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Acid-Modified Biochar from Municipal Solid Waste for Rhodamine B Dye Adsorption

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Abstract

This study investigates the synthesis and application of acid-modified biochar derived from municipal solid waste (MSW) for the adsorption of Rhodamine B (RhB) dye from aqueous solution. Biochar was produced by pyrolyzing MSW at 450°C and subsequently modified using an acidic treatment to enhance its surface properties including porosity and surface functional groups. Characterization of the biochar was performed using techniques such as Fourier Transform infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). Adsorption experiments were conducted to evaluate the effectiveness of the acid-modified biochar in removing RhB dye under various conditions including initial dye concentration, contact time and adsorbent dose. The results showed that initial dye concentration of 10 mg/L, adsorbent dosage of 0.4 g and contact time of 100 mins gave the maximum dye removal from the adsorbent. The result showed that the modified biochar exhibited a significantly higher adsorption capacity of 20.24mg/g, with the adsorption process fitting well with the Langmuir isotherm and Pseudo second-order kinetics. This study demonstrates the potential of acid-modified biochar from MSW as an effective and sustainable adsorbent for removing organic pollutants like RhB dye from wastewater.

Key Words: **Adsorption, Adsorbent, Biochar, Rhodamine B and Pyrolysis**

Introduction

The rapid urbanization and industrialization in the 21st century have led to an alarming rise in municipal solid waste (MSW) generation, creating significant challenges for waste management systems worldwide. In addition to being a disposal concern, MSW contains valuable organic carbon that can be converted into biochar through pyrolysis, offering a promising pathway for waste valorization. Biochar, a highly porous and stable carbon material, has gained considerable attention due to its potential applications in environmental remediation, particularly in wastewater treatment [1]. Its high surface area, abundant functional groups, and ability to adsorb a wide range of contaminants make biochar an effective material for removing pollutants, including heavy metals, organic compounds, and dyes [2,3].

Rhodamine B (RhB), a synthetic organic dye commonly used in the textile, paper, and food

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industries, is notorious for its environmental persistence and toxicity. It is resistant to degradation and can contaminate aquatic ecosystems, posing significant risks to human and environmental health [4]. Traditional methods for dye removal, including chemical oxidation, coagulation, and membrane filtration, are often costly, produce toxic byproducts, or suffer from inefficiencies under certain conditions [5]. As such, adsorption techniques using low-cost adsorbents, particularly biochar, have emerged as an attractive alternative for the removal of dyes from wastewater [6].

While raw biochar is effective in adsorption, its capacity can be further enhanced through surface modification. Acid modification is one of the most widely used methods to increase biochar's surface area and introduce additional functional groups, such as carboxyl, hydroxyl, and phenolic groups, which improve the material's interaction with organic pollutants like Rhodamine B [7]. By increasing the material's surface charge and functional diversity, acid-modified biochar can significantly enhance its ability to adsorb dye molecules [8]. In recent years, various acids, including hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and nitric acid (HNO_3), have been utilized to modify biochar derived from different feedstocks, including agricultural waste, forestry residues, and MSW [9].

Several studies highlighted the effectiveness of acid-modified biochar in adsorbing Rhodamine B. For instance, [10] demonstrated that acid-treated biochar derived from rice husk exhibited a 50% increase in dye removal efficiency compared to untreated biochar. Similarly, [2] reported that biochar modified with sulfuric acid showed significantly enhanced adsorption capacities for RhB due to the creation of more reactive sites on the surface.

In addition to dye adsorption, using MSW-derived biochar aligns with the growing interest in sustainable waste management practices and circular economy principles. By valorizing MSW, biochar production not only addresses waste disposal challenges but also provides a carbon-neutral material for environmental remediation [11]. Furthermore, the acid modification process, which introduces environmentally benign functional groups, offers an opportunity to improve the adsorption efficiency of biochar while maintaining it is sustainability credentials.

This study examines the acid modification of biochar derived from municipal solid waste for the removal of Rhodamine B dye from aqueous solutions. The impact of various acid treatments on the physicochemical parameters of biochar and its adsorption efficacy is carefully analyzed. This study's findings will enhance the creation of more efficient and sustainable adsorbents for wastewater treatment and provide insights into the twin advantages of waste valorization and environmental pollution mitigation. This research investigates the efficacy of acid-modified biochar

obtained from municipal solid waste as an economical and efficient adsorbent for the elimination of Rhodamine B.

Materials and Methods

Raw material & pretreatment

Municipal Solid Waste (MSW) was randomly gathered from various households. The waste primarily consisted of varying amounts of materials such as orange peel, banana peel, pineapple peel, watermelon rind, potato peel, fish bones, animal bones, bread crumbs, chicken droppings, and paper scraps. After collection, the MSW was thoroughly mixed and washed first with tap water, followed by distilled water to eliminate any physically attached impurities. The cleaned waste was then dried in an air oven at 110°C for 24 hours.

Preparation of biochar

The Pretreated Municipal Solid Waste (MSW) was placed in a silica crucible and heated in an air-tight furnace (Vecster Ltd, Furnace Division Ecrotherm) at 450°C for 5 minutes. The resulting biochar was carefully transferred to an airtight container for further processing [12]

Modification of biochar

About 110 g of biochar was soaked into 300 ml of nitric acid at 90^0C for 4 hours. The modified biochar was cooled and repeatedly washed with distilled water to remove residual traces of the activating agent. After washing, samples were placed in a heating/drying oven (Fisher Scientific) at 110^0C for 24 h. Finally, the modified biochar was ground, sieved, and passed through a 0.2 mm sieve and then stored in a plastic bottle for further use.

Characterization of modified biochar

The surface morphology and characteristics of the modified biochar were examined using a PHENOM Prox SEM 800-07334 scanning electron microscope (SEM) at various magnifications. The functional groups on the biochar surface were identified using a VERTEX 70/70V spectrometer (Agilent Technologies). The point of zero charge (pHpzc), which corresponds to the pH at which the biochar's surface has a neutral net charge, was determined using the pH drift method as described by [13].

Preparation of adsorbate

The cationic dye Rhodamine B ($C_{28}H_{31}N_2O_3Cl$), with a maximum absorption wavelength of 556 nm, was used to evaluate the adsorption capacity of the prepared biochar. The dye, purchased from Revertex Chemicals Limited (Abuja, Nigeria), was used. Its chemical structure is shown in Figure 1. A stock solution of 1000 mg/L Rhodamine B was prepared by dissolving 1 g of the dye in 1000 cm^3 of distilled water. Working solutions of lower concentrations were then prepared through serial dilution. Absorbance measurements were taken using a UV-Vis spectrophotometer.

