GIET UNIVERSITY JOURNAL, 2023, VOL.2, NO 8,
Manuscript received 1-4-2023; revised 10-4-2023; Accepted 17-4-2023
ISSN Number: 2583-5955

Adsorption of hazardous materials from aqueous environment using activated carbon synthesized from agricultural and industrial waste: A Review

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Abstract— **In this review we have studied the removal of various harmful waste materials such as heavy metals (Pb(II)), dyes (methylene blue, Amaranth azo dye, methyl orange and Janus Green B azo dye), and herbicides (2,4-dichlorophenoxyacetic acid and paraquat) from wastewater using activated carbon derived from agricultural waste and industrial wastes. The agricultural wastes like corncob, pineapple shell, soapnut shell, jute waste, black cumin seeds, shrub waste, lemon, orange peel and industrial waste such as industrial coal, magnetic nanoparticles are utilized in the preparation of AC. These studies suggest that the activated carbon not only efficiently helps in the removal of toxic pollutants from wastewater but also reduces the waste generated in the environment.**

***Keywords*— Adsorption, activated carbon, heavy metal, agricultural waste**

Overview of the studies

Sayed et. al. has studied the evaluation of corncob-derived activated carbon produced chemically by using phosphoric acid and applied for the removal of the methylene blue. The main waste generated from corn agriculture was corncob in Egypt. The ACs were prepared utilising corncob as a raw material. Chemical activation with concentrated H_3PO_4 acid was used prepare ACs; carried out by pyrolysis for 2h at (400,500 and 600°C) temperatures. After pyrolysis the pH made up to 6-7 by washing with distilled water and the sample was kept for drying at 100°C. The generated AC sample produced AC(1), AC(2) and AC(3) as per the activation temperature are used in the elimination of MB dye from aqueous medium, by batch adsorption experiment. In this the, surface area (m^2/g), micropore volume(cm^2/g) and iodine number(mg/g) for AC1 is (700,0.011,6.32), for AC2 is (633,0.009,0.003) and for AC3 is (600,0.003,485) respectively. The initial dye concentration(5-50mg/g) had an effect on the sorption process. On increasing the dye concentration adsorbent of dye removal is decreases, the results show that on increasing initial dye concentration from 5 up to 50mg/l for AC1, AC2 and AC3 the adsorption potency of dye increases from 4.9 to 46.0, 4.8 to 39.3 and 4.6 to 37.5 mg/g, respectively. The adsorption of MB increased with an increase in pH of the mixture. The pH was attained at pH higher than 8. With increase in the adsorbent dosage the removal percentage of MB increases. While increasing adsorbent dosage from 1 to 5 g/l the dye removal percentage of AC(1), AC(2) and AC(3) increases from 99.2% to 99.6%, 98.6% to 99.4% and 41.6% to 91.2% respectively. One of the most crucial parameters is the contact time between adsorbate and adsorbent. For AC1 the removal of dye increases rapidly in 10 mins of contact time and then steadily until equilibrium was reached at time 45 mins. For AC1 and AC2 the rate of removal is slow at first and gradually increased with time until 120 min it reaches equilibrium. The Freundlich and Langmuir adsorption isotherm models were utilised for the adsorption. The correlation coefficient values are

calculated as AC1(R^2=0.9868) and AC (R^2=0.9810), the both data were satisfactory with Langmuir isotherm model for AC(1) and AC(2) and Freundlich for AC(3) with maximum adsorption potency of 28.65 and 17.57 mg/g,. The Adsorption of dye AC(3) follows Freundlich isotherm model (R^2=0.9823) better fits in adsorption. With the removal capacity of 0.810 mg/g indicates that the sorption of MB on AC3 is favourable[1].

