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A short review on thermodynamic and equilibrium study on various activated carbon synthesized from different biomass and application for the adsorption of water pollutants

Nikahat Banu, M.sc Chemistry, 21pgch008.nikahatbanu@giet.edu
Sivalanki Madhuri, M.sc chemistry, 22pgch012sivalankimadhuri@giet.edu

Abstract: In this chapter we have discussed about the removal of different toxic waste materials like dyes (methylene blue, organic-dye, C.I BB2 and BB3 (basic blue 3 and basic yellow 2) and heavy metals (Chromium (VI)), Phosphate and organic contaminants, Uranium ions) from waste-water using various AC synthesized from different agro-waste. The agro-residue used here are Crescentia cujete fruit shell, orange-peel-powder, coconut leaves, almond leaves, *Padina* sp. and Biomass for the mixture of AC. From the analysis along with obtained results, it is clear that these AC helps to remove the pollutant from waste-water as well as used to minimize the water generation and successfully applied for waste-water treatment.

Keywords—**Activated carbon; agricultural waste; dyes; heavy metals.**

1. **Introduction:** Joseph et al. Has studies the activated carbon synthesized from crescentia fruit shell for the methylene blue removal. The AC is not only the essential absorptive of the dye emission but also can adsorb bacteria, humic substance and humic like organics from wastewater. There are three major technologies available for removing dyes from water are oxidation, adsorption and flocculation-precipitation. In this paper the AC was synthesized from Crescentia cujete fruit shell present in Thiruvottukai. The preparation of AC follows two fundamental steps. The first step include activation and second process was carbonization which was carried out through the gasification or pyrolysis technique in an ideal atmosphere with high temp. for the biochar production. The parameter study includes agitation time (persistent and sub-stained attempt), the elimination percentage decreases when initial dye concentration and carbon dose increases. To reach the equilibrium, for the batch equilibrium experiment, the concentration is 50-250 mgL^{-1}, 0.1g of AC, and temperature 2.5 hours. The MB onto CCSC shows monolayer Langmuir type isotherm from its adsorption behavior. Considering b as Langmuir's adsorption constant and C_o as the initial concentration of solute (mgL^{-1}), for an effective adsorption of MB, the R_L (0 and 1). If R_L is equal to zero then the adsorption process will be irreversible. In this paper, the R_L value was 0.087, by the above values the adsorption shows favorable process. The kinetic values of the model for adsorption of MB are, the R^2 value of PFO (0.954) and

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PSO (0.993) model was respectively. The Freundlich isotherm and Langmuir isotherm constants being MB adsorption are as follows, the R^2 value of Freundlich and Langmuir was 0.925 and 0.998 respectively. The q_m mgL^{-1} value of Langmuir is 66.6666 and b (L/mg) value of Langmuir is 0.05415. By Freundlich and Langmuir isotherm the adsorption equilibrium can be determined. So, from the R^2 value, Langmuir and Freundlich isotherm both are best fitted [1].

Jawad, and co-worker have utilised the Malaysian low-grade charcoal and transformed to a mesoporous AC to emission of MB removal from water. For the preparation of SC-AC possessing large surface area (SA) prepared through microwave induced KOH method, by using low-rank precursor such as Malaysian Selantik (SC). The degree of unsaturated fatty acids based on the alkyl double bond present in iodine number, bulk density, ash content and moisture were used for analyses of the SC-AC and SC. Without activation, iodine number of SC-AC after activation was 1019.8 mgg^{-1} whereas the SC was 38.2 mgg^{-1}. Using the pore structure analysis technique (Brunauer-Emmett-Teller), X-ray spectroscopy (EDX), with energy dispersion scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and determination of the X-ray diffraction (XRD Fourier transform infrared (FTIR), point zero charge (pH_{PZC}), elemental determination (CHNS), the surface and structure characterization was done. By the comparison of SC-AC and raw SC, a structure of SC-AC was determined along increase in ca. by 1160 times (BET surface area =1094.3 m^2g^{-1}) as comparation to the SC before activation (BET surface area=1.23m^2g^{-1}). By using batch mode adsorption along with the optimum conditions, pH (2 to12), initial dye concentration (25 to 400 mgL^{-1}), adsorbent dosage (0.2 to 1.6 gL^{-1}) and contact time (0 to 290 minutes) the adsorption properties of mesoporous activated carbon SC-AC with MB were caried. When the AC of kinetic variables follows pseudo-second-order than there arises an equilibrium up take of MB which confirms the Langmuir isothermal model having max. Single layer adsorption capacity of 489.9mgg^{-1} at 29.85^{o}C. Through, thermodynamic parameters it concludes about the endothermic nature having spontaneous adsorption capacity. The Malaysian Selentik coal (SC) for the synthesis of activated carbon (SC-AC) has a greater pore volume with surface area (1161.3 m^2g^{-1}) and iodine number (1019.8 mgg^{-1}). The total procedure of adsorption consists of π-π stacking interaction, electrostatic attractions and hydrogen bonding. For the preparation of low cost and effective AC with substantive SA, the above process is promising precursor [2].