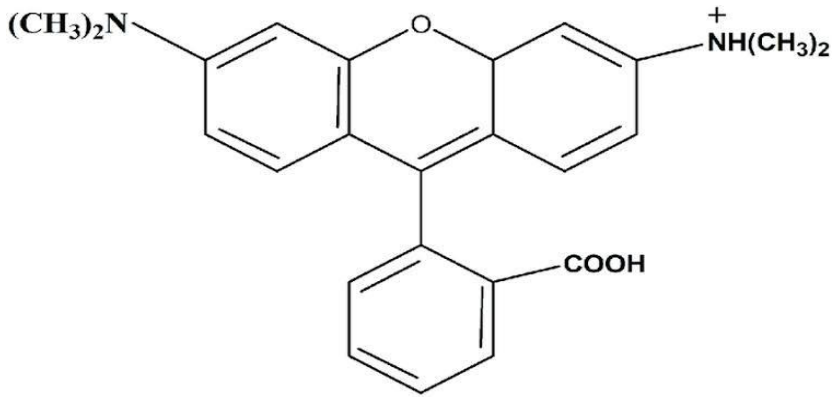


Figure 1 Chemical Structure of Rhodamine B

Batch adsorption experiment

A series of batch adsorption experiments were conducted in 250 cm³ Erlenmayer flasks, each containing 50 mL of Rhodamine B dye solution. A measured amount of modified biochar was added to the dye solution, with various parameters being adjusted, including contact time (20–160 minutes), adsorbent dosage (0.1–0.5 g), initial dye concentration (10–50 mg/L), and temperature (25°C–60°C), while other parameters were kept constant. The mixture of modified biochar (adsorbent) and Rhodamine B dye solution (adsorbate) was sealed in the conical flasks and agitated in a temperature-controlled water bath shaker (Flask Shaker, Barloworld Scientific Limited, Model ST1505A, UK) at 200 rpm. Samples were taken at predetermined intervals, centrifuged, and the supernatant was separated from the adsorbent by filtration using Whatman No. 41 filter paper. The concentration of unabsorbed dye was then measured using a UV-Vis spectrophotometer, operating at the maximum absorption wavelength of 556 nm for Rhodamine B. The removal efficiency of RhB and the amount of dye adsorbed per unit weight of modified biochar (qt in mg/g) were calculated using the following equations:

$$Removal\ Efficiency\ \% = \frac{Co - Ct}{Co} \times 100 - - - (1)$$

$$\text{Adsorption Amount } (\text{mg. g} - 1) = \frac{(Co - Ct)}{Co} \times \frac{V}{m} - - - - - - - - (2)$$

Where, C_o (mg. g^{-1}) is the initial Rhodamine B concentration (mg/L); Ct (mg/L) is the Rhodamine B concentration at time t (min); And V (L) is the volume of Rhodamine B solution; and m (g) is the weight of Biochar (adsorbent) used.

Kinetics of Rhodamine B adsorption onto modified biochar

To investigate the mechanism and characteristics of the adsorption of Rhodamine B dye onto Modified Biochar, two kinetic models. The pseudo

first-order kinetics model of [14,15] pseudo second-order were used to test the experimental data. The linear form of the pseudo first-order rate expression is given as;

$$\ln(\mathrm{qe} - \mathrm{qt}) = lnqe - k1\mathrm{t} \quad -----(3)$$

Where, k_1 (min^{-1}) is the rate constant of the pseudo first order adsorption, qe is the equilibrium adsorption capacity and qt is the amount of adsorbate adsorbed at time. The pseudo second-order kinetic model is expressed by the following:

$$\frac{\mathrm{t}}{\mathrm{qt}} = \frac{1}{K2qe2} + \frac{1}{qe} \times \mathrm{t} \quad ------(4)$$

Where, k_2 ($g/(mg^{-min})$) is the rate constant of the pseudo second-order model, qe is the equilibrium adsorption capacity (the maximum amount adsorbed) and qt is the amount adsorbed at time.

Adsorption isotherms

Adsorption isotherms provide crucial information that reveals the equilibrium relationship between the adsorbate concentration in the liquid phase and the solid phase at a constant temperature. Two isotherm models, Langmuir, and Freundlich equations, were chosen to describe the equilibrium characteristics in this study.

The linear form of Langmuir isotherm is given by the following Eq. (5):

$$\frac{\mathrm{Ce}}{\mathrm{qe}} = \frac{1}{qmKL} + \frac{\mathrm{Ce}}{qm} ----(5)$$

Where qe and qm are the corresponding adsorption capacity and maximum adsorption capacity (mg g^{-1}), respectively, Ce is the concentration of the RhB solution at equilibrium (mg L^{-1}), and K_L is the Langmuir constant (L mg^{-1}).

The Freundlich isotherm is described by the following Eq. (6):

$$\mathrm{Logqe} = \log \mathrm{KF} + \frac{1}{\mathrm{n}} \log \mathrm{Ce} ----(6)$$

Where, K_F (L g^{-1}) and n are the Freundlich constants that indicate the adsorption capacity and adsorption intensity, respectively.

Adsorption thermodynamics

The effect of temperature is paramount and a major factor influencing the adsorption, the temperature was monitored in the range of 25^0- 60^0. The change in Gibb's free energy, enthalpy and entropy of adsorption were calculated using the following equations,

$$\Delta \mathrm{G}^\circ = -\mathrm{RT} \ln \mathrm{Kc} ----- \ (7)$$

Where R is the gas constant, Kc is the equilibrium constant and T is the temperature According to van't Hoff equation;

$$\ln \mathrm{Kc} = {}^{\Delta \mathrm{H}^\circ}/_{\mathrm{RT}} + {}^{\Delta \mathrm{S}^\circ}/_{\mathrm{R}} ----(8)$$

Where ΔS^O and ΔH^O are change in entropy and enthalpy of adsorption respectively. A plot of Kc *versus* 1/T was plotted and values of ΔS^O and ΔH^O were evaluated from the slope and intercept of van't Hoff plots.