Chen and co-worker have analysed the progress of porous property and surface chemistry of textile scrap Jute-base activated carbon produced by physical activation. The expansion of porous nature and surface chemistry of activated carbon by physical activation process is used for the preparation of AC from textile waste Jute. By physical activation in presence of atmospheric N_2 at different temperature (400,500 or 600°C) for 30,60, or 90 mins the carbonized jute is named as C-temperature-time. The carbonized material is again heated at 700, 800, 900°C for 30, 60,90 min, then the CO_2 is stimulated to a flow rate of 300ml/l. The increasing carbonization has an effect on the carbon content of the raw material and also has effect produce preliminary pore structure. The activation temperature(700°C) and time (60 min) is highly affected by porosity and surface chemistry. Carbonization performed at a temperature of 500˚C for about 60 min fulfils the optimal balance in production and pore structure. The analysis of pore volume distribution shown at different temperature the activation carbon produces micropores at 800˚C and mesoporous at 900°C. More carbonaceous structure can be created by changing surface chemistry and porosity by physical activation[2].

Thabede et. al examined the adsorption of methylene blue dye utilising pineapple and soapnut shell waste as activated carbon. This review investigates and analyses adsorption potency of AC derived from pineapple and soapnut shell waste for elimination of MB dye from aqueous medium. By treating the adsorbent with phosphoric acid (H_3PO_4) the activated carbon was prepared. The efficiency of adsorption is influenced by different parameters like run-time(120min), initial concentration (10-50 mg/l), and adsorption dose (0.5g). On increase in the initial concentration adsorption capacity MB dye is increases. The studies say that, depending on initial concentration adsorption capacity is higher in soapnut shell comparison with pineapple. With increase initial concentration adsorption capacity increases in soapnut AC is 0.6g to nearly 100%. As per experiment the sorption efficiency of AC prepared from soapnut shell is much greater than that of the pineapple waste. The dye removal capacity is about 99% and 96% for soapnut shell and pineapple waste respectively. The adsorption isothermal studies show that Langmuir isothermal appropriate for homogeneous adsorption with (R^2 =0.9851) and the Freundlich isothermal use for multilayer adsorption with (R^2=0.9618)[3].

Elimination of lead ions and methylene blue dye from the aqueous medium using activated carbon prepared from black cumin seeds are examined by Patel et.al. The main aim of this work report was to remove MB dye and Pb(ll) ions from aqueous solution using AC derived from BCS. The BCS was carbonized at 300°C, then the carbonized BCS are used to prepare AC by using sulfuric acid (H_2SO_4) in two different concentration (10% and 20%) to prepare two types of AC from BCS such as BCAC-10 and BCAC-20. These two AC are used in the adsorption process as adsorbents. For characterization and analysis of the surface cavity of adsorbent by XRD, BET, TGA, SEM and FT-IR. While studying SEM images of both BCAC-10 and BCAC-20 it was found that they have cavities with rough irregular surfaces. The functional groups ($-COO^-$), ($-NH_2$), ($-HSO_4^-$), (-C=O) are shown in FTIR which are used in absorption process. For both BCAC-10 and BCAC-20 there is an increment surface area and pore size are compared with BCC by using nitrogen adsorption process. Batch adsorption model helps to estimate the various parameters such as contact time, pH, initial dye concentration, contact time and temperature in removal of lead ion and MB. The effect of concentration on sorption capacity of BCAC-10, BCAC-20 and BCC is calculated by using different initial concentration (20 to 100 mg/l) at constant temperature 298K. It was seen that with an increase in initial dye concentration the absorption capacity increases. The adsorption capacity of Pb (11) and MB dye in BCC, BCAC-10 and BCAC-20 is maximum at 100mg/l that is (17.19, 17.71, 17.98 and 11.63,12.71,16.58) mg/l respectively. The absorption capacity is maximum at high contact time and pH such as 120 min and pH=9. In increment of the temperature from 298 to 313K the adsorption capacity of Pb (II) and MB dye increases. To calculate thermodynamic parameters by using

different temperatures, such as enthalpy (ΔH°) that gave positive value indicates the removal of MB and Pb (II) on the adsorbents was endothermic process and the entropy (ΔS°) gave positive value as it indicates the degree of freedom and randomness in aqueous medium during the adsorption method. The equilibrium data is fit in Freundlich isotherm model with correlation coefficient value (r^2) nearly 1. The kinetic data were studied using pseudo first order, pseudo second order, and intra particle diffusion models. When r^2 value is close to 1 than the adsorption data is good fit for PFO and PSO. By using Intraparticle diffusion kinetic model can determine the adsorption taking place on the surface (ESA) or pores (EPA). It shows that EPA for Pb (II) ion and MB onto BCC, BCAC-10, BCAC-20 is 65.85, 94.28, 78.43 and 73.37, 70.82, 95.74% respectively[4].

