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The synthesis of activated carbon from ground nut shells and its characteristics for the active removal of textile dyes

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Key words: Biomass, Ground nut shell, Langmuir, Freundlich isotherm, Activated carbon

Abstract

Conversion and utilization of agricultural waste biomass into activated carbon is an alternative for high cost green adsorbents. The preparation of Activated carbon from Ground nut shell, and agricultural waste was investigated and presented here. Ground nut shell activated carbon is infused with Potassium hydroxide and carbonized (600°C, 1hrs). The obtained substance was activated to improve the surface area. On increasing the pore volume maximum adsorption capacity will be attained. The resulting activated carbon was characterized for its functional groups, Thermal Stability, surface morphology, and Elemental Identification using FTIR, TGA/DTA, and SEM. The dye removal efficiency of the prepared activated carbon was evaluated by using Congo red. Parameters like dosage, concentration, and pH are monitored to improve the properties of the prepared material for adsorbing synthetic dyes and industrial effluents. The monolayer adsorption (Langmuir) and the multilayer adsorption (Freundlich) isotherm models were determined to identify the maximum uptake (qmax) of Congo red by the adsorbent.

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Introduction

Dyes liberated from industries are a major problem for water pollution. The presence of heavy metals, dyestuffs, and metalloids in an aqueous medium leads to health and socioeconomic causes (Hazrat Ali *et al.*, 2019) Toxic substances present in dye water enter into the food chain of humans and several diseases are caused. This became a worldwide concern, because of emerging various diseases. Toxic substances liberated from industries in the form of heavy metals can damage the central nervous system, energy level, and vital organs. Long-term effects will lead to neurological and degenerative processes. Some toxic compounds in dye can damage human cells and leads to cancer (Jaishankar *et al.,* 2014). Parkinson's disease, muscular dystrophy, etc is some of the major problems caused due to the intake of water containing heavy metals. Major illnesses and deaths are occurring in Asia and Africa due to the intake of contaminated water. Around 50 million deaths occur globally. Getting purified water became a major challenge nowadays. The conventional methods and regulations in drinking water should be made strict to avoid the illness caused worldwide. Water treatment methods also should be made advanced to get healthy drinking water to avoid diseases (Rahman *et al.,* 2014).

For the past few years, developing a low-cost adsorbent is a challenging task for researchers. Eco-friendly technologies are emerged to treat wastewater at domestic and industrial levels (Rajasulochana *et al.,* 2016). Development and demonstration of methods like Ion exchange, membrane filtration, Microbe assisted, and nanomaterials are made successful. The high capital and operational cost of treating water using these technologies become a major threat (Muzammil Anjum *et al.,* 2019). To overcome these demerits a new technology was introduced, it was adsorption technology. Green adsorbents were used in the adsorption technique to remove contaminants. These green adsorbents were of high cost. This made the entire process costly. To overcome this demerit activated carbon prepared from agricultural waste is utilized. It is a bio-adsorbent also it can be recovered. Materials or adsorbates that possess high pore volume and surface area are best-suitable for wastewater treatment. When compared activated carbon possesses these properties (Kwikima *et al.,* 2021). Activated carbon prepared from agricultural waste biomass is a preferable and cheapest adsorbent that can be employed in wastewater treatment plants. This will reduce the capital investment and purification cost. In this study, the adsorbent is synthesized from Ground nut shell, which is a waste material from an agricultural source. Ground nut shell biomass is activated by using Potassium hydroxide. On activation, the prepared activated biomass enhances in surface area and its properties. Due to the change in the surface area of the adsorbent after the activation process, the adsorption capability of the activated biomass increased.

Materials and methods

Collection and preparation of activated carbon

Chemicals employed for the synthesis and activation are purchased from Sigma Aldrich USA with 100% purity. Ground nut shell was collected from a near Tholayavattam, Kanyakumari District, Tamilnadu, India.

To remove the dirt in the Ground nut shell, it was washed with distilled water. After washing the shells with water, it was spread under sunlight to eliminate the water content. After drying, the shell was placed in a muffle furnace for 1 h at 600^{o}C.The chemical activation process is done to improve the property of the material. For that, the shells are dipped in saturated potassium hydroxide solution for nearly 24 hours followed by weighing the sample in order to know the impregnation of 1M KOH to the sample and is followed by the activation in muffle furnace at temperature 350^{o}C for 2 hrs. The carbonized material was washed with distilled water to remove the free alkalis and dried in oven at110^{o}C for 2hrs. Ground nut shell-activated carbon (GNSAC) will be obtained. After the formation of activated carbon again it was crushed and sieved (250µm and 150µm) to increase the surface area of the material.