Results and Discussion

Characterization

The point of zero charge (pHzpc) of a solid surface refers to the pH at which the concentrations of acidic and basic functional groups on the surface are balanced. Adsorption of cations is favored at pH values above the pHzpc, while anion adsorption is favored below it. In this study, the pHzpc of the

modified biochar was determined to be 6.65, as shown in Figure 2. The pHzpc is closely related to the one found in shells of *Jatoba*, which was pH 6.25 [16] and well below that of waste processing mustard oil, which was pH 9.0 [17] but well above that of waste radish which was pH 3.4 [18] and seed of *AleuritesMoluccana* which was 5.84 [19].

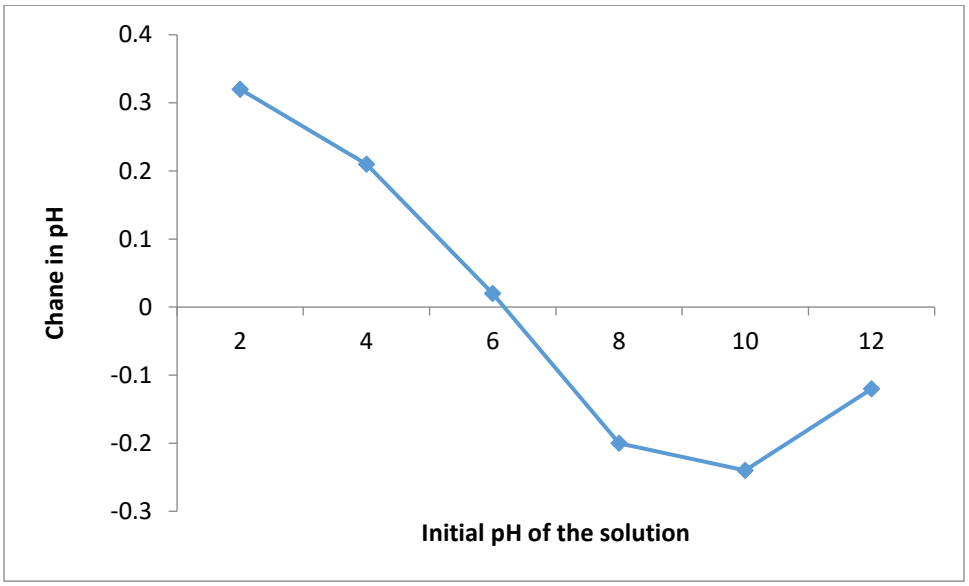


Figure 2. The pH of zero charge of the Adsorbent

The surface morphology of the modified biochar before and after adsorption was examined using scanning electron microscopy (SEM), as presented in Figure 3. A noticeable change in surface structure was observed: prior to adsorption, the biochar exhibited a smooth surface with distinct pores. After the adsorption of Rhodamine B dye, the surface became rough and uneven. This transformation occurred because the pores on the biochar surface became clogged with dye particles, leading to a less uniform texture.

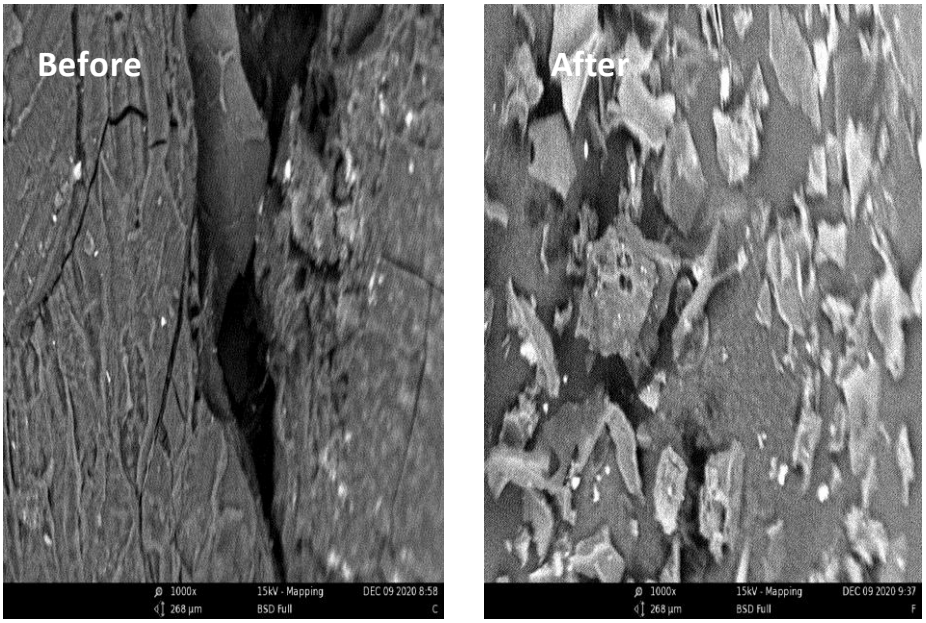
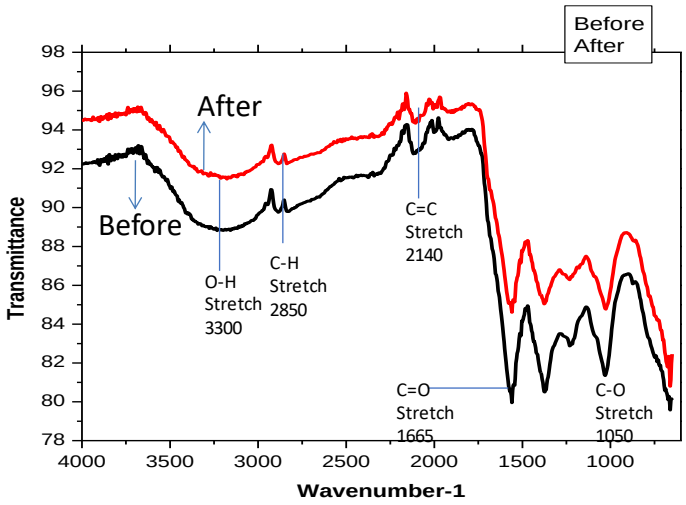


Figure 3. SEM Images of Modified Biochar Before and After Adsorption (1000× Mag.)

Additionally, large pores with rough cavities were observed on the biochar surface, which could be attributed to the modification of the adsorbent material (MSW) or the dehydration and oxidation of organic compounds during the carbonization process. These gives established the range size of mesoporous materials are well-suited for the adsorption of dyes. The porous structure of the biochar is likely responsible for the increased specific surface area, and these irregularities and pores reduce mass transfer resistance, thus facilitating the diffusion of dye molecules and improving biosorption efficiency. Previously reported work identified such pores as medium for dye removal [20].

