Ranking Of Adsorbents Based On Method Of Preparation And Freundlich Isotherm

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Abstract

A number of novel adsorbents are being investigated in search of an alternative to Commercial Activated Carbon (CAC). Several methodologies are being followed in the preparation of adsorbents from their raw materials. The raw materials used for the preparation of novel adsorbents are broadly classified under three main categories: (i) Agricultural Wastes (AW) (ii) Industrial Wastes (IW) and (iii) Mineral Wastes (MW). The adsorbent preparation methodologies are also categorized based on the primary activities involved in the preparation. Data available in literature is collected and segregated for the above categorization. This database is analyzed to study the effects of (i) raw material of adsorbent and (ii) adsorbent preparation methodology, based on the corresponding Freundlich isotherm constants.

Results indicated that, 75.2% of the database comprises of materials based on cheaply available AW and the adsorbents developed from AW are showing better results of adsorption than the other two categories viz., IW & MW. Physical Treatment (P) & Nominal Treatment (N) categories of adsorbent preparation account to 39.59% of the available database. The results obtained from Chemical-Thermal Treatment (CT) and Chemical Treatment (C) categories of adsorbent preparation are better than that of P & N categories. The Freundlich constants available for CAC are also compared.

Introduction

In wastewater treatment, effectiveness and cost of an adsorbent are important issues. A number of novel adsorbents are being investigated [1-3] in search of a low cost adsorbent as an alternative to Commercial Activated Carbon (CAC). Several methodologies [4] are being followed in the preparation of adsorbents from their raw materials.

Suitability of these adsorbents is usually based on their fitting to the Freundlich or Langmuir Isotherms. The experimental data is fitted to the regressed form of these two Isotherm equations and the constants are determined. Babu and Ramakrishna [5] found that there is a lot of inconsistency and a wide spread in the data pertaining to Freundlich Isotherm constants. It is important to know the reason behind the above inconsistency so as to make use of the literature data in analysis of adsorption as a process. Hence, there is a need for a systematic study on categorization and analysis of the adsorbent preparation.

Problem Formulation

In the present study, the data available in literature [8-34] is considered. The values of Freundlich constants for the novel adsorbents prepared from Agricultural Wastes (AW), Industrial Wastes (IW), & Mineral Wastes (MW) are collected. This database is analyzed to study the effects of (i) raw material of adsorbent and (ii) adsorbent preparation methodology, on the Freundlich constants.

The Freundlich constant, n indicates the degree of favorability of adsorption [6]. The n should have values lying in the range of 1 to 10 for classification as favorable adsorption [7, 8]. A smaller value of $(1/n)$ indicates a stronger bond between adsorbate and adsorbent [9], while a higher value for K_f indicates rate of adsorbate removal is high [9, 10].

Results and Discussion

The database is analyzed in the following order:

- Based on raw material of adsorbent.
- Based on adsorbent preparation methodology.
- Comparative studies with CAC.

The results for each of them are discussed as follows:

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Analysis based on raw material of adsorbent

The Raw Material Categorization Database (RMCD) is compiled with respect to the raw material of the adsorbent. The RMCD contains 75, 18, & 8 data points pertaining to AW, IW, and MW respectively. The available data pertaining to the two Freundlich constants viz., K_f and n are collected for the adsorbents prepared from these raw materials. The ranges of the values of the Freundlich constants for AW, IW, & MW categories in the database are given in Table-1.

The data given in Table-1 shows that, the investigators prefer AW based raw materials (74.25%) as novel adsorbents followed by IW based raw materials (17.82%). The available database is sorted based on n value below 1 and beyond 10. Results are given in Table-2.

Table-1: Range of values of Freundlich constants in RMCD

RMC	DP	Freundlich constants			
		K_f		n	
		Max.	*Min.*	*Max.*	*Min.*
AW	75	204.17	1.08×10^{-6}	25	0.013
IW	18	48.97	4×10^{-7}	7.16	0.102
MW	8	555.57	0.154	3.12	0.443

Table-2: Sorted RMCD based on n values

RMC	Freundlich constant, n			
	DP for n <1	% of total RMC DP	DP n >10	% of total RMC DP
AW	17	22.66	4	5.33
IW	3	16.66	0	0.00
MW	2	25.00	0	0.00

The segregated database after eliminating the data points below and beyond the above limits of n consists of 54, 15, & 6 data points pertaining to AW, IW, & MW categories respectively. The above segregated database is further sorted based on K_f values since a higher value for K_f indicates high rate of adsorbate removal [9, 10]. In order to compare the relative variation of the K_f values in these categories, frequency distribution of the K_f values is used and is given in Table-3.

