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A Systematic Approach for Screening and Performance Assessment of Novel Adsorbents

V. Ramakrishna
Professor, Department of Civil Engineering,
LBR College of Engineering,
Mylavaram, Krishna District-AP

Abstract:- **Activated carbon prepared from various raw materials are being examined for water and wastewater treatment purposes. The investigators are reporting for more characteristics than prescribed under the relevant IS codes, IS 2752:1995 and IS 8366:1989, while some of the characteristics prescribed by the IS codes are not being examined. Under these circumstances, selection of a suitable adsorbent for a specific purpose becomes difficult. The present study is taken up with an objective of screening the adsorbents based on (i) performance in terms of pollutant removal (ii) available IS Codes (iii) available physico-chemical characteristics. A database comprising the physico-chemical characteristics of the activated carbon prepared from various raw materials is generated from literature and is compared with the limits prescribed under available IS codes. A four scale linear ranking model is also developed in this study for the systematic assessment of the suitability of activated carbon for a specific purpose and is illustrated with a data source where the information pertaining to the relevant physico-chemical characteristics is fully available. It is concluded from the present study that, (i) adsorbents prepared from agricultural wastes are more suitable than those prepared from industrial wastes (ii) a separate IS code is desirable for defining the suitability of activated carbon for wastewater treatment; (iii) identification of characteristics for the activated carbon prepared from a specific raw material category is desirable; (iv) a standard/common method should be prescribed for the preparation for commercially available activated carbon; and (v) a possible re-examination of the characteristics selected and prescribed under IS 2752:1995 and IS 8366:1989 (vi) it is possible to rank the activated carbon based on its physico-chemical characteristics**

1. INTRODUCTION

A number of low cost novel adsorbents are developed and reported by several investigators [3, 10, 21, 23, 31, 32, 39] in pursuit of an alternative to the commercial activated carbon used for the treatment of a number of pollutants from contaminated water. Materials such as fly ash [15, 17, 28, 30, 36], bituminous coal [34, 35], blast furnace slag [38], coconut shell [13, 20], mango seed and shell [1, 19], bagasse [9], rice-husk ash [40], coconut fibre pith [18], sawdust [14, 24, 25, 29], groundnut husk [22], used waste tea leaves [37], wood barks [2, 16, 41] etc. have been attempted. The physico-chemical characteristics have also been reported by the investigators along with the methods of preparation of adsorbents.

Two codes of Bureau of Indian Standards (BIS), viz., IS 2752:1995 (originally published in 1963 and revised in 1978, 1989, and 1995)[11] and IS 8366:1989 (originally published in 1977 and revised in 1989) [12] are available for classification of adsorbents for their use in specific purposes based on their physico-chemical characteristics.

IS 2752:1995 defines the activated carbon for two specific purposes viz.,

- Respirator carbons and Solvent recovery (Type-1)
- Water treatment (Type-2)

IS 8366:1989 defines the activated carbon for three specific purposes viz.,

- Decolorizing vegetable oils, fats, and waxes (Type-1)
- Decolorizing sugar solutions, corn sugar solutions etc. (Type-2)
- Decolorizing pharmaceuticals (Type-3)

It is observed that, there are no guidelines for defining the activated carbon suitable for wastewater treatment. The activated carbon of Type-2 under IS 2752:1995 is suitable for water treatment whereas the Type-3 under IS 8366:1989 is categorized for decolourisation of pharmaceuticals. The wastewater from pharmaceuticals causes pollution that needs to be treated.

2. OBJECTIVES OF THE STUDY

Both the available IS codes are not suitable for directly classifying the adsorbents for wastewater treatment. Further, it is noticed that [5], the physico-chemical characteristics reported by the investigators are beyond the prescribed characteristics of the above two IS codes.

The present study focuses on the aspects for selecting adsorbents suitable for contaminated water treatment. The developed adsorbents should be screened based on-

- performance in terms of pollutant removal
- available IS codes
- any model based on physico-chemical characteristics for deciding the suitability of adsorbent based on the compliance of their characteristics prescribed under the two IS codes.

