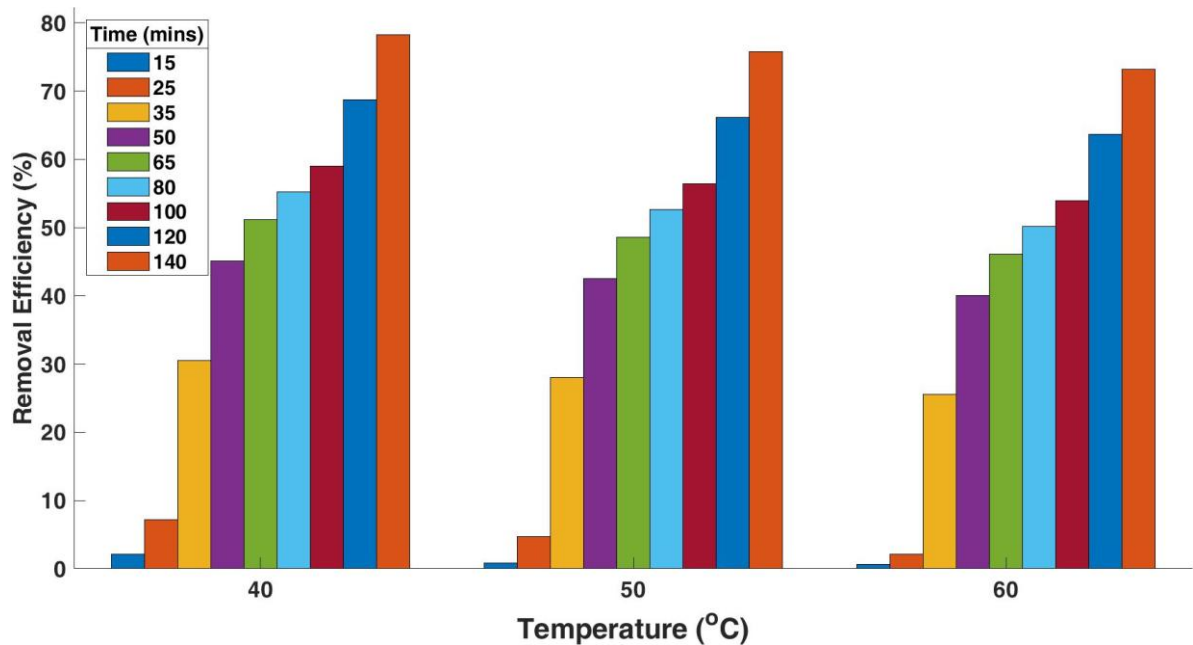


Fig. 4. Percentage Yield of Carbonized Rice Husk

3.4 Variation on Temperature

Contrarily, the temperature has a slight inverse relationship with removal efficiency, the removal efficiencies at 120 mins were 68.69, 66.16 and 63.64% for 40, 50 and 60 °C respectively. The decrease in removal efficiency as temperature rises is due to the molecular movement reduction. This result suggested that the adsorption process of sulfate by modified RH was temperature-dependent and represents an exothermic reaction since the extent of adsorption decreased with the temperature rise [13]. The activated carbon has higher efficiency at low temperatures and higher contact time.

3.5 Variation on Dosage

The experiment was carried out with the variation of adsorbent dosage (1-2 g) at constant temperature and varying contact time 15 to 140 min and was repeated in a similar way for acid and salt treatment. The effect of adsorption dose on the sulphate ion removal efficiency at varying contact times is presented in **Error! Reference source not found.**. The removal efficiency increases with the adsorbent dose. More adsorbent implies an increase in the adsorbent surface area and a large number of active sites for sulphate ion adsorption [9].