The FT-IR spectra of the biochar before and after dye adsorption are shown in Figure 4. A broadband of around 3300 cm^{-1} is attributed to O-H stretching vibrations, while a peak at 2850 cm^{-1} corresponds to C-H aliphatic stretching. A band at 2140 cm^{-1} indicates C=C stretching, and a peak at 1665 cm^{-1} represents C=O stretching vibrations. Additionally, C-O stretching was observed at 1050 cm^{-1}. The intensities of all these peaks slightly increased after the adsorption of Rhodamine B, indicating the involvement of functional groups in the adsorption process.



Absorption bands and FTIR Spectra of Modified Biochar Before and After Adsorption

Figure 4. Absorption bands and FTIR Spectra of Modified Biochar Before and After Adsorption

Effect of contact time

The effect of contact time on the adsorption process was evaluated in a batch system, with time intervals ranging from 20 to 160 minutes. The experiment was conducted using a fixed initial concentration of Rhodamine B (100 mg/L), an adsorbent dosage of 0.1 g, and a room temperature of 27°C. Contact time was identified as a key factor influencing the adsorption capacity of the adsorbent. The results showing the amount of Rhodamine B adsorbed onto the modified biochar at different contact times are presented in Figure 5.

The findings reveal that the adsorption rate was initially rapid, with the amount of dye adsorbed increasing quickly during the early stages of the process. This fast adsorption continued until equilibrium was reached, after which the rate slowed down or declined. The initial rapid uptake of the dye can be attributed to the availability of the most accessible active sites on the surface of the modified biochar [21].

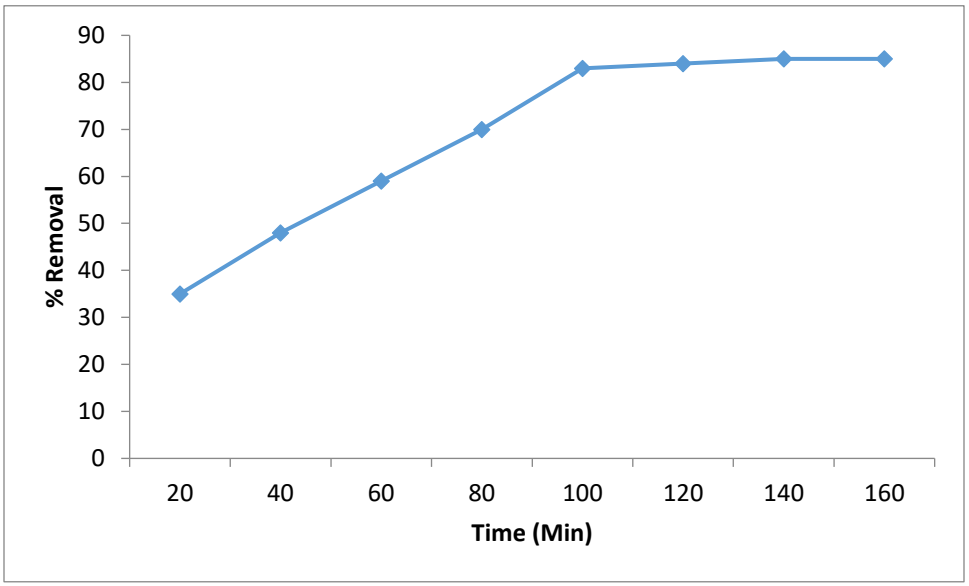


Figure 5: Effect of Contact Time

Effect of adsorbent dose

The effect of adsorbent dosage was investigated on each adsorbent at different dosages under the following conditions: Initial Concentration 100 mg/l, Contact time 30 minutes and temperature 27^{o}C. The effect of the adsorbent dose is presented in Figure 6. The result shows the percentage of the amount adsorbed with adsorbent dosage ranges from (0.1- 0.5 g) for modified Biochar. The result clearly shows that the removal efficiency (amount adsorbed) of Rhodamine B was initially increasing with the increase in dosage of the produced biochar until it reached a stage after which insignificant increases were noticed, the amount adsorbed gradually increased from around 60% to 90%, as adsorbent increases from 0.1 g to 0.3 g. Subsequently, a negligible increase was observed when the dosage was further increased.

However, an increase in available surface adsorption site enhances Rhodamine B removal when the adsorbent dosage was increased [22] subsequent saturation of adsorption sight as well as overlay of adsorbent may have resulted in removal equilibrium/reduction in percentage removal [23]. Moreover, it is well understood that the number of available adsorption sites & the surface area increase by increasing the adsorbent dose and therefore, result in an increase in the amount of adsorbed dyes [24].