Preparation of adsorbate

The adsorbate azo dye (Congo red) is prepared by weighing 500mg of dye in 1000ml water. From this stock solution, various concentrated solutions are prepared from 10- 70 mg/l for the adsorption studies.

Adsorption studies

To conduct batch equilibrium experiments the congo red dye was prepared by adding dye in deionized water. For getting the required concentration, the water and dye are added in the proper ratio. In a conical flask, 1g of Ground nut shell-activated carbon was added. After that 10 to 70mg/L of varying dye concentration was treated to GNSAC. Equilibrium studies show that 24 hours of time is required to reach the point of equilibrium. By carrying out a series of isotherms at adsorbent dosages (1.0, 2.0, and 3.0 g/l) and pH (3, 7.8 and 9.6.) the effect of adsorption isotherm was determined. The concentrations of dyes are determined by using a UV/visible spectrophotometer. Using the mass balance relationship equation the amount of dye absorbed onto the activated carbon, qe (mg g-1), was calculated. At regular intervals of time, the samples in an aqueous medium were collected to determine their dye concentration. The amount of dye adsorption in a particular period at time t, qt (mg g-1), was determined by an equation given below.

$qt = (C_o - C_t)xV/M$

Liquid-phase concentrations of solutes at initial at any time (t) are denoted by Co (mg L-1) and Ce (mg g-1). The volume of the solution is denoted by V, and the dosage of adsorbent in the solution (g L-1) is denoted by M. Relations between the mass of dye adsorbed at a particular dosage, pH, and liquid phase of dye concentration are determined by Langmuir (1918) and Freundlich (1906) isotherm model (Jayarajan *et al.,* 2011).

Results and discussion

Characterization of activated carbon

FTIR- spectroscopy

Fig. 1 represents the FT-IR spectroscopic study of Ground nut shell-activated carbon. A maximum peak with a wide band is noticed at 3346 cm^{-1} is Imino compound, =N-H stretch. The band at 2925 cm^{-1} is attributed to the interaction between carbon and hydrogen on the surface of the carbon. In the region of 2856 cm^{-1} is symmetry stretch. Two peaks at 1565 and 1381 cm^{-1} are due to the presence of functional groups, which are obtained during the activation process. This will leads to the presence of ammonia and a primary amine (Sun *et al.,* 2019). The band at 1381 cm^{-1} is due to the aliphatic nitro compound. The absorption band at 1020 cm^{-1} may be due to the Si-O or C-O stretching in alcohol, ether, or hydroxyl groups. Peroxide, C-O-O stretch can be noticed at 874 cm^{-1}. Due to the activation process, alkaline groups of cyclic ketones and their derivatives can be noticed at 605 cm^{-1} peak assigned out of the plane as C-H bending mode.

