Utilization of Waste Plastic- Wrappers for the Production of Potential Activated Carbon

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Abstract
Although recycling of waste plastic is one of the controlling measures of plastic wastes, some plastics like wrappers of food items cannot be recycled. These wastes finally lead to accumulation in landfills causing environmental problems. So alternate way to reduce this environmental pollution is converting them to some value added material such as activated carbon which not only reduces waste generation but is also worth economical. Among various technologies, adsorptive removal of these toxins by the usage of activated carbon as the adsorbent is more promising and economical, as it is known for its high adsorption capacity. The preparation of activated carbon from waste food packaging polymers which amount about 35% of the total plastic wastes accumulated would not only reduce the large quantities of plastics but also help in water treatment. A relatively new technique, Hydrothermal Carbonization (HTC) was used for the carbonization of the raw material in addition to the traditional carbonization process. Initially the waste plastic wrapper was cut in small pieces and processed to produce char which was further processed to prepare activated carbon. The samples were characterized before and after the process. The obtained char is activated with 1N KOH solution at optimized activation time of 23hrs and impregnation ratio (KOH : char) of 6:1. The obtained activated carbon is named as dry pyrolysed activated carbon (DPAC) and it was characterized by several means such as EDX, XRD, FTIR, Iodine value, Methylene blue adsorption and FESEM analysis which confirmed the production of activated carbon from plastics.

Key words: waste plastic wrapper, waste management, activated carbon, carbonization, pyrolysis and methylene blue adsorption.
1. Introduction:
Due to the incredible properties of plastics like durability and low cost, these materials became inseparable from humans’ day-to-day life at every corner in the world right from electrical appliances to food packaging materials. Nowadays, synthetic polymers are being used in several industries out of which packaging application covers about 35% of plastic use throughout the world [1, 2]. The multi layered flexible food packaging wrappers are mainly composed of three layers of aluminum metalized film-inner layer, low density poly ethylene (LDPE) - middle layer, biaxial oriented polypropylene (BOPP) - outer layer [3, 4]. How much useful role these plastics are playing at the same time that much adverse effect also they are causing, the problems that is being created by these plastics include effect to environment, effect to animals and effect to humans. Due to urbanization the generation of municipal solid waste is enhancing at a very high rate. Plastic wastes account for 7% of the municipal waste. Due to these reasons, attempts are being made continuously by many researchers on this issue to find a better solution. Although recycling is one of the methods for waste plastic management but the plastic recycling is not always green because it usually results in the down cycling of plastics into a poor quality product that consists of high levels of toxic additives which may be present in the form of stabilizers. A recycling plant also produces larger amount of effluents during the cleaning and washing processes, which produces a large volume of wastewater. In addition to that, plastic waste generation is increasing every year at a higher rate than the recycled fraction and more over there are some plastics, which cannot be recycled and are finally diverted to landfills. Therefore under these circumstances, one of the ways for such waste plastic management is converting them to useful materials like industrial fuels (viz. crude oil, petroleum gases) and activated carbon.

2. Literature:

Based on their particle size activated carbons are classified into three types they are powdered activated carbon (0.15 to 0.25 mm), granular activated carbon (0.6 to 4 mm) and activated carbon fibers. Industrial applications of powdered activated carbon include pharmaceutical, food industry, waste water treatment, sugar decolourisation, and mercury and dioxin removal from a flue gas stream [5, 6]. The granular activated carbon being larger [7, 8] as compared to powdered activated carbon presents a smaller external surface. Granular activated carbon is advantageous as compared with powdered activated carbon as it offers less pressure drop, high apparent density, high hardness, low abrasion index and also it can be reused more than once.
Applications of granulated carbons include water treatment, deodorization and separation of components of flow system. Compared to granular activated carbons and powder activated carbons, the activated carbon fibres have their unique characteristics like fast intra-particle adsorption and ease of handling. It can be applicable in both gas and aqueous phase adsorption processes [9-11].

Activated carbon can be produced from any materials those have high carbon content in them. However, literatures indicate that many experiments are being carried out to obtain a cost effective activated carbon from coconut shells, coffee industry wastes, wood, olive, almond shells, rice husk, date pits, nutshells, plum stones, lepsi-seeds and PVC etc. [12 -17]. Some researchers have mentioned that low-cost adsorbents can be developed by using waste materials which in turn will reduce the production cost of activated carbon. Four different methods namely, physical activation, chemical activation, carbonization followed by activation and hydrothermal carbonization are being used by different researchers for production of activated carbon. Again, different researchers have used different chemical activation agents for different source materials at different activation temperatures and times [18-21].