Adsorption of MB from aqueous medium by Facile synthesis of Fe_2FeO_4 magnetic nanoparticle are analyzed by Dinh et. al**.** to extract methylene blue from wastewater by using $FeFe_2O_4$ magnetic nanomaterial which is prepared by using facile and simple chemical preparation methods. $FeFe_2O_4$, a magnetic nanomaterial is characterized by using TGA, DTG, FT-IR, XRD, SEM and BET methods. The effective factors for the extraction of MB dye are adsorption time, including pH and concentration was studied. To investigate the adsorption capacity by batch adsorption, process the affective factors are pH (2-11), ion strength (0-0.5 ml of KCl), adsorption time (5-240 min) and the initial dye concentration is (664 nm) was calculated by using UV -vis method. On increasing the pH form 2-10 and initial concentration from 15 - 320 mg/L , the adsorption capacity of MB dye is maximum, after 80 min the adsorption of MB dye is maximum. On increase the ionic strength of KCl from 0 - 0.5 mol/L, the adsorption capacity decreases from 64% to 5%. To explain the quantity of adsorbate on the surface by using sorption isotherm, shows the data for non-linear isotherm modal is Langmuir (X^2 =1.325, RMSE=1.823 and R^2=0.9725), Freundlich (X^2=5.53, RMSE=3.443 and R^2=0.9018) Sips (X21.236, RMSE=1.819 and R^2=0.9726) and Temkin (X^2=2.0370, RMSE=2.4290 and R^2=0.9511) isotherm models. The best result fitted data shows in slip model, confirming the heterogeneous characteristics of the adsorption systems. At the same time, the mechanism and kinetic studies have shown that the electrostatic force of attraction plays as a primary mechanism for the elimination of MB from aqueous medium by Fe_2FeO_4 magnetic nanomaterial. The maximum adsorption capacity obtained from Langmuir model well fitted the experimental data with q_{max} = 42.35mg/g under favourable conditions of sorption time equal to 80 minutes and pH equal to10. The synthesized material has rough surface with two kinds of shape including nanorods and nanospheres, which are used as adsorbent in adsorption process[5].

Georgin et. al. investigated on turning shrub waste into highly efficient adsorbent: Application of Physalis Peruvian chalice treated with strong acid to eliminate 2,4-dichlorophenoxyacetic acid herbicide. Adsorption of 2,4-D was carried out by chalice originated by the production of physalis peruvian fruit were treated with H_2SO_4 and employed as a viable adsorbent in the sorption mechanism. The sorption process was examined by various methods, like FT-IR, SEM and XRD. The surface of the material changed favorably after the treatment with acid. After the treatment with acid the surface changes from smooth to an uneven surface and with irregular cavity size. The batch adsorption experiments were used to calculate critical parameters that can affect the sorption mechanism such as surface chemistry, cavity size, pH (2-10), adsorption dosage (0.6-1.4 g/l) and pollutant concentration. The adsorption was supported at pH=2 with concentration of $0.8gL^{-1}$. The kinetic data well suited pseudo second order model and Langmuir and Toth isothermal models with R^2=0.9855 significantly suggested the higher adsorption efficiencies, 244 and 320 mg g^{-1}, representatively. The sorption of 2,4-D was exothermic and spontaneous found from computed thermodynamic results[6].