M.H.khani has studied on the isotherm and statistical data of uranium (u) biosorption via *padina* sp. By using *Padina* sp. the emission of U ions from saturated solution was carried out, a brownish aquatic algal biomass was applicable by the response of the surface methodology. An interactive effect of the four significant parameter that are initial concentration U solutions, pH, temperature and wet time are taken in the BWC composite design which be taken to evaluate on uranium uptake. By diluting 1 gram of

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Uranium/I stock solution the Uranium solution was prepared. In analysis of uranium concentration and batch sorption program, pH, uranium concentration and temperature at 152 rpm are present. Whereas the initial metal concentration of C_o (mg^{-1}) of the solution, the bio sorbent (g), M is the amount, and after some time **t** (mg^{-1}) C_t = metal concentration. The data were satisfactory shaped to fill a space of second order polynomial model the surface determination was allowed. A very high determination coefficient value R^2=0.9746 and adequately second order with less developed state model was analyzed. The most conducive uranium initial concentration in the solutions and temperature, pH and time where participle was 4.08, 778.47 mg^{-1}, 74.31 min, and 37.47^{o}C, was respectively. To increase as much as possible the U uptake was conjecture verified. The maximum monolayer adsorption capacity (376.73 mgg^{-1}) was evaluated by Langmuir isotherm and the stability details for biosorption of U onto the *Padina* sp. having good or sufficient representation [3].

B. chen along with their co-researchers studied on the new magnetic biochar which effectively adsorbs phosphates and organic pollutants. For environmental and agricultural application, biochar is recognized as multifunction material. By the treatment of synthetical arrange of Fe^{3+}/Fe^{2+} upon later pyrolyzing and orange-peel-extract under various temperature (2500, 400 and 700^{o}C) a novel magnetic biochar (MOP700, MOP400, MOP250) were prepared, resulting in the formation of biochar and the iron oxide magnetite was prepared in eligible step. In OP250 sample, when the temperature in 250^{o}C the percentage of ash was 3.17%, C yield was 20.7%, TPV (0.0592 cm3/g), SA (51.6m^2/g) and the percentage of C and H content were 56.5% and 5.11% respectively. The non-magnetic-charcoal (OP400) shows less sorption capability for the organic pollutants as compared to MO400 that exhibits highest sorption ability. The non-magnetic biochar shows less sorption capability than phosphate magnetic biochar especially MOP25. In regression parameter of isotherm of organic pollutants to magnetic biochar, R^2 value of Freundlich 0.996 and linear in high concentration R^2 value is 0.986 and the Q_A^{max} value is 2.99 mg/g. By the regression of parameters of isotherms, the R^2 value of Freundlich 0.382 and R^2 value of Langmuir 0.339. By using potential sorbent and considering the above data the magnetic biochar were utilized for simultaneous emission of phosphate and organic contaminants from waste water [4].