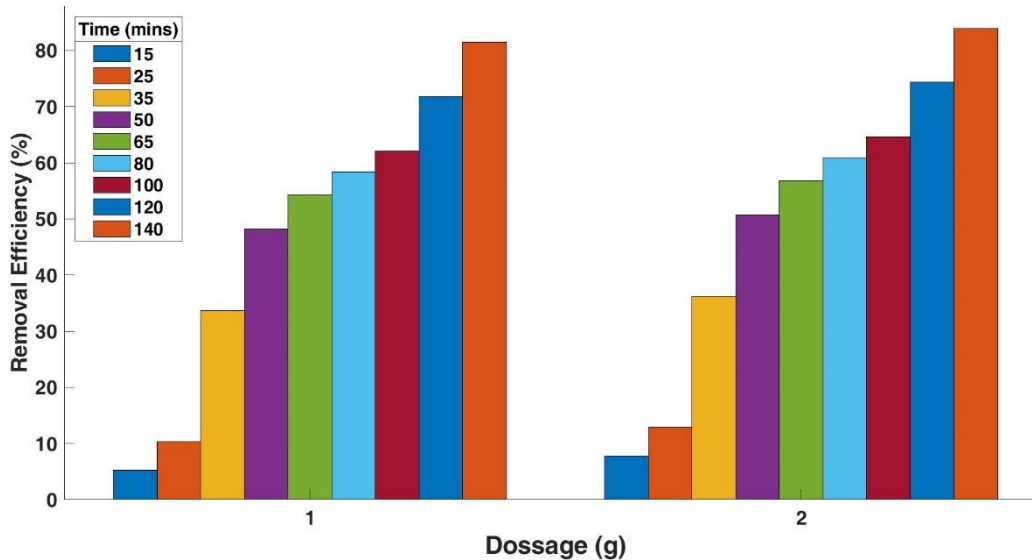


Fig. 5. Percentage removal of sulphate versus adsorbent dose and contact time

3.6 Variation in Acid and Salt Treatment

Chemical modification enhance adsorption capacity via liberation of new adsorption sites, enhancement of adsorbents' ion-exchange properties and the emergence of functional groups that favours pollutant uptake. Acids and bases are the most common chemicals used for adsorbents treatment, others include oxidizing agents and organic compounds [13]. However, adsorption capacity differs based on the choice of chemical. The removal efficiency of acid (H_3PO_4) and salt ($ZnCl_2$) treated RHA is compared in

. Both adsorbents have similar performance with time, dosage and temperature. However, the salt-treated adsorbents have higher removal efficiency successively. The acid treatment enhances the adsorbents binding sites with a more negative charge suitable for metal adsorption. Hence, the high efficiency of acid-treated adsorbents in removing heavy metal ions [8], [13]. Moreover, several authors have reported that base treatment tends to remove base soluble materials and inorganic compounds like carbonate and silica on the rice husk surface that might interfere with its adsorption property [9]. Specifically, $ZnCl_2$ enhanced the stability and mesoporosity of carbonaceous material resulting in higher adsorption capacity compared with other agents [6], [24]