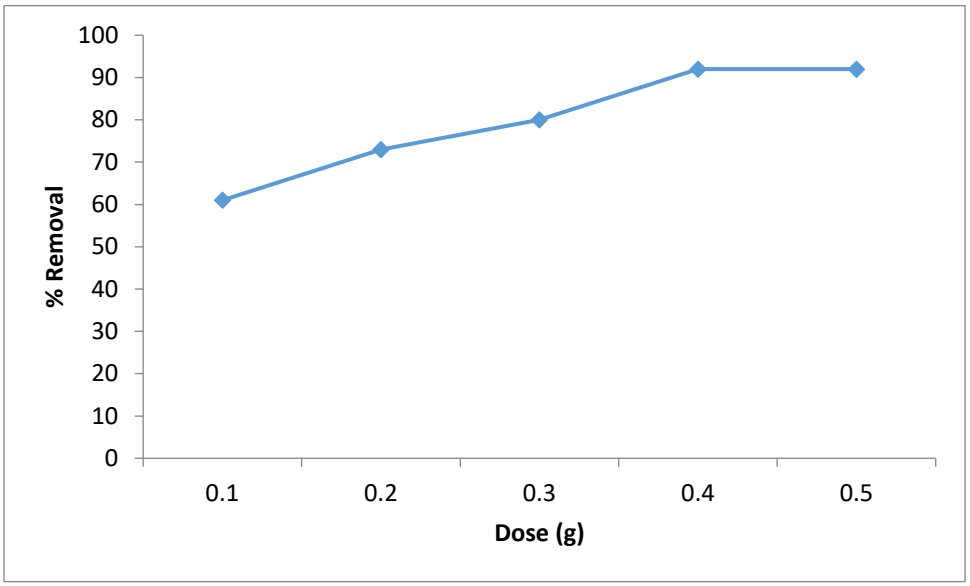


Figure 6 Effects on Adsorbent Dose

Effect of initial concentration

The effect of initial concentration was evaluated under different initial concentration (10 – 50 mg/L) with the following condition: Adsorbent dose (0.1 g), Contact time of 30 minutes and temperature of 27^{o}C. The effect of initial concentration is presented in Figure 7. The result revealed that when initial concentration was increased from 10 to 30 mg/L removal efficiency of RhB dye decreased from 97 to 70 % and 40 to 25 % respectively. The result also showed that removal efficiency was found to decrease progressively when the initial concentration was increased from 10 to 50 mg/L. It was also witnessed that adsorption of lower concentrations of dyes reached equilibrium earlier than those with higher concentrations. Furthermore, adsorption was reached remarkably rapidly within a range of 10 to 30 min. This might be due to the fact that biochar produced at higher temperatures is rendered highly absorptive in nature [25]. Such dehydrated biochar takes up water rapidly when subjected to water solutions containing dye for adsorption. This leads to an interaction of the dissolved dye molecules with the surface moieties in the adsorbate, thereby leading to prompt adsorption of synthetic dyes. A similar observation was reported by [25], where the removal of Malachite Green (MG) dye was found to be 95% percent within 40 minutes at pH 5 and temperature 25^{o}C. Rapid adsorption of dyes by biochar may prove advantageous for its probable commercial application for adsorptive removal of dye-containing effluents.

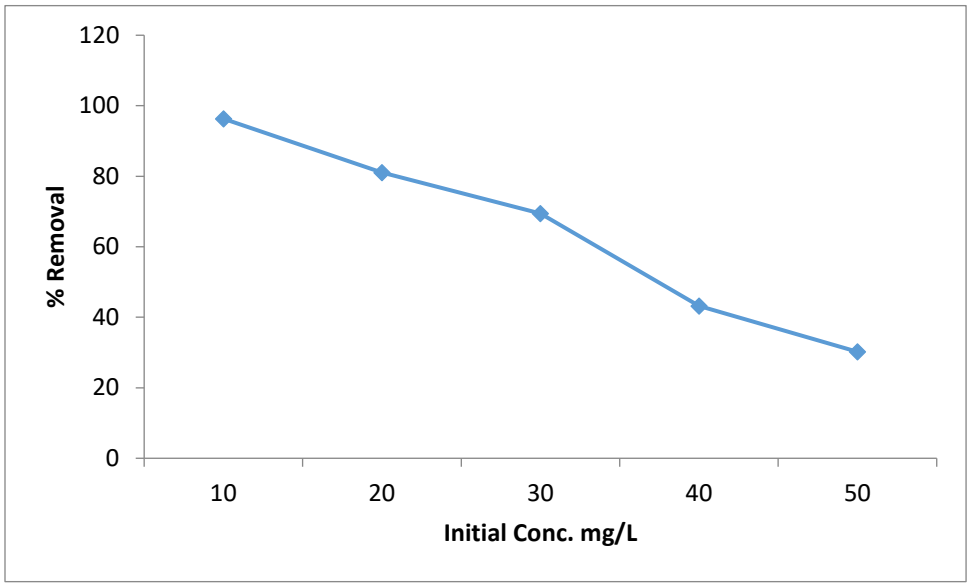


Figure 7. Effects on Initial Concentration

Kinetic studies

The adsorption kinetics and model parameters provide crucial insights for the design and modeling of adsorption processes. The kinetic model parameters for Rhodamine B (RhB) adsorption onto the adsorbents used are presented in Table 1. The correlation coefficient for the first-order model was found to be relatively low, with a value of 0.465. The experimentally determined equilibrium adsorption (qe_{exp}) differed significantly from the calculated values (qe_{cal}) for the pseudo-first-order kinetics, indicating that the adsorption of Rhodamine B onto the biochar-modified biochar (BMB) did not follow first-order kinetics. Similar findings were reported by [26] and [27] who studied kinetic models of Cd removal by AC derived from wood and olive stone, respectively. Moreover, [28], who investigated the removal of Pb from single and competitive solutions by AC produced from Van apple pulp, reported results that are in agreement with those reported in the current research.

In contrast, the correlation coefficient for the pseudo-second-order model was much higher, reaching 0.999 (Table 1). The calculated adsorption capacities (5.0) closely matched the experimental values (4.89), showing strong agreement. These findings suggest that the adsorption of Rhodamine B dye follows a second-order kinetic model. This observation supported the assumption that the adsorption could predominantly be due to chemisorption [29].

Table 1. Kinetic Model

Kinetic Models	Constant Values	AMB
Pseudo First Order	qe (exp) mg/g	21.93
	qe (cal) mg/g	5.260
	K_1 min^{-1}	0.031
	R^2	0.465
Pseudo Second Order	qe (exp) mg/g	4.89
	qe (cal) mg/g	5.0
	K_2	0.1732
	R^2	0.999