n. z. rosly and rest co-worker modified the lead sulphide through calix [6] arene, the adsorption of MB dyes and study of optimization was used by the response surface methodology. For the adsorption of MB dye, lead sulfide modified with calix [6] arene was synthesized and regenerated and possible adsorbent was characterized via field FE-SEM and energy-dispersion X-ray spectroscopy, FTIR. The optimum pH, temperature, initial concentration and adsorbent dose (44.01mg) calix [6] arene was modified with lead sulpide, temperature (31.00^{o}C), initial concentration (22.00 mg^{-1}) and pH (6) were

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inspected. With the help of elimination percentage of MB dye, the adsorption process was evaluated. The Langmuir model isotherm was best fitted, a mono layer chemisorption shows maximum adsorption efficiency (q_{max}) 5.495 mg. g^{-1} and kinetic study display that it obeys PSO related to its high co-relation and co-efficient value (R^2=0.999). The parameters of Langmuir and Freundlich isotherm along with regression information are as flows, the R^2 value of Langmuir 0.941, K_L value was 0.3233 L/mg and q_{max} value was 5.495 mg/g, whereabout the Freundlich R^2 value was 0.909, N value was 2.268 and K_F value was 2.630 L/mg [5].

y. kuang, x. zhang, and s. zhou used surfactant modification method for the emission of MB from waste water by AC**.** The AC for the adsorption of MB dye ion was modified through three surfaces. The change of AC was over by using the two CTAB (cationic surfactant-hexadecyl trimethyl ammonium bromide) and SDS (sodium dodecyl sulfonate) and anionic surfactant-sodium lauryl sulfate (SLS). When cationic dye interacts with cationic surface (CTAB (activated carbon modified by cationic surfactant)) whereas, adsorption ability of cationic dye eventually increases by anionic surfactants (SLS). The influence of the adsorption efficiency of MB modified by AC was done in batch adsorption process, such as initial methylene blue (MB) concentration (10,30,50 mg/L), pH (1-12), temperature (298,398,318,328 k). When MB dye solution contains Na^+, Ca^{2+}, NH_4^+, Mg^{2+}, and K^+ the cations have no result on adsorption. The adsorption performance rapidly gets improved in the presence NO^{2-} ions. In PSO model the dynamic of adsorption describe very well. In PFO model and PSO model, the MB removal by SLC-C the R^2 value of PFO model was 0.0644 and the R^2 value of PSO was 1 and the C_o value is 10 mgL^{-1}. The MB dye adsorption in both waters (real and modeling water) shows effective when the AC was modified by anionic surfactant. Isotherm parameters of Freundlich, Temkin and Langmuir models are as follows, the adsorption model of Langmuir isotherm R_L value was 0.106, Q_{max} value was 232.5 mgg^{-1} and R^2 value was 0.999. Thermodynamic variables for good removal efficiency of MB (methylene blue) on SLC-C were, ΔG (11.78 Kj/mol), C (10 mg/L), ΔS (0.059 KJ/mol) and ΔH (5.90 KJ/mol). The adsorption process was very fast process and endothermic processes which was confirmed when ΔG has negative values and ΔH possess positive values [6].

z. jia, z. li and other co-rescrechers analysied the adsorption performance and mechanism of MB on chemically AC sphere obtained through hydrothermally Synthesized polyvinyl alcohol microsphere. Through carbonization and sulfonation of PVA (polyvinyl alcohol) microspheres the CACms (chemically activated carbon microspheres) are synthesized, with the assistance of $FeCl_3$ by hydrothermal method. SEM, XRD and FTIR are applied for the characterization of as-prepared sample. For emission of cationic dye with higher adsorption, the functional carbon microsphere with sulfonic groups tends to be an excellent adsorbent. For the evaluation of the adsorption performance of CACms, a typical kind of