The wastewater from pharmaceuticals causes pollution that needs to be treated. Decolourisation of pharmaceuticals is assumed as a treatment option for comparative study.

Hence, it is decided to restrict the comparative study to the activated carbons prescribed under the following heads:

- Type-2 under IS 2752:1995
- Type-3 under IS 8366:1989

3. NOVEL ADSORBENTS

An exhaustive literature survey [3, 21, 26, 39] is carried out for the variety of activated carbons reported for their use in thetreatment of contaminated water with respect to the pollutant they are attempted to remove in the batch/column studies, and given in Table-1.

Table-1 Novel adsorbents studied for their use in wastewater treatment

Adsorbents	**Studied for the removal of**
Crushed coconut shell, Rice straw, Rice husk ash, Fly ash, Sawdust, Granular amorphous peat, Ricehulls treated with zinc chloride, Bituminous coal, Coal, China clay, Lignite, Lime, Activated carbon, Modified acacia bark, *Chrolella vulgaris*, Rice husk powder, Waste tea and coffee powder, Exhausted coffee nuts, Walnut shells, Blast furnace flue dust, Fly ash regenerated with 0.1 N HCl/H_2SO_4, Bagasse, Coconut jute carbon, Acacia arabica bark, Waste tea leaves carbon, Rice husk carbon, Carbonaceous waste slurry of fertiliser plant, Road dust.	Cr^{+6}
Fly ash, Sawdust, Modified acacia bark, *Chlorella vulgaris*, Coconut coir dust, Blast furnace slag, Ground nut hull treated with EDTA, Waste tyre rubber, Commercial activated carbon, Fly ash regenerated with 0.1 N HCl/H_2SO_4, Polymerised grafted tin oxide gel, Jute, Montmorillonite, Kaolinite, Serpentine; Coal, Fly ash and Cement matrix; Waste tea leaves,	Pb^{+2}
Fly ash, Sawdust, Bituminous coal, Coconut shell, Raw rice husk, Chitosan, Hair, Modified acacia bark, Coconut coir dust, Rubber from scrap tyre, Groundnut hull treated with EDTA, Waste tea/ coffee powder, Exhausted coffee nuts, Walnut shells, Peanut skin, Coconut husk hull, Waste tyre rubber, Wollastonite, Montmorillonite, Kaolinite, Serpentine, Waste tea leaves.	Cd^{+2}
Pyrrhotite pyrite, Wool fibers modified with polyethyl amine, Coal, Waste rubber, Hair, Modified acacia bark, Tannery hair, Maize starch bark, Modified cellulose, Cattle hair, Chemically modified cotton, Waste tyre rubber, Sawdust, Jute, Modified cotton N-amino-deoxy cellulose, Foamed natural rubber.	Hg^{+2}
Granular amorphous peat, Fly ash, Alumino-silicates, Cowdung, Peat, Modified acacia bark, Coconut coir dust, Wollastonite, China clay, Fly ash-China clay, Peanut skin, Coconut husk hull, Sawdust, Jute, Serpentine; Coal, Fly ash, and cement matrix; Chitosan.	Cu^{+2}
Granular amorphous peat, Fly ash, Clay, Coconut coir dust, Blast Furnace slag, China clay; Coal, Fly ash, and cement matrix; Waste tea leaves.	Zn^{+2}
Granular amorphous peat, Fly ash, Modified acacia bark, Coconut coir dust, Peanut skin, Coconut husk hull, Wollastonite, China clay.	Ni^{+2}

For the present study, the available information for the raw materials of the novel adsorbents are divided into two categories viz.,

- Industrial wastes/by-products
- Agricultural wastes

The above information (Refer Table-1) is segregated based on the above two categories of materials along with that of the adsorption studies using Commercial Activated Carbon (CAC) procured from local suppliers. A database corresponding to a total of sixty-five different materials reported is compiled. This total comprises of 26 & 28 different materials of Industrial-wastes/by-products, and agricultural wastes respectively; and 11 different types of CAC. It is noted from the compilation that the investigators are reporting for more characteristic properties than that prescribed by the IS codes. Barring moisture and ash contents, the characteristic properties prescribed by the BIS codes (IS 2752:1995, IS 8366:1989) are different for both the water treatment and decolourisation purposes.