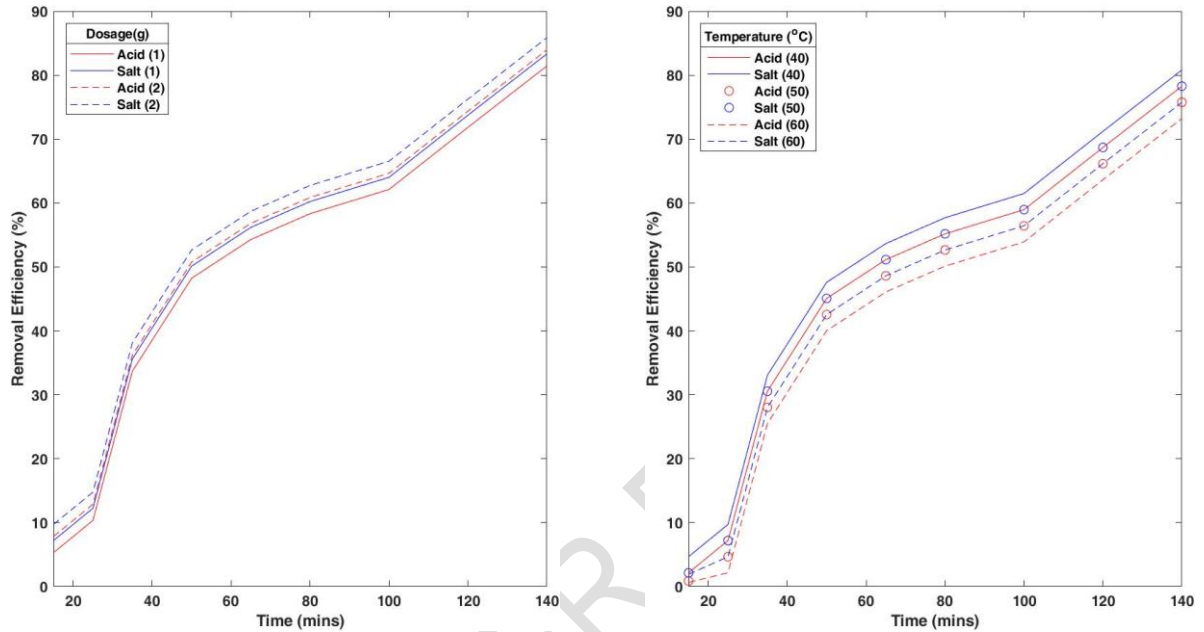


Fig. 6. Percentage removal of sulphate versus adsorbent dose

4. CONCLUSION

As outcomes of this study, thermal treatment of RH at temperature range of 300- 400 °C for 2 h enhances carbon to silica conversion rate and ultimately the adsorption potential. The adsorption process of sulphate from ADW suggest both surface and pore diffusion as sulphate adsorption efficiency increases with adsorbent dosage and adsorption time. The process was temperature-dependent and reaction since the extent of adsorption decreased with the temperature rise. The removal efficiency of acid (H_3PO_4) and salt ($ZnCl_2$) treated RH adsorbents differs. The salt-treated ($ZnCl_2$) adsorbent has a higher efficiency at all adsorbent dosages, temperature and time successively due to its ability to enhance the stability and mesoporosity of carbonaceous material. The thermal and chemical modification of RH adsorbents proved effective in sulphate minimization of ADW as the excess sulphate can be reduced by 80%, making the treated water suitable for reuse.

DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

REFERENCES

- [1] J. Mateo-Sagasta, S. M. Zadeh, H. Turrall, & J. Burke. "Water pollution from agriculture: a global review Executive summary. Food and Agriculture Organization of the United Nations and the International Water Management Institute," *CGIAR*, p. 35, 2017, [Online]. Available: <http://www.fao.org/3/a-i7754e.pdf>.
- [2] C. A. Hejase *et al.*, "Opportunities for Treatment and Reuse of Agricultural Drainage in the United States," *ACS ES&T Eng.*, vol. 2, no. 3, pp. 292–305, 2022, doi: 10.1021/acsestengg.1c00277.
- [3] W. Gao, Z. Duan, C. Yan, and C. Liu, "Influence of nutrient mitigation measures on the fractional export of watershed inputs in an urban watershed," 2020.
- [4] L. M. Dudley, A. Ben-Gal, and N. Lazarovitch, "Drainage Water Reuse: Biological, Physical, and Technological Considerations for System Management," *J. Environ. Qual.*, vol. 37, no. S5, p. S-25-S-35, 2008, doi: 10.2134/jeq2007.0314.
- [5] E. Ashour, B. Zeidan, and M. Elshemy, "Assessment of agricultural drainage water reuse for irrigation in El-Behira Governorate , Egypt ABSTRACT," *Water Sci.*, vol. 35, no. 1, pp. 135–153, 2021, doi: 10.1080/23570008.2021.1982336.
- [6] M. N. Mahamad, M. A. A. Zaini, and Z. A. Zakaria, "Preparation and characterization of activated carbon from pineapple waste biomass for dye removal," *Int. Biodeterior. Biodegrad.*, vol. 102, pp. 274–280, 2015, doi: 10.1016/j.ibiod.2015.03.009.
- [7] F. Akoh, H. Bouchoum, M. El Bouchti, O. Cherkaoui, A. Jada, and M. Tahiri, "Sulfate removal from aqueous solutions using esterified wool fibers: Isotherms, kinetic and thermodynamic studies," *Desalin. Water Treat.*, vol. 194, pp. 417–428, 2020, doi: 10.5004/dwt.2020.25461.
- [8] T. G. Chuah, A. Jumariah, I. Azni, S. Katayon, and S. Y. Thomas Choong, "Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: An overview," *Desalination*, vol. 175, no. 3, pp. 305–316, 2005, doi: 10.1016/j.desal.2004.10.014.
- [9] S. B. Daffalla, H. Mukhtar, and M. S. Shaharun, "Preparation and characterization of rice husk adsorbents for phenol removal from aqueous systems," *PLoS One*, vol. 15, no. 12 December, 2020, doi: 10.1371/journal.pone.0243540.
- [10] M. Ahmaruzzaman and V. K. Gupta, "Rice husk and its ash as low-cost adsorbents in