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cationic dye such as MB was chosen. By the adsorption performance of (CACms), there is no change in adsorption capacity to wide range of pH from 2-10. By the kinetic parameter for the adsorption of MB on to CACms, the R^2 value of PFO kinetic model tends to be 0.8391 and R^2 value of PSO kinetic model was 0.9989. In isotherm parameter for MB onto CACms, the R^2 value of Freundlich and Langmuir constants was 0.7429 and 0.99 with temperature 25ºC. The highest adsorbing capability can extend up to 925.9 mg g^{-1} at 45ºC and Langmuir adsorption design was best fitted from the original data. The change in temperature have a remarkable impact on adsorption process. The adsorption shows endothermic and spontaneous process which was determined by thermodynamic parameters such as enthalpy, entropy and free energy. Thermodynamic parameters for adsorption of MB on CACms, ΔG^o value was -12.46 KJ mol^{-1}, ΔH^o value was 13.78 $KJmol^{-1}$ and ΔS^o value was 88.24 $JK^{-1}mol^{-1}$ with temperature 25ºC. Moreover, as-prepared CACms shows strong adsorption ability for MB [7].

s. h. zhang *et al* investigated on the mechanism of chromium (vi) emission by nZVI based on XPS analysis. In this work, the morphology of chain structure was properly characterized and synthetizations was performed, here nZVI (nanoscale zero-valent iron) possess greater surface area (182.97 m^2g^{-1}). After 60 minutes of reaction just 43% of Cr(VI) get removed in an oxic condition, whereas complete removal of Cr(VI) was taken place after 20 minutes of reaction under anoxic disorder. In the new process it is confirmed by experimentally that the $FeCrO_4$ with less compactness was generated under acidic condition. After 60 min reaction the pH was 9. Furthermore, Cr-spiked waters shows fast emission of traced Cr (VI) with the help of as-prepared nZVI. By the normal process, the formation of layer containing hydroxides, chromium oxides and iron oxides can be present but only $FeCr_2O_4$ having low concentration has been generated. The initial concentration of Cr (VI) was 60 mgL^{-1}, pH was 3, adsorbent (nZVI) dosage 0.51 gL^{-1}, reaction time seems to be 60 min and temperature 25°C. By the process under acidic conditions and anoxic ($3<pH<6$) most significant efficiency as the as-prepared nZVI and Cr (VI) removal rate was reported. For the first time the removal of Cr(VI) was detailed and the mechanism of nZVI was proposed [8].

s. moosavi and the co-workers studied on the wastewater color emission and the utilization of AC with their effective magnetic properties. From the beginning of 21st century, water contamination is still a crucial problem which is predominantly caused by dyes. For the dye removal present in aqueous solution, adsorption method is widely used. Using EDX, XRD, FTIR, VSM, SEM and TEM, the adsorbent was characterized. Meanwhile, the induce of AC derived from biomass, agro-waste etc. onto magnetic content material can leads to effective emission of organic-dye from waste water. The range between 5-17 nm was for the NP size of iron oxide. After treatment the adsorbent recovery and separation process shows less favorable even though AC prepared from agro-waste, biomass and from

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the abundant and low-cost materials exhibits high potential for the waste water treatment in industry. The chemical and physical properties of activation include BET surface area ranging from 500 to 3362 m^2/g, adsorption capacity 5−5000 mg/g, specific mass density 120−240 g/m^2, ash content was 0.2%−37%. The optimum contact time (3 hours), adsorbent dose was 5 g/L and pH (2). The adsorption shows maximum when temperature was 303 K at pH (3-4) and contact time 60 mins. As well as the recovery and magnetic separation was explained in this literature review in this which it provides the evidence of the effective use of magnetic adsorbents[9].

a. hassani along with the co-researchers compared the elimination of optimization of two materials with structurally dissimilar harmful dye treated with charcoal as an inexpensively and available absorbent. For the emission of the two dyes C.I. BB3 and BY2 (Basic yellow 2 Basic Blue 3) low-cost coal and easily available adsorbent has been used, the effect of operational parameters was determined through RSM. For experimental designing, process modeling and optimization the quadratic central composite design (CCD) is required. From the analysis the parameters were, adsorbent dosage (0.4-2 gL^{-1}), dye initial concentration (10-50 mgL^{-1}), contact time (5-45 minutes) and temperature (12-60^oC). By the residuals analysis, t-test statistics and analysis of variance (ANOVA) the regression coefficients model were tasted. The model which was obtained has highly significant and 99% content present. The optimum adsorbent dosage was $1.5L^{-1}$, initial concentration of dye was 30 mgL^{-1}, temperature 25^oC and contact time 10 min. The major characteristics of adsorbent are as follows, the value of moisture is 4.46, value of ash yields 29.64, value of volatile material 34.28, and value of fixed carbon was 31.62. F-value for percentage of BY2 was 14.77, the F-value for percentage of BB3 was 30.74. The BY2 and BB3 dyes shows high emission efficiency (91.29% and 97.08% respectively for BB3 and BY2) under optimum conditions [10].