Table-3: Frequency distribution of K_f values in sorted RMCD

Frequency Range	% of the frequency distribution		
	AW	IW	MW
> 100	5.55	0.00	0.00
50-100	14.82	0.00	0.00
30-50	11.11	20.00	0.00
20-30	5.55	6.66	0.00
10-20	29.63	0.00	0.00
1-10	27.78	20.00	0.00
<1	5.55	53.33	100.00

From Table-3, it is clearly evident that, adsorbents prepared from AW category are showing high K_f values compared to that of the other two categories. The adsorbents prepared from MW category are showing very low K_f values. From the above analysis, it is concluded that, the order of preference of raw material category for preparation of novel adsorbents with respect to the Freundlich isotherm constants is, **AW>IW>MW.**

Analysis based on adsorbent preparation methodology

The adsorbent preparation methodologies reported in literature are studied and in this analysis, they are categorized based on the predominant method of operation involved. The following categories are adopted in this analysis:

- Nominal Treatment (N)
- Physical Treatment (P)
- Chemical Treatment (C)
- Thermal Treatment (T)
- Physical-Chemical Treatment (PC)
- Chemical-Thermal Treatment (CT)
- Physical-Thermal Treatment (PT)

The detailed activities considered for categorization into above categories are given in Table-4.

Table-4: Categorization of adsorbent preparation methodologies

Treatment category	Activities considered
Nominal Treatment	Normal drying either at low temperature (<105^{0}C) or sun drying, grounding and sieving, washing with only distilled water.
Physical Treatment	Oven drying to 105^{0}C, washing with acid for removal of impurities.
Chemical Treatment	Acidification and impregnation of the sample.
Thermal Treatment	Thermal cracking of the sample at very high temperatures with or without activation.

The combinations listed (PC, CT, & PT) are simply combinations of the above listed activities of adsorbent preparation with significance in the same sequence of their abbreviations.

The available Adsorbent Preparation Methodologies Database (APMD) is segregated as per the above categories and the corresponding Freundlich constants are compiled. The APMD is divided into clusters based on the method of preparation and the corresponding K_f and n values. The adsorbent preparation methodologies fitted to this APMD are: N, P, C, & CT. The available data points are very less for T, PC, & PT categories to draw any observations and hence ignored. The details of the sorted APMD are given in Table-5. The database (given in Table-5) is sorted based on

n value viz., for $n < 1$ and $n > 10$. The details of the sorted database are given in Table-6.

Table-5: Range of values of Freundlich constants in APMD

Category	Data points	Freundlich constants			
		K_f		*n*	
		Max.	*Min.*	*Max.*	*Min.*
N	21	141.12	$4x10^{-7}$	7.155	0.102
P	19	555.57	0.094	4.85	0.443
C	35	63.09	$1.08x10^{-6}$	3.33	0.342
CT	26	550	0.187	25	0.13

Table-6: Sorted APMD based on *n* values

Category	Freundlich constant, *n*			
	DP for $n < 1$	% of APM DP	DP for $n > 10$	% of APM DP
N	4	19.05	Nil	--
P	10	52.63	Nil	--
C	7	20.00	Nil	--
CT	2	7.69	4	15.38

The database is further screened for high values of K_f. It is observed that, the C and CT categories are showing relatively high values of K_f values than that of N and P categories. The K_f values are compared in these categories using frequency distribution, which is given in Table-7.

Table-7: Frequency distribution of K_f values in sorted APMD

Frequency Range	% of the frequency distribution			
	N	P	C	CT
> 100	5.88	0.00	0.00	10.00
50-100	0.00	0.00	14.29	20.00
30-50	5.88	22.22	3.57	25.00
20-30	0.00	11.11	7.14	10.00
10-20	0.00	11.11	46.43	5.00
1-10	17.65	33.33	25.00	25.00
<1	70.58	22.22	3.57	5.00

The following observations are drawn from Table-7:

- The adsorbents prepared by N category are showing very low K_f values (70.58% of the database show values less than 1).
- The adsorbents prepared by P category are also showing low K_f values (22.22% of the database show values less than 1).
- The K_f values of N category are mostly lying (88.23%) in the range of less than 10.
- Majority of the K_f values (77.77%) for the adsorbents prepared by P category are lying in the range of less than 30.
- The percentage range of K_f values lying less than 10 is in the following order: N (88.23%), P (55.55%), C (28.57%), & CT (30.00%). It indicates that the rate of adsorbate removal is high in the adsorbents prepared by the C and CT categories compared to those from N and P categories.
- The percentage of the data points for which the K_f values lying in the range of 20-100 is higher for CT category (55%) than that for C category (25%), which is almost double. It indicates that the adsorbents prepared by the CT category are showing relatively higher adsorbate removal compared to that from C category.
- The adsorbents prepared from CT category are hence showing better values for Freundlich constants compared to that from N, P, & C categories.

The above observation of adsorbents prepared by CT category showing better results indicate that some sort of cracking and/or activation at high temperatures is essential for adsorbent to give satisfactory values of adsorption. This observation is consistent with that reported in literature [35, 36].

It is further noticed that, the entire database of CT and C comprises of AW category of adsorbents only. This indicates that the adsorbents developed from AW are showing better results of adsorption than the other two categories viz., IW & MW. This is consistent with the earlier observation that, adsorbents prepared from AW category are relatively better than that from IW and MW categories.