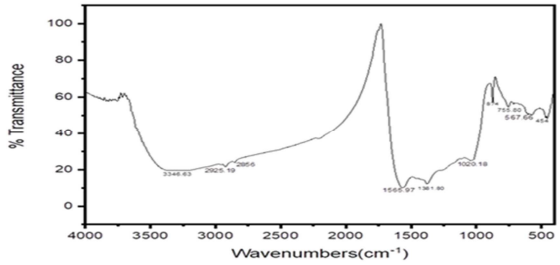

Fig. 1. FT-IR spectroscopy of GNSAC

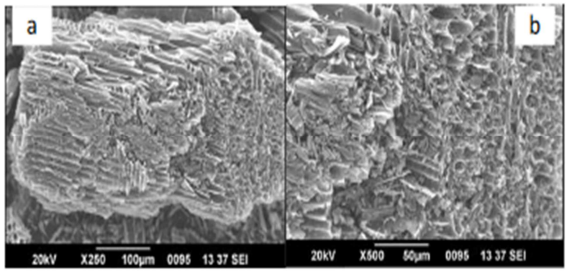

Fig. 2. SEM analyses of ACGNS at different magnification

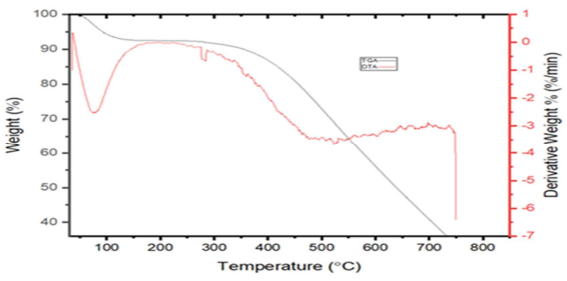

Fig. 3. TGA/DTA Analysis of ACGNS

Scanning electron microscope analysis (SEM)

The surface morphology of GNSAC was detected by using scanning electron microscopy (SEM). SEM images of GNSAC at different magnifications are indicated in Fig. 2. The SEM images clearly describe the pore volume and cracks with rough surfaces. The appearance of voids and irregular and uneven projections are due to the formation of volatile gases during the carbonization process. SEM image of GNSAC shows the micropore at different magnifications (a) and (b). These microspores are present on the surface of the particle. Chemical activation helps to create a micropore of various forms on the particle's surface that favours adsorption properties. When the surface area and pore volume of the material gets increased, its efficiency to adsorb get also gets increased. From this surface morphological study, it is evident that GNSAC has a large surface area therefore it can be used as an adsorbent (Singh *et al.,* 2019).

TGA/DTA analysis

To identify the thermal stability of the prepared activated carbon, the thermal behavior was investigated using TGA/DTA technique for GNSAC at a temperature range of 30-750°C. Fig. 3 represents the corresponding results of the TGA/DTA analysis. An initial weight loss of 3-5% is identified from Thermo gravimetric analysis. This may be due to the adsorbed water at lower temperatures not exceeding 100°C. Also at 450°C, a slight weight change is noticed this is due to the burning of functional groups over the surface of the activated carbon. When the temperature moves towards 400°C there is no change in weight this may be due to the high stability of activated carbon (ACGNS). There is a loss of water present in the micropore on increasing temperature this can be considered as the first endothermic event. An increase in a broad exothermic band is noticed, this is due to the decomposition of functional groups and partial gasification of the least stable fragments of the carbon structure. From the above observations, GNSAC shows higher thermal stability and at the higher temperature, the loss of mass occurs (Abisha *et al.,* 2021).

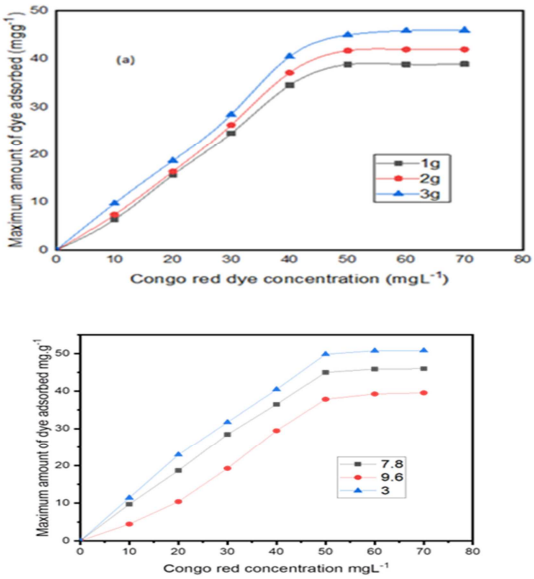

Fig. 4. Adsorption effect of Azo Dye (Congo red) on Ground nut Shell (a) at various dosages with varying dye concentration and (b) varying pH with concentration of dye

Adsorption studies

Effect of dosage and ph

Adsorption of dye using environmentally benign Ground nut shell biomass (GNSAC) at various dosages and pH are shown in Fig. 4(a) and (b). In the preliminary stage, there is a sudden increase in adsorption due to the concentration of dye (Yadav *et al.,* 2021). After a certain limit, it reached a constant value. On increasing the concentration the adsorption increases slightly. During the adsorption process, electrostatic interaction between adsorbent versus adsorbate is governed by pH. Due to the influence of positive charge on the surface of the sorbent and the rate variation of adsorbent occurs. This will accept the negatively charged dye molecule and helps to promote the rate of adsorption. On increasing the dose of adsorbent, the adsorption is increased (Rajeev Jain *et al.,* 2013). The effect of pH is described in Fig. (b). From this, it is evident that at pH 3 and 7.8 the adsorption rate is higher. This happens because of lowering pH levels, and H^+ ions increase on the surface of the prepared activated carbon. Dye molecule gets a negative charge between them due to their electrostatic force of attraction (Sushmita Banerjee *et al.,* 2017).