j. zhang and their co-researchers has studied the characterization, production and the reaction of Hemp stem based on AC. In this study, by activation of KOH and with the help of Hemp stem the high surface area AC was prepared. The N_2 desorption-adsorption isotherm, FTIR spectroscopy and TG-MS were used for the characterization, structure identification, structure and thermal analysis upon reaction and mechanisms of AC. By the KOH activation, the reaction and mechanism of activated carbon from Hemp atoms are composed of two activation steps/stages. Polycyclic reactions between the carbon and KOH forms oxide as intermediate in second activation stage [11].

a. h. jawad *et al* prepared mesoporous activated carbon through coconut leaves (pocos nuclefera) with microwave-assistant by H_3PO_4 activation for the emission of MB dye. The fallen coconut (Cocos nucifera) leaf was use for the preparation of MAC, where agricultural waste was microwave-induced with H_3PO_4. The ash content, iodine number,

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moisture content and bulk density was evaluated for the characterization of the CAC. SEM, BET surface area, XRD, pH_{pzc} and FTIR spectroscopy are used for the characterization. From BET data it was analyzed that CAC has wide-ranging surface area of 632 m^2g^{-1}, it contains 84% of mesopore with an average pore size of 36.52 Å. The uptake properties of MB by CAC were analyzed at initial pH (3-10), different CAC dosage level (0.21-10gL^{-1}), time (0-360min) and MB concentration (50-30mg/L). By the Langmuir and Freundlich isotherm parameter value for the adsorption of MB onto CAC at 30°C, the R^2 value of Langmuir was 0.9822 and R^2 value of Freundlich was 0.8800. As it shows maximum single layer absorption capacity was 250 mgg^{-1} at 30ºC, therefore the Langmuir model was well fitted according to equilibrium data. Thermodynamic parameter value for the adsorption of MB onto AC, the R^2 value was 0.9997, ΔG^o value was -5.95 KJ/mol, ΔH^o value was -107.72 KJ/mol and ΔS^o value was 375.04 J/mol K. In the work, it was analyzed that a sufficient mesoporous-activated (MAC) can be prepared from the renewable precursor (coconut leaves) [12].

J. M. Jabar along with the co-workers used African almond leaves biochar for the production of AC through pyrolysis assisted with H_3PO_4 as a chemical activating agent for sequestering the MB dye from wastewater. By pyrolytic at 700ºC for the adsorption of MB dye from aqueous. The absorbent was prepared by using African almond leaves (ALs). By using SEM, FTIR, XRD, pH_{pzc} and BED techniques the characterization of H_3PO_4 activation PALB are analyzed. For determining the optimum parameters for sequestration of MB dye the influence of various adsorption parameters were analyzed. The kinetic models and equilibrium adsorption isotherm are assessed equally. The adsorption dosage of 0.2 gL^{-1} and contact time 30 min., the PALB with high surface area (816 $m^2g^{-1)}$ and the radius 1nm shows tremendous removal efficiency because MB removal was > 98% from aquatic media at pH 8 and at temperature 303k. The PFO kinetic models and Freundlich were to best fitted with adsorption isotherm value of Langmuir constants was 0.941, R^2 value of Freundlich constants was 0.984 and R^2 value of Temkin constants was 0.0974. The thermodynamic parameters for MB dye uptake onto PALB are, the ΔH^o value was 24.27 KJ/mole, ΔS^o value was 0.82 KJ/mole. K and ΔG^o value were -224.34 KJ/mole with temperature (T) 303ºC. For the removal of MB dye from aquatic media. PALB shows a good single layer adsorption efficiency (Q_{max}) of 264.95mgg^{-1}. By these studies, it indicates that adsorption of MB dye from aquatic media due to PALB has great potential ability for adsorption purpose proves as an eco-friendly absorbent [13].