Tsai and co-workers researched on Herbicide paraquat adsorption kinetics from aqueous medium onto activated bleaching earth**.** In this review, bleaching earth was utilized for removal of herbicide paraquat from aqueous medium. The batch adsorption experiment determined the rate of sorption and adsorption kinetics depends on different controlled methods parameters like initial paraquat concentration (2g/l), agitation speed, temperature (25 and 45°C), at 25°C q_e is 31.65 mg/g and

when the temperature increases to 45°C fitted the sorption capacity decreases to 28.49 mg/l equilibrium time(60-120min) and adsorbent dosage(2g/l). By the equation of pseudo second order kinetic model, the adsorption kinetics can be explained. we can find the rate constant of adsorption, time of half-adsorption, equilibrium adsorption efficiency, and equilibrium concentration by using experimental data. The isotherm data was fitted in Freundlich model with R^2 value 0.999. Comparing with the published data in literature the effective diffusion coefficient was evaluated based on the restrictive diffusion model. The results of this study were found to be satisfactory with those of the similar surface sorption system[7].

Senthilkumaar et. al. examined the removal studies of methylene blue using jute fiber carbon: equilibrium and kinetic studies**.** The jute fiber procured from the plant stem was utilized in the preparation of AC by using H_3PO_4. The jute fiber carbon (JFC) is used as a sorbent in the elimination of MB from aqueous medium. The parameters that influence adsorption method are initial dye concentration of MB. In increment from 50 to 200 mg/L the removal efficiency increases from 45.35 to 73.86 mg/g, with time (259 min) and pH (5-10). Langmuir isotherm model well fitted with the equilibrium data with R^2value 0.99. The sorption capacity yielded to be 225.64 mg/g. The range of resulted pH was 5-10. To explain the adsorption of MB onto JFC was examined by the kinetic data obtained at various concentration has been studied by Elovich equation, pseudo first order, pseudo second order equation, intraparticle diffusion. Therefore, intraparticle diffusion was the best model to study the removal of MB onto JFC[8].

Characterization of nZVI are analyzed by Sun and Co-workers. The iron nanoparticles have drawn worldwide attentiveness because of its uniqueness in their properties and practical applications. It is employed in the treatment of ground water and site improvement. Fe nanoparticles were prepared by the reduction of $NaBH_4$ process and have been characterized with the techniques of XANES, TEM and XRD. The size of the particle is 60nm with majority greater than 90 in the nano-domain (1-100). Due to the weak surface charge, the nanoparticles have greater inclination of forming microscale aggregates, and iso electric point is in the range of pH range 8.1-8.3. Iron nanoparticles have a shell generally of (FeO) and a core composed of nZVI. The dual characteristics of iron nanoparticles should be thoroughly researched because they may be valuable for the transformation and isolation of numerous pollutants for environmental and other applications[9].

Mechanism study and parameters of nano activated carbon prepared from industrial mine coal as adsorbents for elimination of dyes from textile wastewater are examined by Shokry et. al. For the removal of MB dye from aqueous medium by using (NAC) were synthesized using maghara coal which are collected from the industrial mine. These materials are highly available, economically and environment friendly. By using chemical activation process with NaOH, NAC was prepared. The prepared NAC was utilized as viable sorbent in the adsorption of MB dye. From carbonization NAC, the average size of the particle was 0.478mm at 550°C for 90min with 50% NaOH and with an impregnation ratio 35. The absorbent having surface area $49m^2/g$ with minimum pore size of 14.7nm. The adsorption efficiency is recognized by electrostatic interaction which was proved by FTIR and SEM analysis of AC after adsorption mechanism. Adsorption equilibrium data was better fitted with Langmuir isotherm demonstrating the single-layer coverage of NAC with a greater single layer removal efficiency of 28.09 mg/g. It was resulted that the, for the removal of methylene blue dye and organic contaminants by using NAC synthesized from maghara coal is cost-effective, environment friendly and has less toxic effect on the ecology[10].