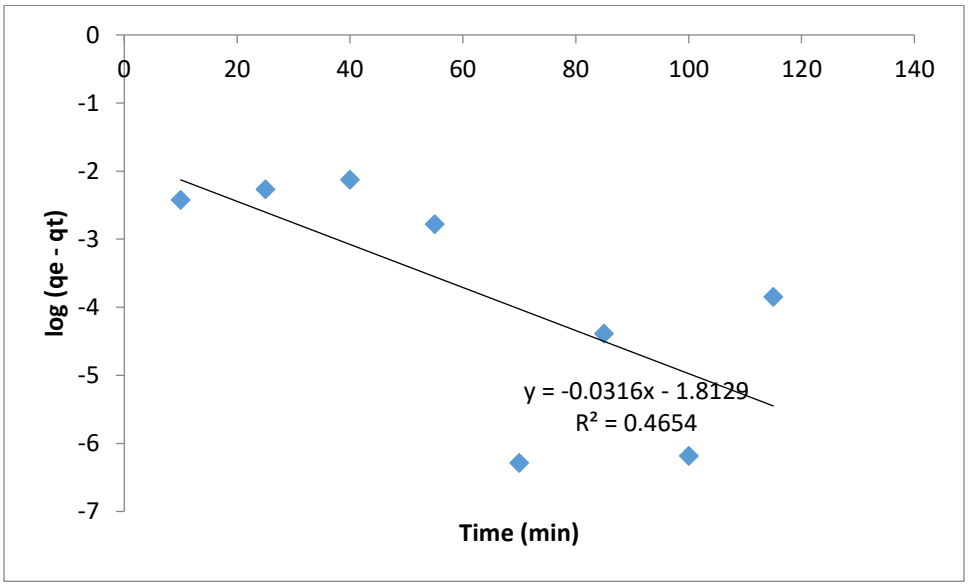


Figure 8 Pseudo First order kinetics adsorption model of RhB on AMB

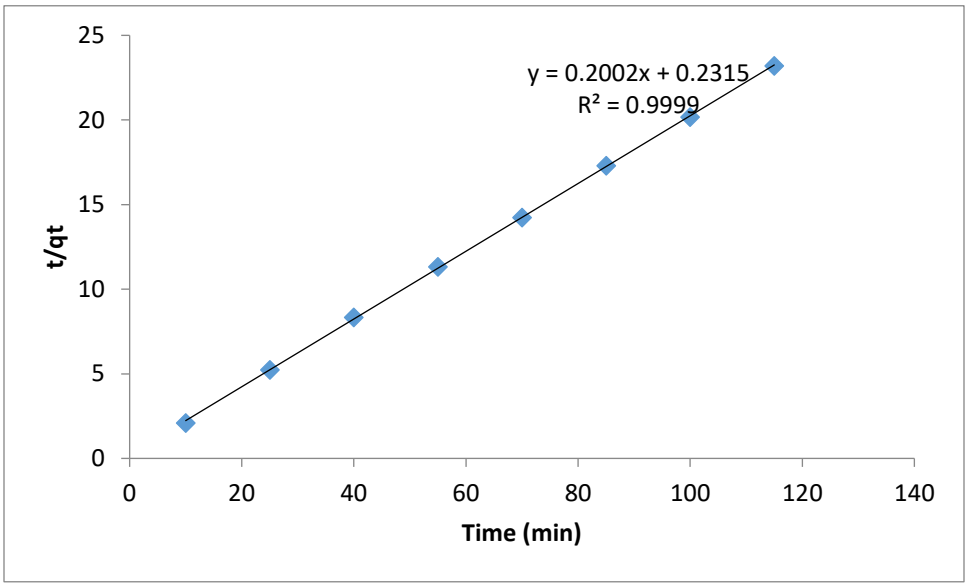


Figure 9 Pseudo Second order kinetics adsorption model of RhB on AMB

Adsorption isotherms

Adsorption isotherms provide crucial insights into the equilibrium relationship between the concentration of adsorbate in the liquid phase and its concentration in the solid phase at a constant temperature. In this study, two isotherm models—Langmuir and Freundlich—were used to describe the equilibrium characteristics. The constants for each model, along with the corresponding adsorption isotherm parameters, are presented in Table 2. This table summarizes the Langmuir and Freundlich adsorption constants observed for the uptake of Rhodamine B (RhB) dye in the experiment.

The Langmuir isotherm model assumes that maximum adsorption occurs when a saturated monolayer of adsorbate molecules is formed on the adsorbent surface, with no interactions between the adsorbed molecules [21]. As shown in Table 2, the adsorption of Rhodamine B onto the adsorbent follows the Langmuir isotherm, as indicated by the higher regression coefficient (R^2 = 0.999). These high values confirm that the adsorption process is well described by the Langmuir model. The maximum adsorption capacity (qmax) was found to be 20.24. Additionally, the value of the separation factor (RL) was between 0 and 1, which suggests that the uptake of RhB is favorable [21].

On the other hand, the Freundlich isotherm model, which describes a heterogeneous adsorption process, showed lower regression coefficients (R^2) of 0.6457 compared to the Langmuir model, as presented in Table 2. The Freundlich constant (K_F) for RhB adsorption was found to be 5.64. Higher K_F values typically indicate better adsorptive removal and stronger affinity of the adsorbent material used [30].

Table 2 Parameters of Langmuir and Freundlich isotherms.

Isotherm Parameters	**Constants**	**AMB**
Langmuir	q_{max}(mg/g)	20.24
	K_L	2470.36
	R_L	0.4951
	R^2	0.999
Freundlich	K_F	5.642
	n	2.320
	R^2	0.6457