4. RESULTS AND DISCUSSION

A. *Screening based on performance with respect to pollutant removal*

The performance of activated carbon is assessed based on its pollutant removal efficiency. The efficiency is usually tested based on its compliance with isotherms such as Langmuir or Freundlich for batch studies of adsorption. To understand this objective, a large database is generated [7, 8, 27] corresponding to activated carbons prepared from materials pertaining to industrial wastes, agricultural wastes along with that of commercial activated carbon for comparison. The information based on Freundlich constants k_f and n is compiled for each of the materials. Higher the value of k_f higher is the pollutant removal. Ramakrishna and Babu [27] analyzed the data by developing models based on multiple regression and artificial neural networks and concluded that, adsorbents prepared using agricultural wastes are more effective than those prepared from industrial wastes.

B. Compliance studies with reference to IS codes

The physico-chemical characteristics for the novel adsorbents prepared from agricultural and industrial wastes reported in literature are given in Table-2. It is noticed that:

- The investigators have examined more characteristics than those prescribed under IS codes.
- Data for most of the characteristics described by IS codes (IS 2752:1995, IS 8366:1989) is missing.

Table-2 Characteristics reported in literature

S. No.	Characteristic	S. No.	Characteristic
1	Apparent density	14	Calcium (CaO)
2	Porosity	15	Sulphur
3	Cation exchange capacity	16	MgO
4	Surface area	17	MnO
5	Particle size	18	FeO
6	Moisture content	19	Loss on ignition
7	Ash content	20	Fe_2O_3
8	Decolorizing power	21	Combustible matter
9	Matter soluble in water	22	Specific gravity
10	Matter soluble in acid	23	Phenol number
11	Bulk density	24	Iodine number
12	Silica	25	pH
13	Alumina		

The frequency of reporting each of the physico-chemical characteristics in literature is compiled. From this database, the characteristics that are more frequently reported are identified and are given below:

- Bulk density
- Moisture content
- Ash content
- Particle size
- Surface area
- Silica
- Alumina

The following aspects are observed when the above information is compared with the characteristics prescribed by the IS codes:

- The characteristics such as moisture content, ash content, particle size, and surface area are prescribed in the IS codes.
- The characteristics such as bulk density, silica, and alumina are not prescribed in the IS codes but are frequently reported in literature.

The available database for the characteristics listed in Table-2 is segregated based on the characteristics prescribed by BIS codes. The database is examined with the above selected list of characteristics and their prescribed limits as per the relevant IS codes.

The information pertaining to the details of particle size is available in literature for about 47 materials. However, it is noted that none of the investigators reported the particle size as per the guidelines prescribed under IS 8366:1989. Similarly very little information (for 2 materials out of 65 materials) is available for the Iodine number prescribed under IS 2752:1995. Hence the information available for particle size and Iodine number are ignored for the comparative study purpose. For the remaining characteristic properties, studies are carried out by Babu and Ramakrishna [5] in terms of the following compliance of characteristics with that of IS codes.

- Compliance of one of the characteristics (C1)
- Compliance of any two characteristics (C2)
- Compliance of all three characteristics (C3)
- No compliance of any of the characteristics (CN)
- No compliance based on partial data reported (CNP)
- Data not reported for any of the characteristics (DNR)

The percentage share of compliance is calculated based on the compliance data for each sequence of the category and the total number of materials under each of the three categories. The above results for the compliance data under IS 2752:1995 are given in Table-3. It is to be noted from Table-3 that,

- 11.54% to 36.36% of the activated carbons for which data is reported are complying with at least one characteristic.
- There is no compliance for any two of the characteristics for the activated carbons prepared from Industrial wastes/by-products.
- The compliance information for any two of the characteristics for the other two categories is also not much encouraging (3.57% and 9.09%).

- Most of the data is either not fully reported (36.36% to 71.43%) or not complying based on partial data reported (9.09% to 26.92%) under IS 2752:1995.