3. Experimental work :
Initially the sample was cut into small pieces. A known amount of the cut sample was taken into a crucible and was carbonized using muffle furnace at different temperatures. The sample was converted to char after 2 hours. The char was collected in a beaker and was impregnated with KOH solution at different impregnation ratios and the beaker was kept on a magnetic stirrer for different activation time periods. To know the optimum values of activation time, temperature and impregnation ratio, the obtained char was tested for its iodine value. Iodine value test was carried out according to ASTM D4607-94(2006) at various time periods of activation, impregnation ratios and carbonization temperatures. The char was collected in a beaker and was impregnated with 1N KOH solution with an optimized impregnation ratio (KOH to char) of 6:1 and the beaker was kept on a magnetic stirrer for an optimized activation time of 23 hours. Now the activated carbon (AC) was produced which was washed with dilute hydrochloric acid for 1 hour and then washed several times with distilled water till the pH of the sample comes to a range of 6-7. The obtained AC was dried in an oven for 4h and stored in a desiccator. The final yield of dry pyrolysed activated carbon (DPAC) thus obtained was measured.
4. Results and discussions

The activated carbon sample prepared from waste plastic wrappers was then characterised by different analysis which are discussed below.

4.1 CHNS Analysis

CHNS elemental analyser helps in determination of carbon, hydrogen, nitrogen and sulphur in organic matrices and other types of materials. Before converting the waste packaging materials to activated carbon, it is essential to know the carbon content of the sample for which CHNS analysis and proximate analysis were carried out for the selected sample. The results of these analyses are shown in Table-1 and Table-2. The carbon content of the source material i.e. selected waste food packaging wrapper was found to be 74.24% and 71.38% (Table-1 and Table-2). These results of high carbon content indicate its suitability for using in activated carbon preparation. The activated carbons thus prepared by dry pyrolysis was also analysed by proximate analysis to check the compositions. The analysis results are shown in Table-2. It is observed that a good amount of fixed carbon is present in the considered waste plastics.

4.2 Iodine value

The char obtained from the carbonization was impregnated with 1N KOH solution at a particular impregnation ratio (viz. 6:1) of KOH to char which was then put on a magnetic stirrer for different activation time periods (i.e. 5, 10, 15, 20, 21, 22, 23, 24, 25, and 30 hours). Iodine value test was carried out for these dried activated carbon samples whose results are shown in Fig.-1. The optimum activation time is noted corresponding to highest iodine value. It is observed from the Fig.-1(A) that with increase in activation time, iodine value is increasing up to 20 hours of activation time and then decreasing drastically with further increase in activation time beyond 20 hours. With a detail analysis for transition period (Fig.-1 (B)), it is found that iodine value is decreasing after 23 hours. Maximum Iodine value of 680 is observed at 23 hours implying it to be the optimized activation time. Then, the char was impregnated with different impregnation ratios of alkali to char (i.e. 2:1, 4:1, 6:1 and 8:1) and was activated with the optimum activation time period of 23 hours. Iodine value test was performed for all the prepared activated carbon samples and the results are shown in Fig.-2(A). The impregnation ratio at which highest iodine value was measured is considered as optimum one. It is observed that with increase in impregnation ratio, iodine value is increasing up to 6:1 and then decreasing which implies that the optimum
impregnation ratio is 6:1. Effect of carbonization temperature on activated carbon was also studied. The iodine number was found to be increased with the carbonization temperature (Figure-2(B)). The iodine number was found to be maximum at 350°C having a value of 561.32 mg/g. Although the iodine value was found to be increasing with temperature, but beyond 350°C, the material was burning completely leading to the formation of porous carbon because of high temperature carbonization. Thus 350°C was considered as optimum carbonization temperature.

4.3 Elemental analysis (EDX analysis)

The elemental analysis was carried out for the selected sample before and after processing by using Energy-dispersive X-ray (EDX) analyzer. EDX analysis of waste plastic (food packaging wrapper) is shown in Fig.-3(A). It is observed from this figure that one major peak and some smaller peaks are present there indicating the presence of higher percentage of carbon than other components in the sample. Elemental analysis of char (obtained just after carbonization) and activated carbon (finally obtained after proper activation) were also carried out whose results are shown in Fig.3(B) and Fig.3(C) respectively. Composition of different components present in plastic, char (obtained just after carbonization) and activated carbon (finally obtained after proper activation) are shown in Table-3. It is observed from these Figures and table that carbon content is very significant in all the cases implying its suitability for preparation a proper activated carbon.