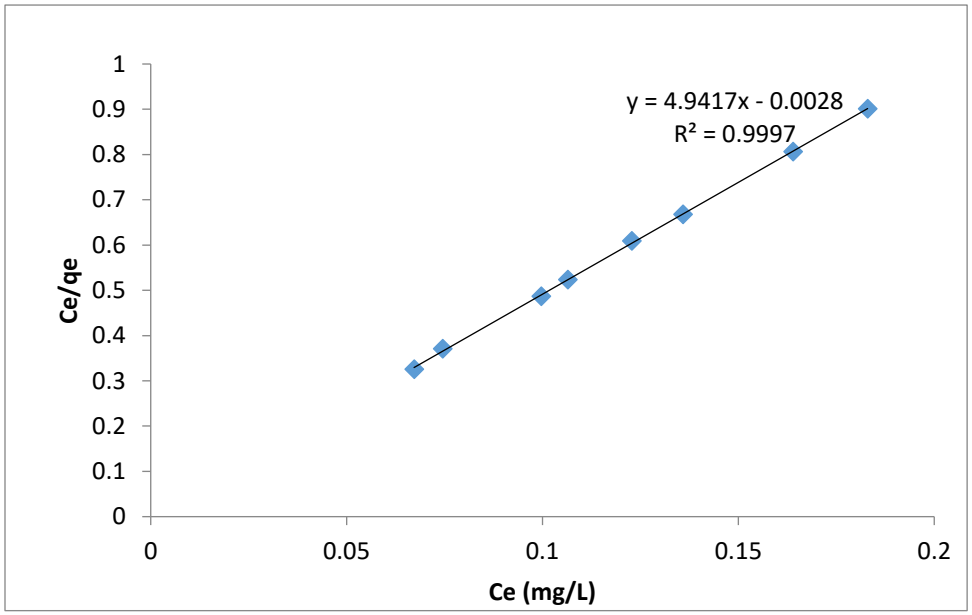


Figure 10. Langmuir Isotherm for AMB Adsorption

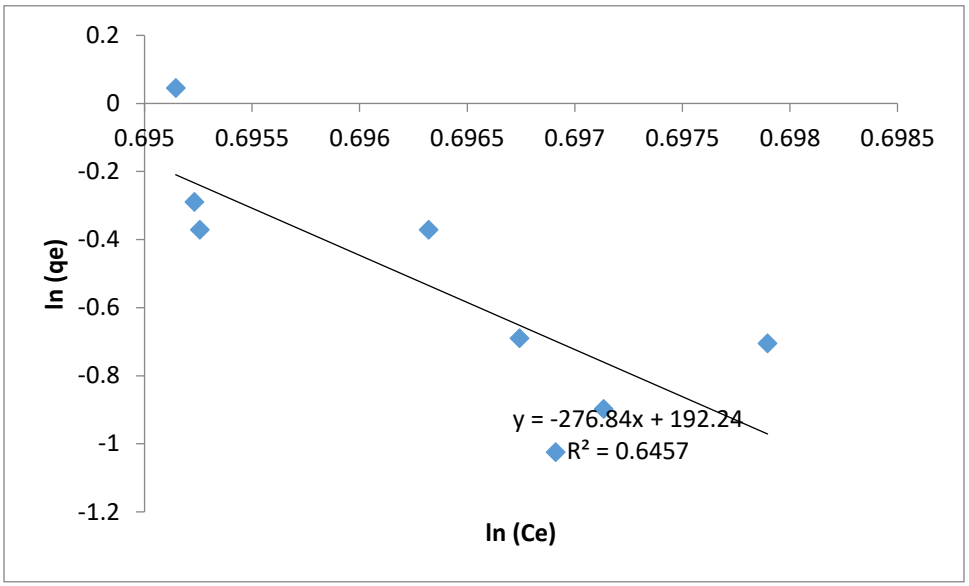


Figure 11. Freundlich Isotherm for AMB Adsorption

Adsorption thermodynamics

The effect of temperature is a crucial factor influencing the adsorption process. In this study, temperature was varied within the range of 25°C to 60°C. The thermodynamic parameters, including the changes in free energy (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o), are presented in Table 3. The negative values of ΔG^o indicate that the adsorption process is spontaneous. Furthermore, the more negative the ΔG^o value, the more energetically favorable the process becomes (-1868.45 – 2086.99 kJ/mol) [31]. The positive value of ΔS^o suggests an increase in disorder or randomness at the solid-liquid interface during the adsorption of Rhodamine B (RhB) onto the adsorbent's active sites [32]. This implies a strong affinity between the dye and the adsorbent, and indicates that significant changes occur in the internal structure of the adsorbent as a result of the adsorption [33]. The negative ΔH^o values indicate that the adsorption process is exothermic in nature. The values of ΔS^o and ΔH^o were determined from the slope and intercept of the van't Hoff plots shown in Figure 11.

Table 3 Thermodynamic Parameters

Adsorbent	ΔH^o (kJ/mol)	ΔS^o (J/mol/K)	Temperature (K)	ΔG^o (kJ/mol)
ABM	-7.67	6.24	298	-1868.45
			303	-1899.66
			308	-1930.88
			313	-1962.11
			318	-1993.33
			323	-2024.55
			328	-2055.77
			333	-2086.99

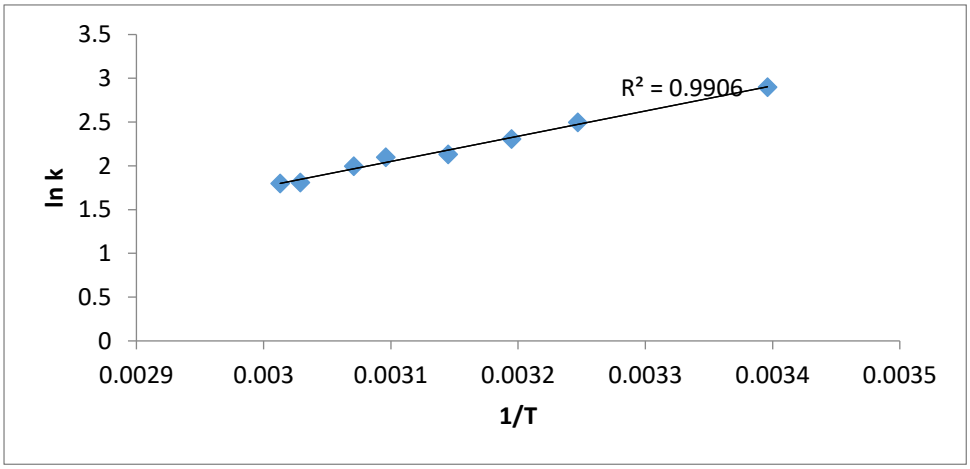


Figure 11. Van't Hoff Plot for Adsorption of RhB onto AMB

Conclusion

The experimental results demonstrated that biochar derived from the pyrolysis of municipal solid waste is an effective and low-cost adsorbent for the removal of the cationic dye Rhodamine B. The point of zero charge (pHz) value was determined to be 6.65 highlighting its suitability for cationic dye adsorption. Surface morphological properties were analyzed using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). Batch experiments revealed that the adsorption kinetics followed the pseudo-second-order model, while equilibrium data aligned with the Langmuir Isotherm. Thermodynamics analysis indicated that the adsorption process is predominantly chemisorption, spontaneous and exothermic in nature.

References

[1] Zhang, Y., Liu, Z. & Wang, J. (2022). Biochar and its modified forms as adsorbents for removal of organic pollutants from water: A review. *Environmental Science and Pollution Research*, 29(28), 42702–42720.

[2] Mohanty, S., Patra, A. K. & Mishra, B. K. (2021). Sulfuric acid-modified biochar for the removal of Rhodamine B from aqueous solution: Equilibrium,

kinetic, and thermodynamic studies. *Environmental Science and Pollution Research*, 28(12), 14592–14606.

[3] Sharma, S., Yadav, A. & Jadhav, H. (2023). Removal of toxic dyes from wastewater using biochar derived from waste materials: A review of current progress and future perspectives. *Bioresource Technology*, 364, 128159.

[4] Li, H., Yang, X. & Zhang, Z. (2023). Adsorption of Rhodamine B from aqueous solution using modified biochar: Mechanisms and applications. *Journal of Hazardous Materials*, 431, 128563.

[5] Gupta, V. K. & Saini, V. K. (2021). Adsorption of Rhodamine B dye on biochar: A comprehensive review. *Environmental Science and Pollution Research*, 28(16), 20094–20112.

[6] Zhao, F., Wang, Q. & Li, Z. (2023). Adsorption of Rhodamine B from aqueous solution using modified biochar: A review. *Environmental Pollution*, 316, 120622.