Table-3 Percentage share of compliance under IS 2752:1995 with respect to the category of activated carbon

Category of activated carbon	C1, %	C2, %	C3, %	CN, %	CNP, %	DNR, %
Industrial wastes/ by-products	11.54	0	0	7.69	26.97	53.85
Agricultural waste	21.43	3.57	0	3.57	0	71.43
Commercial Activated Carbon	36.36	9.09	0	9.09	9.09	36.36

C1: Compliance of one of the characteristics; C2: Compliance of any two characteristics
C3: Compliance of all three characteristics; CN: No compliance of any of the characteristics
CNP: No compliance based on partial data reported; DNR: No compliance based on partial data reported

Similarly the percentage overall compliance is computed based on the compliance data for each sequence and the total number of materials available under all the three categories (i.e., 65). The percentage overall compliance for the activated carbon of all the above three categories under IS 2752:1995 and IS 8366:1989 respectively. The following observations are made:

- 20% of the activated carbons for which data is reported are complying with at least one characteristic.
- None of the activated carbons from the three categories under study are complying fully under both the IS codes.
- Data is not reported for any of the characteristics for 58.46% of the activated carbon classified under the three categories listed earlier.
- No compliance for more than two out of the six selected characteristics.
- The compliance for only one of the characteristics is high (20% and 15.38%) under both the IS codes.

C. Anamolies with respect to reported physico-chemical characteristics

The IS codes prescribed certain characteristics for classification of activated carbon based on physico-chemical characteristics. However, the investigators have been examining [5] for few additional characteristics (Refer Table-2) and at the same time not reporting few characteristics prescribed by the IS codes. For example, the characteristics such as bulk density, silica, and alumina are being reported more frequently (24.26%) but they are not required as per the IS codes. The available database is compiled [5] for the characteristics that are reported for each of three categories under study and is analyzed.

The following observations are arrived at from the analysis:

- For the activated carbons prepared from industrial wastes/by-products all the 25 characteristics are reported over the entire database though all of them are not prescribed by IS codes.
- For activated carbon from agricultural wastes and CAC very few characteristics are reported (14 and 11 respectively).
- The information pertaining to characteristics such as decolorizing power, matter soluble in water, matter soluble in acid, pH, and Iodine number is missing for commercial activated carbon.

In view of the above aspects and improve clarity of understanding, there appears to be a need to prescribe a set of characteristics separately for the activated carbons prepared from each of the raw material category viz., industrial waste/by-products, agricultural wastes etc.

D. Linear ranking model based on physico-chemical characteristics prescribed by IS codes

The available information pertaining to physico-chemical characteristics other than that prescribed by IS codes is misleading the investigators for verification of the properties with a correct reference. Babu and Ramakrishna [5] studied in detail these anomalies and reported that no specific set of guidelines are available to develop a commercial activated carbon with uniform characteristics. Under these circumstances, it becomes the need of the hour to assess the suitability of the novel adsorbent (or even commercial activated carbon) for contaminated water treatment. A ranking model is hence explored for defining suitability of the activated carbons for a specific purpose when the information is fully available for the relevant characteristics.

The linear ranking model developed by Babu and Ramakrishna [6] is based on the data available in the literature [33] with an objective to rank the activated carbons for their suitability for contaminated water treatment based on the compliance of their characteristics prescribed under the two IS codes mentioned earlier. The data is compared with the permissible limits prescribed under IS 2752:1995 and IS 8366:1989. Rengaraj et al., [33] prepared six different types of activated carbons (M-1 to M-6) and examined their physical characteristic properties along with that of commercial activated carbon (CAC) as per the IS codes.

Babu and Ramakrishna [6] determined the percentage compliance of the characteristic properties as per the IS codes. The percentage of compliance is calculated with respect to the frequency of compliance for the prescribed limits and the maximum possible chances of compliance of the material under each IS code. The results are shown in Fig. 1.