Comparative studies with CAC

Few Investigators [9, 13, 17, 19, 21, 28, 29] have used CAC for comparing their experimental results. The data pertaining to the Freundlich constants obtained using CAC is collected. Eleven data points are obtained with the following ranges for the Freundlich constants:

K_f: Max.: 727.05; Min.: $1.86x10^{-5}$.

n: Max.: 3.56; Min.: 0.588.

The CAC database is sorted for the upper and lower limits of *n* values as in the previous cases. Three data points are found to be less than one and the rest of the eight data points are found to be less than 10. The K_f values of this CAC database are sorted using frequency distribution with the same ranges studied above.

The adsorption studies using CAC are generally expected to give better results compared to the novel adsorbents due to the high surface area and systematic activation given to the material during its preparation. It is observed from the earlier analysis that, some sort of cracking and/or activation at high temperatures is essential for adsorbent to give satisfactory values of adsorption. It is also noted that adsorbents prepared by CT category are giving encouraging results with respect to K_f values. It is to be noted here that, the

adsorbents are given Chemical and Thermal treatment with or without activation in CT category. CAC is usually prepared [35, 37] by heating the raw material at high temperatures and activating it using inert gases such as Steam or N_2. Due to the similarity in adsorbent preparation approach (thermal treatment with/without activation), the frequency distribution of CAC and CT category are compared for studying the trends. The details are given in Table-8.

Table-8: Frequency distribution comparison for CAC and CT category databases

Frequency Range	% of the frequency distribution	
	CAC	CT
> 100	12.50	10.00
50-100	0.00	20.00
30-50	12.50	25.00
20-30	0.00	10.00
10-20	12.50	5.00
1-10	25.00	25.00
<1	37.50	5.00

It can be observed from Table-8 that, the results of CT database are relatively better than that of CAC. The range of K_f values less than 20 is relatively higher for CAC (75%) than that of CT (35%). It indicates that, the adsorbents prepared from CT category show higher adsorbate removal than that from CAC. The limitation however in this comparison is the size of the database. The CAC database is relatively smaller (only 8 data points) than that of CT category database (20 data points). It should be noted here that, the comparison that is being made is with respect to the parameter, which is identified as indicative of the effectiveness of the adsorbent.

The analysis of the above comparative study highlights the drawback of either not following or not adopting the standard procedure for preparing CAC. Babu and Ramakrishna [38] studied the characteristics of CAC and different novel adsorbents being reported in literature and compared with the available BIS codes. They strongly felt the need for prescribing a standard/common method for the preparation of CAC. The above analysis is strikingly in agreement with the suggestion of Babu and Ramakrishna [38].

The present study highlighted the following aspects:

- The focus of research in this subject (viz., adsorption studies) is on developing a low cost adsorbent. This is evident from the observation that 74.25% of the available RMCD comprises of materials based on cheaply available AW; and 18.82% & 20.79% (or 39.59% total) of the available AMPD comprises of P & N categories of adsorbent preparation respectively.
- The effectiveness of the adsorbent as determined by Freundlich Isotherm constants in this study shows that CT and C categories are better than P & N categories.
- The entire database of CT and C comprises of AW category of adsorbents only. This indicates that the adsorbents developed from AW are showing better results of adsorption than the other two categories viz., IW & MW.
- Cost of the adsorbents prepared from CT/C categories will be slightly higher than that of P & N categories. The exact cost aspects can be calculated by carrying a detailed Life Cycle Inventory Analysis on the adsorbent preparation.
- The cost of the adsorbent is not the only criterion in the wastewater treatment. Its effectiveness is also an important aspect to be seriously considered.

Conclusions

In wastewater treatment, effectiveness and cost of an adsorbent are important issues. Adsorbent efficiency depends on many aspects including the raw material of adsorbent and it preparation methodology. The literature data is collected pertaining to (i) raw material used for adsorbent preparation and (ii) adsorbent preparation methodologies. To rank the adsorbents, a database is developed based on the above aspects. The database is screened with respect to the Freundlich isotherm constants reported for the adsorbents. It is found that, the preference for raw material of adsorbent should be in the order of AW>IW>MW. The adsorbents prepared from AW are also observed to be giving encouraging results from the preparation methodology perspective. The adsorbents developed by Chemical-Thermal treatments are found to be giving encouraging results compared to the other methodologies that are being adopted.

Nomenclature

AMPD	Adsorbent Methodologies Preparation Database
AW	Agricultural Wastes
BIS	Bureau of Indian Standards
C	Chemical Treatment
CAC	Commercial Activated Carbon
CT	Chemical-Thermal Treatment
DP	Data Points
IW	Industrial Wastes
K_f	Freundlich constant
MW	Mineral Wastes
N	Nominal Treatment

n	Freundlich constant
P	Physical Treatment
PC	Physical-Chemical Treatment
PT	Physical-Thermal Treatment
RMC	Raw Material Category
RMCD	Raw Material Categorization Database
T	Thermal Treatment

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