[7] Wu, F., Xie, Z. & Liu, S. (2022). Enhancing adsorption performance of biochar via acid modification for organic pollutant removal. *Journal of Cleaner Production*, 356, 131752.

[8] Chen, Y., Wang, Z. & Jiang, L. (2023) Surface modification of biochar for enhanced organic dye adsorption: A review of methods and mechanisms. *Science of the Total Environment*, 789, 147800.

[9] Kumar, A., Sethi, M. & Ahuja, R. (2023). Biochar-based materials for environmental remediation: Role of surface modification in improving pollutant uptake. *Environmental Chemistry Letters*, 21(2), 679-696.

[10] Hossain, M. K., Islam, M. A. & Ali, M. I. (2023). Acid-modified biochar for enhanced removal of organic pollutants: Effect of modification methods on adsorption capacity. *Journal of Environmental Management*, 311, 113079.

[11] Singh, R., Ranjan, R. & Mishra, P. (2021). Biochar as a sustainable material for environmental management: Challenges and opportunities in waste valorization. *Environmental Technology & Innovation*, 20, 101088.

[12] Jin, H., Capareda, S., Chang, Z., Gao, J., Xu, Y. & Zhang, J. (2014). Biochar pyrolyticallyproduced from municipal solid wastes for aqueous As(V) removal: adsorption property and its improvement with KOH activation. *Bioresour Technol 169:622–629.*https://doi.org/10.1016/j.biortech.2014.06.103

[13] Rivera-Utrilla, J., Bautista-Toledo, I., Ferro-Garcia, M. A. & Moreno- Castilla C. (2001). Activated carbon surface modifications by adsorption of bacteria and their effect on aqueous lead adsorption. *Journal of Chemical Technology and Biotechnology*, 76(12): 1209–1215.

[14] Lagergren, S. & Svenska, B.K. (1898) On the theory of socalled adsorption of materials. *R. Swed. Acad. Sci. Doc, Band,* 24, 1, 1898.

[15] Ho, Y.S., & Mckay, G. (1999). Pseudo-second order model for sorption processes, *Proc.Bioche*,. 34, 451, 1999

[16] Demarchi, C.A. A. & Debrassi, C.A. (2012). Rodrigues, The use of Jatoba´ bark for removal of cationic dyes, *Color. Technol*. 128 1– 10.

[17] Ribeiro, R.F.L., Soares, V.C., Costa, L. & Nascentes, C.C. (2012) Efficient removal of Cd2+ from aqueous solutions using by-product of biodiesel production, *J. Hazard. Mat.* 237 (2012) 170–179.

[18] Magriotis Z.M., Vieira, S.S., Saczk, A.A., Santos, N.A.V. & Stradiotto, N.R. (2014). Removal of dyes by lignocellulose adsorbents originating from biodiesel production, *J. Environ. Chem. Eng., 2 (2014) 2199–2210*

[19] Postai, D., Luiza, C. A., Demarchi, F., Danielle, C. C., Melo, C. & Antonio, R. (2016). Adsorption of rhodamine B and methylene blue dyes using waste of seeds of AleuritesMoluccana, a low cost adsorbent. *Alexandria Eng. J.* (2016), http://dx.doi.org/10.1016/j.aej.2016.03.017

[20] Inyinbor, A. A., Adekola, F.A., & Olatunji, G.A. (2015). Adsorption of Rhodamine B dye from aqueous solution on Irvingiagabonensis biomass: Kinetics and thermodynamics studies *Afr. J. of Chem.* 68, 115, 2015

[21] Dey, M. D. & Mukhopadhyay, R. (2015). Adsorptive removal of methylene blue by biomass of Aspergillus versicolor: a mechanistic study. *International Journal of Advanced Research in Science and Technology 4 (4), 398–405.*

[22] Angin, D. (2014). Utilization of activated carbon produced from fruit juice industry solid waste for the adsorption of Yellow 18 from aqueous solution. *Bioresour Technol.**168**, 259.*

[23] Pirbazari, A.E., Saberikhah, E., Habibzadehkozani, S.S. (2014). Fe3O4 – wheat straw: preparation, characterization and its application for methylene blue adsorption. *Water Resour Ind **7–8**, 23.*

[24] Malik, R., Rnteka, D.S. & Wte, S.R. (2007). Adsorption of malachite green on groundnut shell waste based powdered activated carbon. *Waste Management,* 27,1129-1138.

[25] Mohan, D., Sarswat, A., Ok, Y. S. & Pittman, C. U. (2014). Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent–a critical review. *Bioresource Technology* 160, 191–202.

[26] Bohli, T., Ouederni, A., Fiol, N. & Villaescusa, I. (2015). Evaluation of an activated carbon from olive stones used for heavy metal removal from aqueous phase. *C.R. Chim.* 88–99

[27] Mohan, D., Pittman, C.U., Bricka, M. Smith, F. Yancey, B. Mohammad, J. Steele, P.H. AlexandreFranco, M.F. Go´mez-Serrano, V. & Gong, H. (2007). Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. *J. Colloid Interface Sci.* 310, 57–73

[28] Depci, T. A. R. & Kul, Y. O. (2012). Competitive adsorption of lead and zinc from aqueous solution on activated carbon prepared from Van apple pulp: Study in single and multi-solute systems, *Chem. Eng. J.* 224–236.

[29] Malash, G. F. & Mi, E. K. (2010). Methylene blue adsorption by the waste of Abu-Tartour phosphate rock. *Journal of Colloid and Interface Science*, 348 (2), 537–545.

[30] Mahvi, A.H., Maleki, A., & Eslami, A., (2004). Potential of Rice husk ash or phenol removal in aqueous system. *American Journal of Applied Science* (4): 321-326.

[31] Li, S., & Tan, Z. (2010). Application of activated carbon derived from scrap tires for adsorption of Rhodamine B. *Journal of environmental sciences,* (22): 1274- 1280

[32] Gupta, V.K. and Rastogi, A. (2007). Biosorption of lead from aquoues solutions by Green Algae Spirongyraspeciaes: Kinetics and Equilibrium studies. *J Colloid Interface Sci.*, 296:59-63.

[33] Akar, S. T. Gorgulu, A., Kaynak, Z., Anilan B. & Akar, T. (2009) Biosorption of Reactive Blue 49 dye under batch and continuous mode using a mixed biosorbent of macrofungusAgaricus bisporus and Thujaorientalis cones, *Chem. Eng. J.*, 148(1), 26 34.