4.4 FTIR analysis

FTIR analysis was carried out to determine the bonds which were present in the sample and in the prepared activated carbon. The FTIR analysis graphs for raw plastic sample and prepared activated carbon sample are shown below in Fig.-4. FTIR analysis of plastic sample and activated carbon samples with corresponding functional groups are listed in Table-3(A) and Table-3(B) respectively. The presence of –O-H is due to the absorption of water molecules as result of an–O-H stretching mode of hydroxyl groups and adsorbed water as well as hydrogen bonded –O-H group of alcohols and phenols. –C - O bonds are expected due to stabilizing chemicals which are present in the parent raw material. – C= C -, =C-H- and –C-H- bonds are present due to the polymeric nature of the raw material and also because of C-H interaction with the surface of the carbon. These bonds could be found in both aromatic and aliphatic structures.
4.5 XRD analysis

Many crystalline compounds are found in food packaging wrapper and char as observed in XRD plots [Fig.-5(A) and 5(B)]. Most identified crystalline compounds are Titanium dioxide and Aluminum compounds. XRD plot for the DPAC is shown in Fig.-5(C). The presence of Titanium Dioxide at \(2\theta = 32.09, 42.279, 48.489, 46.054, 48.489, 64.141, 66.353, 74.609, 76.284\) and Titanium Carbide at \(2\theta = 25.026\) in Fig.-5 (C) confirms that Aluminum compounds are removed in AC through the acid wash.

4.6 Methylene blue adsorption

Methylene blue adsorption was carried out on the surface of the prepared activated carbon to know its adsorptive capacity. Percentage of adsorbance and equilibrium sorbate concentration \( (q_e) \) were plotted against the concentration in Fig.-1. From Fig.-6(a), it is observed that with the increase in initial concentration of Methylene blue solution, the percentage of its adsorbance is decreasing. The reason may be due to the fact that same amount of methylene blue might be getting adsorbed when all other factors remain unchanged and only methylene blue amount increases. Adsorbance of Methylene blue on DPAC is found to be 99.9% at 10 ppm concentration while it is found to be 64% at 70 ppm concentration of Methylene blue solution. It is further observed from Fig. 6(b) that the adsorption capacity \( (q_e) \) of Methylene blue on activated carbon is increasing with the increase in its concentration in liquid from 10 ppm to 70 ppm. This may be due to the fact that an increase in capacity with increasing dye concentration mainly suggests that the dye molecules do not completely penetrate the particle or partly that the dye molecules preferentially adsorb near the outer surface of the particle [22] as pore sizes of the DPAC go on decreasing.

4.6 Adsorption equilibrium study

For the identification of the adsorption behavior at constant temperature, the variation in the experimental data (Fig.-7) clearly indicates the current adsorption process behavior is very similar to the adsorption mechanism described by Langmuir. Measured slope, intercept and \(R\) values of the above plot are found to be 0.0594, 0.105 and 0.324 respectively (Table-4). The achieved \(R\)-value indicates that the prepared activated carbon has sufficient potential for adsorption.

4.8 : Field Emission Scanning Electron Microscope (FESEM)
The FESEM micrograph (Figure 8a) shows that the char produced by carbonization of plastic doesn’t consist of any pores and completely dense. The particles are found to be compact with non-uniform distribution.

After carbonization, the particles are also found to be compact with non-uniform distribution (Figures.-8b,8c & 8d) even at higher magnifications. The inner carbonaceous phase is observed to be fragmented and the particles of the activated carbon are seen varying in size and shape thereby indicating that the carbon skeleton is severely broken and is looking like a “loose sponge structure. With the further magnifications from 5000x to 50000x and 100000x as shown in Figures.-8b, 8c & 8d, the surface was also observed to be porous just like a honey comb on the inner walls of larger pores which are arranged in irregular manner.

5. Conclusions
In the current work activated carbon has been produced successfully from waste plastics by dry pyrolysis methodology. For every batch with dry pyrolysis, a yield of around 10-15% of activated carbon was obtained. Time of 2hr was required for carbonizing under dry pyrolysis process. The optimum time of activation and impregnation ratio (KOH : char) for AC were found to be 23h and 6:1 respectively.

The prepared activated carbon was characterized by analyzing the SEM image and data revealed by XRD analysis. In the FESEM images pores have been identified for AC and the carbon skeleton was found to be severely broken. The obtained structure was looking like a “loose sponge”. XRD and EDX analysis reveal the removal of impurities of plastic in the prepared activated carbon. FTIR analysis confirms the presence of stable – C=C-, =C-H- and –C-H-bonds. In addition to the above the obtained Iodine value (673) reveals the adsorption potential.

Adsorption analysis of methylene blue dye solution for activated carbon has been investigated by using UV-Visible spectrophotometer at a wavelength of 663nm. On comparison of adsorption% and adsorption capacity, it has been observed that for 10ppm of solution, activated carbon has shown an adsorption% of 99.9% and the adsorption percent has gradually reduced with increase in concentration till 70ppm of dye solution.
The mathematical expression describing the adsorption behaviour closely matches with the behaviour predicted by Langmuir adsorption Isotherm. The obtained regression coefficient value (0.94) depicts the close agreement between the predicted and experimental data.

Acknowledgement

The authors are thankful to Director, National Institute of Technology, Rourkela, India for providing necessary facilities for the M.Tech. project work.

References