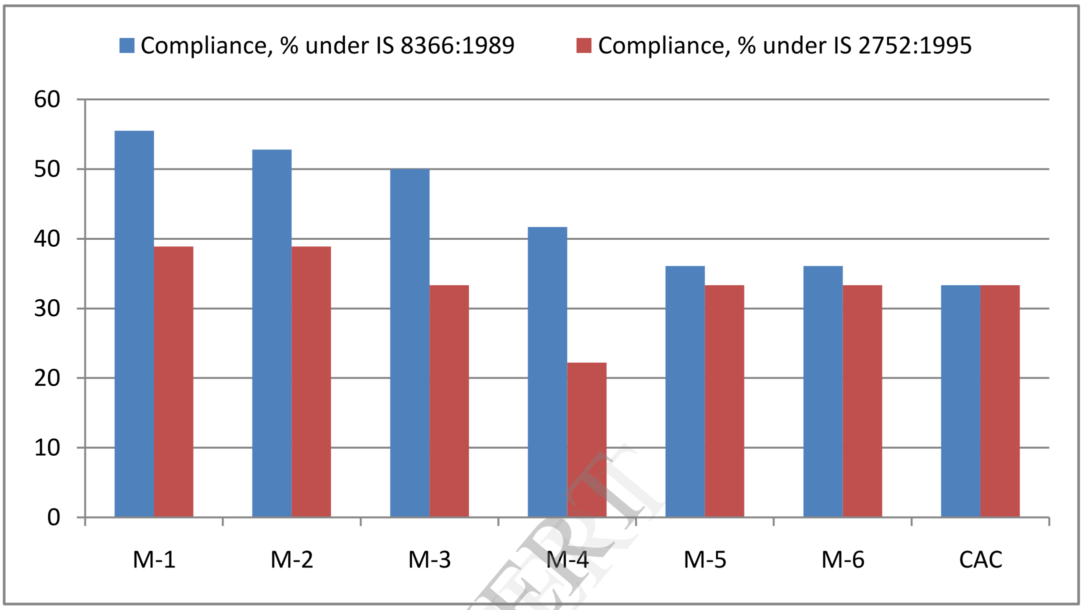

Figure 1 Comparison of activated carbon characteristics in compliance with IS 8366:1989 and IS 2752:1995

The percentage compliance is varying from 22.22 to 38.89 with respect to IS 2752:1995 and from 33.33 to 55.5 with respect to IS 8366:1989 respectively. It is further observed that most of the activated carbons prepared are having better percentage compliance with that of CAC.

The surface area of CAC is very low (296 m^2/g) while three of the other six materials have better surface area than CAC. Babu and Ramakrishna [5] reported a surface area range for CAC from 486-1298 m^2/g, which is higher than that used in the above study. Higher surface area leads to better adsorption and hence it may thus be inferred in this regard that adsorption efficiency of CAC used in the comparison study may be relatively lesser compared with other adsorbents.

These anamolies will hence lead to a need for having a standard and common method of activated carbon preparation, **at least** for the grade that is commercially available. To minimze the gaps in this regard, a linearly distributed model is proposed (Refer Fig. 2) for the **relative ranking** of the activated carbons under study based on the frequency of their complying with the standards. Four ranks are proposed viz., Very Good, Good, Average and Poor.

From Figure 2 it can be understood that, the CAC and all the six activated carbons tested are more suitable (**Good to Average**) for the purpose of decolourization of pharmaceuticals than for water treatment (**Average to Poor**). The above ranking model can be modified by increasing the levels of scale of ranking and can be used to assess the relative suitability of the activated carbons. The ranking model can be improved by studying the significance of each of the characteristics with reference to the objective of the usage of the activated carbon and accordingly awarding relative weightage(s). However, a large database pertaining to complete information of the physico-chemical characteristics for each activated carbon used by the investigators is essential in this regard. The model developed help in a **systematic assessment** of the suitability/classification of an activated carbon for a specific purpose and can be applied where information is fully available for the relevant characteristics.