- water and wastewater treatment," *Ind. Eng. Chem. Res.*, vol. 50, no. 24, pp. 13589–13613, 2011, doi: 10.1021/ie201477c.
- [11] S. B. Daffalla, H. Mukhtar, and M. S. Shaharun, "Characterization of Adsorbent Developed from Rice Husk: Effect of Surface Functional Group on Phenol Adsorption," *J. Appl. Sci.*, vol. 10, no. 12, pp. 1060–1067, 2010.
- [12] P. T. Scaglioni and E. Badiale-Furlong, "Rice husk as an adsorbent: A new analytical approach to determine aflatoxins in milk," *Talanta*, vol. 152, pp. 423–431, 2016, doi: 10.1016/j.talanta.2016.02.042.
- [13] W. S. Wan Ngah and M. A. K. M. Hanafiah, "Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review," *Bioresource Technology*, vol. 99, no. 10, pp. 3935–3948, 2008, doi: 10.1016/j.biortech.2007.06.011.
- [14] J. Kopáček, J. Hejzlar, P. Porcal, and M. Posch, "Sulphate leaching from diffuse agricultural and forest sources in a large central European catchment during 1900–2010," *Sci. Total Environ.*, vol. 470–471, pp. 543–550, 2014, doi: 10.1016/j.scitotenv.2013.10.013.
- [15] J. Rastislav, B. Eduard, K. Martin, K. Ján, and S. Branislav, "Sulphate contamination, pH and conductivity of forest soils in two neighbouring mountains with different pollution in Slovakia from 1989 to 2013," *Soil Water Res.*, vol. 13, no. 3, pp. 129–139, 2018, doi: 10.17221/218/2015-SWR.
- [16] M. K. Sharma and M. Kumar, "Sulphate contamination in groundwater and its remediation: an overview," *Environ. Monit. Assess.*, vol. 192, no. 2, 2020, doi: 10.1007/s10661-019-8051-6.
- [17] O. S. Ismaila, O. A. Samsudeen, O. A. Yusuf, and U. C. Gunu, "Assessment of Physicochemical Characteristics of Selected Borehole Waters in Oke-Oyi Community, Ilorin East Local Government Area, Kwara State," *J. Appl. Sci. Environ. Manag.*, vol. 21, no. 6, p. 1127, 2017, doi: 10.4314/jasem.v21i6.22.
- [18] M. A. Adejumobi, T. A. Alonge, B. A. Mufutau, and M. F. Jatto, "Assessment of Suitability of Oshin River Water for Irrigation : Case Study of Oke-Oyi Irrigation Scheme , Nigeria .," *J. Environ. Sci. Toxicol. Food Technol.*, vol. 10, no. 6, pp. 48–51, 2016, doi: 10.9790/2402-1006034851.
- [19] E. O. Oriola, "Dynamics of soil Chemical Properties in Oke--Oyi Irrigation Project Site of Lower Niger Basin Development Authority, Ilorin, Nigeria," in *Geo-studies forum*, 2004, vol. 2, no. 1, pp. 86–94.
- [20] A. Mandal, P. Mukhopadhyay, and S. K. Das, "The study of adsorption efficiency of rice husk ash for removal of phenol from wastewater with low initial phenol concentration," *SN Appl. Sci.*, vol. 1, no. 2, pp. 1–13, 2019, doi: 10.1007/s42452-019-0203-3.
- [21] M. N. Alaya, M. A. Hourieh, A. M. Youssef, and F. El-Sejarah, "Adsorption properties of activated carbons prepared from olive stones by chemical and physical activation," *Adsorpt. Sci. Technol.*, vol. 18, no. 1, pp. 27–42, 2000, doi: 10.1260/0263617001493251.

- [22] M. Rahmati, G. Yeganeh, and H. Esmaeili, "Sulfate ion removal from water using activated carbon powder prepared by *Ziziphus spina-christi* lotus leaf," *Acta Chim. Slov.*, vol. 66, no. 4, pp. 888–898, 2019, doi: 10.17344/acsi.2019.5093.
- [23] T. Jie, L. Benqiang, C. Jinghua, S. Ying, and L. Huili, "Preparation and characterization of an attenuated porcine epidemic diarrhea virus strain by serial passaging," *Arch. Virol.*, vol. 163, no. 11, pp. 2997–3004, 2018, doi: 10.1007/s00705-018-3968-6.
- [24] A. Santhosh and S. S. Dawn, "Synthesis of zinc chloride activated eco-friendly nano-adsorbent (activated carbon) from food waste for removal of pollutant from biodiesel wash water," *Water Sci. Technol.*, vol. 84, no. 5, pp. 1170–1181, 2021, doi: 10.2166/wst.2021.303.

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