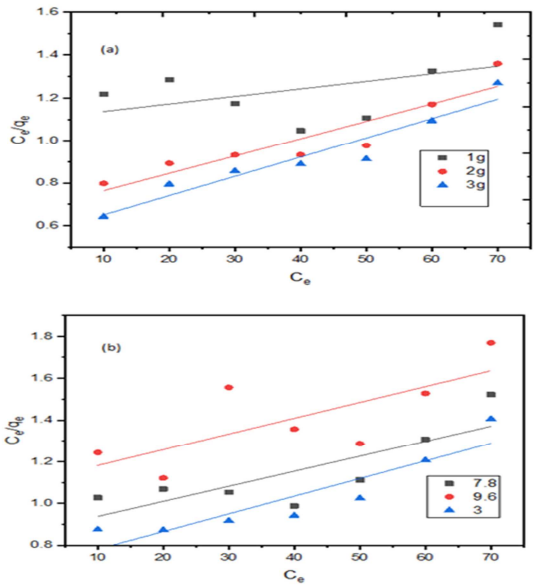

Fig. 5. Determination of the adsorption of Congo red dye using Ground nut Shell by Langmuir isotherm (a) varying adsorbent dosages with various dye concentration (b) varying pH with concentration of dye

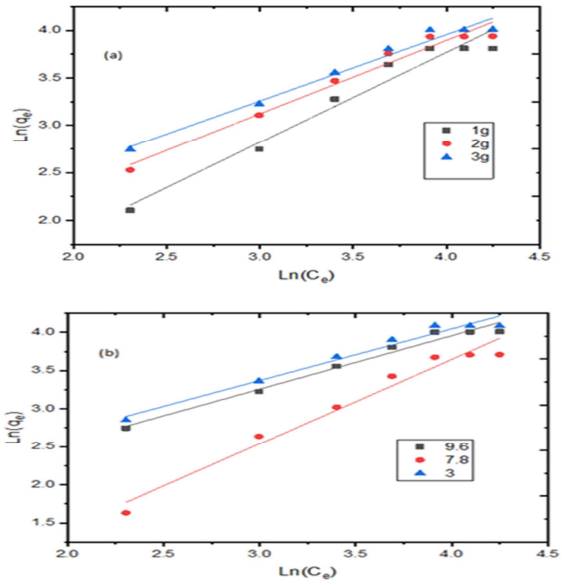

Fig. 6. Freundlich isotherms for the adsorption of Congo red dye using Ground nut Shell (a) at different adsorbent dosages with dye concentration (b) at different pH with dye concentration

The maximum dye removal percentage was obtained for an adsorbent dosage of 3.0 g L^{-1} for Congo red on Ground nut Shell activated carbon (GNSAC) at 70 mg L^{-1} concentration is 45.98 g L^{-1}. The adsorption increased when a dose of adsorbent is increased, it is due to the high surface area of the adsorbent (Singh *et al.,* 2015). In general, when the dye uptakes are compared, the acidic solution is much higher than neutral and alkaline conditions.

Langmuir isotherm

The monolayer adsorption on homogeneous site is determined by Langmuir isotherm. The expression given below is applied to calculate the Langmuir isotherm.