S. Cheng and their co-researchers compared the cerium/iron modified activated carbon with AC for the emission of MB from wastewater. Emission capabilities of MB dye by the adsorption of AC and modified Fe–Ce-AC has been studied in this paper. By zeta potential measurement, N_2 adsorption, SEM, Raman, FTIR, XRD, XPS, and EPS are examined for characteristics information about Fe-Ce-Ac. To separate dye from waste water an external

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magnetic field along with subsequently recycle must be made, by which the Fe_3O_4 lead to Fe-Ce-Ac having magnetic properties. The adsorption isotherm parameters for adsorption of raw AC and Fe-Ce-Ac, the R^2 value of Langmuir constants was 0.999, K_L value was 0.477 mgL^{-1}, R^2 value of Freundlich and Temkin was 0.879 and 0.954 respectively with temperature 30ºC. In addition, the raw AC and Fe-Ce-Ac equilibrium isotherm and kinetics of MB adsorption were systematically examined. By the kinetic and intra particle diffusion parameters for adsorption of raw AC an Fe-Ce-Ac, the R^2 value of PFO isotherm was 0.977 and R^2 value of PSO isotherm was 0.979. The PSO and Langmuir isotherm matches the kinetic data very well due to their adsorption behavior as per the obtained adsorption data. By the maximum single layer absorption capacity Fe-Ce-Ac shows rapid increased by 27.32% as compared with the raw AC. According to the total experimental results, the MB dye emission from the Fe-Ce-Ac proves to have effective adsorption [14].

2. Conclusion

Agriculture waste materials are easily available and used as a renewable precursor. In this work, AC were prepared from various agro-waste, which showed high removal efficiency with greater adsorption capacity. AC synthesized from Crescentia cujete fruit shell for the emission of MB from waste-water shows removal efficiency >91%. Using Malaysian Selantik charcoal (SC) for the synthesis of AC by microwave-induced KOH, 85.4% of MB was removed. AC synthesized from *Padina* sp. for the emission of Uranium ion exhibits adsorption efficiency up to 376.73 mgg^{-1}. By the treatment of chemical co-precipitation of Fe^{3+}/Fe^{2+} upon orange-peel-extract the phosphate and organic pollutants get removed having removal efficiency 99.4±0.4% and the adsorption capability of MOP700 was 1242±18 mg/kg. The removal of MB through lead sulphide modified via Calix [VI]arene shows 88.07% emission efficiency with 5.495mg/g adsorption capacity.

AC was also modified by using two CTAB (cationic surfactant-hexadecyl trimethyl ammonium bromide) and SDS (sodium dodecyl sulfonate) for the removal of MB having adsorption capacity 232.5 mg. g^{-1} with removal efficiency 96.6%. Cr (VI) was removed by nZVI having 43% of removal efficiency with 123.85mg/g adsorption capacity. Using agro-waste material for the preparation of AC for the emission of organic dyes from wastewater by adsorption having adsorption capacity 526mg/g and removal efficiency was 100%. The two dyes C.I. BB3 and BY2 (Basic yellow 2 and Basic Blue 3) were removed with the help of charcoal as an activated carbon, emission efficiency of BY2 and BB3 was 97.08% and 91.29% respectively whereas the adsorption efficiency for BY2 and BB3 was 38.34m^2/g, 8.81cm^3/g. AC synthesis from coconut leaves via microwave-assistant H_3PO_4 has 97.6% of emission efficiency and 250 mg. g^{-1} adsorption capability. Almond leaves was used for the preparation of AC by microwave-assistant H_3PO_4 for adsorption of MB, the emission efficiency and adsorption capability were 98% and 263.95mg/g respectively. Hence AC

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prepared from agro-waste shows potential removal for dyes (MB, BY2, BB3), heavy metal and organic materials and also proven to be effective for the waste-water treatment.

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