Fan et. al analysed the process under potentiostatic model electrochemical degradation of aqueous solution of Amaranth azo dye on ACF. By using potentiostatic electrochemical method in aqueous solution in which the activated carbon fiber (ACF) works as electrode for degradation of amaranth azo dye from the aqueous solution. The working of electrochemical process on ACF was known as adsorption, electroreduction and electrooxidation. Chemical Oxygen Demand (COD), efficient removal of the colour and TOC (Total organic carbon) were favoured when a suitable potential region was chosen. The initial dye concentration of $80mgL^{-1}$ for the electroreduction method was able to be completely removed after 5h. The TOC and COD materials can be deducted for about 60% after same time. At potential of 1000mv, the removal of colour was 95.4%

at the with the TOC and COD removal ratio being about 35% and 30%. The azo bond -N=N- was deteriorated in the range of -800mV to -200mv and 600mV -1400mV[11].

Ramutshatsha-Makhwedzha et. al. examined the AC derived from the peel of lemon and orange for the elimination of MB dye and methyl orange from waste water. The treatment of industrial waste water from large scale waste resource is a major concern. The absorbent behaviour of orange and lemon-peel derived activated carbon (OLPAC) is studied in the laboratory. By chemical activation of phosphoric acid, OLPAC was successfully prepared which was used for the sorption of methylene blue (MB) and methyl orange from waste water. The pH was (2-10), contact time(5-180min), adsorbent mass (0.010-0.8) and dye concentration (50-200 mg/l) were the most influential parameters on the sorption of MO and MB dye. The adsorption isotherms data were best described by Langmuir (R^2=0.987) and pseudo-second order kinetic model (R^2=0.997). The MO and MB adsorption capacity was 33 and 38 mg/g. OLPAC removes MO and MB dye from waste water by using sorption process. The removal capacity of MO and MB dye are 96 and 98%. The adsorption process is inexpensive and OLPAC are successfully utilized in the removal of MO and MB dye from waste water [12].

Chamkouri and co-worker investigated on the generation of a novel pH sensor based upon Janus Green B azo dye immobilized on triacetyl cellulose membrane; It's Optimization and Experimental Design. A novel pH optical sensor was formulated immobilized Janus Green B dye on to triacetyl cellulose membrane. In the immobilization step, condition of the dye solution was employed. The influencing parameters are concentration of the optimum value is 6× 10-5 mol/l), time (60sec.) and pH. On increasing the pH of dye solution there was a decrease in amount of dye immobilized on the film. It states at higher pH immobilization ceased. The calculation of optimized parameters was done by utilising the Box-Behnken design. The sensor favours pH range of 2.0-10.0 for (RSD> 5%). Optical sensor is used in on-line applicability, speedy response time (less than 1min), high selectivity, long-term stability (more than 6 months) and sensitivity as well as better reproducibility and reversibility[13].

Review on MB dye: Its Uses, Photodegradation, Properties, and Toxicity are studied by Khan *et al.*The presence of methylene blue increases toxicity in the aquatic environment. The major pollutants are the industrial dyes that make the water unfit for drinking purpose. MB is hazardous, toxic and are not degradable. This causes harmful effect for living beings and ecosystem. Photodegradation is a favorable oxidation method which is used for removing methylene blue from wastewater. By this method 7.9% MB dye is removed in 10h through photolysis. In this process it was found that dye was converted in to simple nontoxic species by mineralization of dye. The study points on the parameters that influence the photodegradation rate of MB, initial dye concentration, loading pH of reaction media, photocatalyst type, irradiation reaction time, and oxidizing agent. There are few aspects to be explored not only for the effective elimination of MB dye but also improves their practical use in different fields[14].

Conclusion: -

From various literature study, it has been seen that the activated carbon derived from agricultural waste is utilised as an efficient adsorbent in the elimination of hazardous heavy metals, dyes and other pollutants. We have observed that the maximum removal efficiency of activated carbon derived from corncob is 99.6%, soapnut shell is 99 %, pineapple waste is 96%, black cumin seeds is 12.71% and 17.98% for Pb (II) and MB respectively. For amaranth azo dye the adsorption efficiency is 95.4%. From this, it is confirmed that the waste materials based activated carbon can be potentially applied for MB and MO dye and amaranth azo dye removal from aqueous environment.

Acknowledgement: -

We would like to extend our sincere thanks to GIET University, Gunupur for supporting us throughout the work. We also thanked to Dr. Uttam Kumar Sahu for his continuous help and support in this work.

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