$$q_e = \frac{KbC_e}{(1 + bC_e)}$$

$$\frac{1}{q_e} = \frac{1}{K} + \frac{1}{KbC_e}$$

Fig. 5(a) & (b) represents the (Ce/qe vs Ce) is plotted in a linear graphical relation indicating the applicability of the langumir model. The values are calculated from the slope and intercept of the different straight lines representing the different adsorbent dosages, temperature, and pH (b) energy of adsorption and (k) adsorption capacity, and Qo is represented by (K). The Langmuir isotherm constant (Qo) is given in equation 2. It is a measure of the amount of dye adsorbed when the monolayer's completed. The monolayer capacity (Qo) of the adsorbent for the dye is comparably obtained from an adsorption isotherm. The observed statistically significant (at the 95% confidence level) linear relationship as evidence of these by the R^2 values (close to unity) indicates the applicability of the isotherm (Langmuir isotherm) and surface (Nimibofa Ayawei *et al.,* 2017). The Langmuir isotherm constants along with correction coefficients are reported and clear from the shape of the adsorption isotherm, that it belongs to the L2 category of isotherm, which indicates the normal (or) Langmuir type of adsorption (Mula Berhe Desta *et al.,* 2013).

Freundlich isotherm

Multilayer adsorption on heterogeneous surface energies system is determined by Freundlich isotherm. Fig. 6 (a) and (b) represents the Freundlich isotherm of GNSAC at different dye concentration

and pH. From the Freundlich isotherm it is evident that the batch isotherm gives a linear fit (Extross *et al.,* 2022).

$q_e = K_F C_e^{1/n}$

$\ln q_e \ln K_F/(1/n)\ln C_e$

The constants associated with Freundlich isotherm are the intercept, which is an indicator of sorption capacity (kf) and the slope (1/n) sorption intensity. Freundlich isotherm has been illustrated to be a special case of heterogeneous surface energies and it can be easily extended to this case (Rondina *et al.,* 2019). It has been stated by that the magnitude of the exponent 1/n gives an indication of the favourability and capacity of the adsorbent system. The values of n >1 represents the favourable adsorption condition (Kumari *et al.,* 2018). The exponent between 1< n < 10 shows the better adsorption (Shariati Rad *et al.,* 2014). From the figure it is evident that R^2 was fine and sorption was excellent.

Conclusion

Activated carbon prepared from Ground nut shells to absorb the textile dye (congo red) is investigated under bath equilibrium modes. Langmuir model confirms the presence of the formation of a monolayer on the outer space of the adsorbent. Freundlich model confirms the prepared material has high adsorption capacity. Adsorption of Congo red dye at an adsorbent dosage of 45.98g L^{-1} and pH 50.8g L^{-1} is reasonably high. When compared with acidic, neutral, and alkaline conditions, dye utilization is higher in an acidic medium. From this, it can be finalized that the pH of the aqueous solution is a major factor of adsorption using Congo red or GNSAC. Pore size, volume, and particle shape are the major factors that determine adsorption. Surface morphological studies showed well pore size, volume, and crack are formed in GNSAC. After the activation process, the pore size and volume are increased this enhances the adsorption property. The usage of agricultural waste biomass from Ground nut shells paves a new path in water treatment. From this research, advancement can be done in the water treatment process using the data reported here. Activated carbon prepared from Ground nut shells is the best suitable adsorbent that can be employed in water treatment plants. Our research confirms the higher efficiency and low cost of the adsorbent material. Ground nut seed shell-activated carbon is a promising adsorbent for removing textile dyes and also in water treatment.

References

Abisha BR, Anish CI, Beautlin Nisha R, Daniel Sam N, Jaya Rajan M. 2021. Adsorption and equilibrium studies of methyl orange on tamarind shell activated carbon and their characterization. Phosphorus, Sulfur, and Silicon and the Related Elements 197(3), 225-230. https://doi.org/10.1080/10426507.2021.1993849

Extross A, Waknis A, Tagad C, Gedam V, Pathak P. 2022. Adsorption of congo red using carbon from leaves and stem of water hyacinth: equilibrium, kinetics, thermodynamic studies. International Journal of Environmental Science and Technology 20. DOI: 10.1007/s13762-022-03938-x.

Hazrat Ali, Ezzat Khan, Ikram Ilahi. 2019. Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation. Journal of Chemistry 4, 1-14. DOI: 10.1155/2019/6730305

Jaishankar M, Tseten T, Anbalagan N, Mathew BB, Beeregowda KN. 2014. Toxicity, mechanism and health effects of some heavy metals. InterdiscipToxicol. 7(2), 60-72. DOI: 10.2478/INTOX-2014-0009.