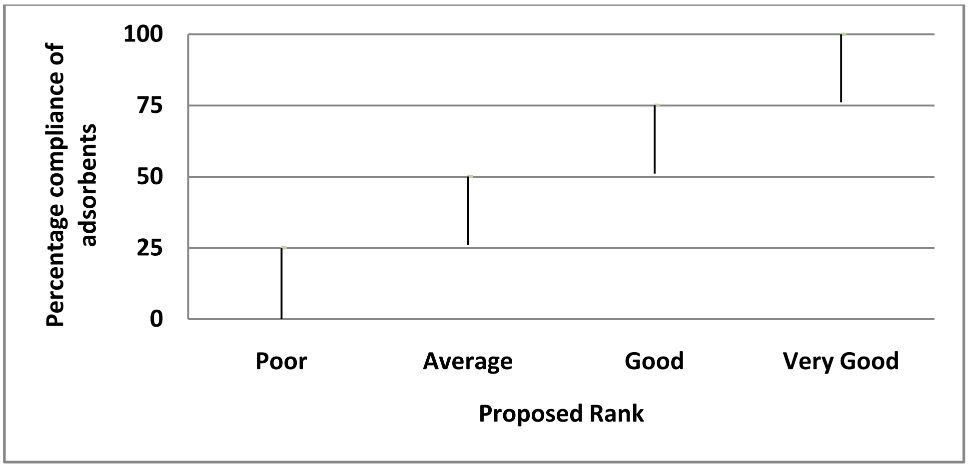

Figure 2 Ranking model of adsorbents based on percentage compliance of characteristics

The results reported by the investigators are satisfactory [26] with regard to their objectives irrespective of any compliance with prescribed IS codes. The performance assessment of activated carbons with respect to percentage compliance needs to be studied further to bridge the gaps created by anomalies in these aspects.

5. CRITICAL COMPARISON OF APPROACHES STUDIED

In the present study, several approaches such as Screening based on performance with respect to pollutant removal, Compliance studies with reference to IS codes, Anomalies with respect to reported physico-chemical characteristics, Linear ranking model based on physico-chemical characteristics prescribed by IS codes are discussed.

The ultimate objective of using any adsorbent is its efficiency of pollutant removal. Since a number of adsorbents with different preparation methodologies are used, their characteristic properties, in particular surface area, are important. The examination of characteristic properties hence becomes critical. Incidentally, the available IS codes are not relevant for determining the suitability of adsorbent for wastewater treatment. Out of the number of materials that are studied, it is concluded that adsorbents prepared using agricultural wastes are more suitable than those using industrial wastes and at times better than commercial activated carbon based on pollutant removal efficiency.

The ambiguity continues with regard to depending on existing IS codes in this regard. In view of the many studies being taken up investigators on low-cost novel adsorbents, this analysis hence suggests a need to have a re-look at the available IS codes for activated carbons, with the following objectives (i) to prepare revised guidelines under the available IS codes for the required physico-chemical characteristics and their limits (ii) to develop a separate IS code for wastewater treatment (iii) to prescribe a set of desired physico-chemical characteristics based on material of preparation such as agricultural wastes, industrial wastes etc. (iv) to prescribe a standard/common method for the preparation of activated carbon that is commercially available (v) to impose a clear labeling requirement that the CAC should satisfy the limits prescribed by the relevant IS code. The ranking model can only be considered as a supporting tool to decide on selection of an adsorbent based on IS codes. The compliance studies will prove to be useful in these types of studies.

Summary and Conclusions

There are two IS codes available for characterization of activated carbons. Incidentally, it is found from literature that the activated carbon prepared from various raw materials are being examined and reported for more characteristics than prescribed under the relevant IS codes. Further, some of the characteristics prescribed by the IS codes are not being examined by the investigators. To address these issues, the present study is taken up with the objectives of screening and assesing the performance of adsorbents based on IS codes using literature database. The database is compared with the limits prescribed under the two specific types of activated carbons in IS codes. The conclusions of the study are as follows:

- The available IS codes are not suitable for wastewater treatment
- A separate IS code is desirable for defining the suitability of activated carbon for wastewater treatment.
- Identification of characteristics for the activated carbon prepared from a specific raw material category such as agricultural wastes, industrial wastes etc. is required.
- A standard/common method should be prescribed for the preparation of activated carbon that is commercially available.
- A possible re-examination of the characteristics selected and prescribed under IS 2752:1995 and IS 8366:1989 is needed.
- The ranking model proposed in the present study based on a specific case study substantiates that it is possible to rank the activated carbon based on its physico-chemical characteristics.
- There is a further scope in the improvement of the proposed ranking model

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