Jayarajan M, Arunachalam R, Annadurai G. 2011. Agricultural wastes of jackfruit peel nano-porous adsorbent for removal of rhodamine dye." Asian Journal of Applied Sciences 4(3), 263-270. DOI: 10.3923/ajaps.2011.263.270

Jayarajan M, Arunachala R, Gurusamy A. 2011. Use of Low Cost Nano-porous Materials of Pomelo Fruit Peel Wastes in Removal of Textile Dye. Research Journal of Environmental Sciences 5, 434-443.

Kumari S, Khan S. 2018. Effect of Fe3O4 NPs application on fluoride (F) accumulation efficiency of *Prosopis juliflora*. Ecotoxicology and environmental safety **166**, 419-426.
DOI: 10.1016/j.ecoenv.2018.09.103.

Muzammil A, Miandad R, Muhammad W, Gehany F, Barakat MA. 2019. Remediation of wastewater using various nano-materials, Arabian Journal of Chemistry **12**(8), 4897-4919.

Mulu Berhe Desta. 2013. Batch Sorption Experiments: Langmuir and Freundlich Isotherm Studies for the Adsorption of Textile Metal Ions onto Teff Straw (*Eragrostis tef*) Agricultural Waste. Journal of Thermodynamics, vol. 2013, Article ID 375830, 6 pages, 2013.
https://doi.org/10.1155/2013/375830

Nimibofa A, Ebelegi AN, Wankasi D. 2017. Modelling and Interpretation of Adsorption Isotherms. Journal of Chemistry, vol. 2017, Article ID 3039817, 11 pages, 2017.
https://doi.org/10.1155/2017/3039817.

Rahman MM, Adil M, Yusof AM, Kamaruzzaman YB, Ansary RH. 2014. Removal of heavy metal ions with acid-activated carbons derived from oil palm and coconut shells. Porous Materials **7** (5), 3634–3650.
DOI: 10.3390/ma7053634.

Rajasulochana P, Preethy V. 2016. Comparison on efficiency of various techniques in treatment of waste and sewage water – A comprehensive review. Resource-Efficient Technologies **2**(4), 175-184.

Jain R, Sikarwar S. 2013. Adsorption and desorption studies of Congo red using low-cost adsorbent: activated de-oiled mustard. Desalination and Water Treatment **52**, 7400-7411.
DOI: 10.1080/19443994.2013.837004.

Rondina DJG, Ymbong DV, Cadutdut MJM, Nalasa JRS, Paradero JB, Mabayo VIF, Arazo RO. 2019. Utilization of a novel activated carbon adsorbent from press mud of sugarcane industry for the optimized removal of methyl orange dye in aqueous solution. Applied Water Science **9**(8), 181.
DOI: 10.1007/s13201-019-1063-0

Sushmita Banerjee, Chattopadhyaya MC. 2017. Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product. Arabian Journal of Chemistry 10(Sup.2), S1629-S1638.

Singh H, Choden S. 2015. Comparison of adsorption behaviour and kinetic modeling of bio-waste materials using basic dye as adsorbate. Indian Journal of Chemical Technology **21**, 359-367.
DOI: 10.1061/9780784412725.ch08.

Sun B, Yuan Y, Li H, Li X, Zhang C, Guo F, Liu X, Wang K, Zhao XS. 2019. Waste-cellulose-derived porous carbon adsorbents for methyl orange removal. Chemical Engineering Journal **371**, 55-63.
DOI: doi.org/10.1016/j.cej.2019.04.031

Shariati-Rad M, Irandoust M, Amri S, Mostafa F, Fattaneh J. 2014. Magnetic solid phase adsorption, preconcentration and determination of methyl orange in water samples using silica coated magnetic nanoparticles and central composite design. Int Nano Lett **4**, 91–101.
https://doi.org/10.1007/s40089-014-0124-5

Kwikima MM, Mateso S, Chebude Y. 2021. Potentials of agricultural wastes as the ultimate alternative adsorbent for cadmium removal from wastewater. A review. Scientific African, vol. 13, e00934.
https://doi.org/10.1016/j.sciaf.2021.e00934

Yadav S, Yadav A, Bagotia N, Sharma AK, Kumar S. 2021. Adsorptive Potential of Modified Plant-Based Adsorbents for Sequestration of Dyes and Heavy Metals from Wastewater - A Review. J. Water Process. Eng. 42.
DOI: 10.1016/J.JWPE.2021.102148.