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PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBON FROM WASTE MATERIAL

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ABSTRACT

A study of the adsorptive property of activated carbon prepared from used tyre, maize cob, coconut shell, guinea corn stem and orange peels is reported. Following carbonisation, the samples were activated at 500°C using orthophosphoric acid, zinc chloride and potassium hydroxide as activating agents. The adsorption capacity of the activated carbons was determined spectrophotometrically by contacting them separately with standard solutions of methylene blue, methyl red and potassium permanganate. The adsorption data were fitted to the Langmuir adsorption isotherm using least-squares linear regression analysis technique. The monolayer coverage (X_m) and specific surface area (S) of each sample was determined from Langmuir adsorption isotherms.

The samples of activated carbon obtained from coconut shell and used tyre compare favourably with commercial activated carbon in terms of adsorption capacity, percent of solute adsorbed and specific surface area. However the samples obtained from maize cob, guinea corn stem and orange peels were inferior to the commercial activated carbon. The various factors that affect the adsorption capacity of activated carbon and the percent solute adsorbed from solution are discussed.

INTRODUCTION

Activated carbon is a product of carbonisation and activation of carbonaceous materials. These processes result in production of large surface area, and provide the carbon with the ability to adsorb gases and vapours from gases or dissolved and dispersed substances from liquids. The adsorptive property lends the carbon to a wide range of applications [1]. The demand for activated carbon is increasing partly due to its use in industries in solution purification and solvent reclamation, and in research laboratories as decolourising agents and catalyst support. Yet activated carbon is not readily available locally and the quantity consumed in Nigeria is largely imported [1,2].

The need for production of activated carbon from locally available raw materials is evident and several research efforts are geared towards this[2-9]. In one study activated carbons produced from Nigerian subbituminous coal, palm kernel and cow bone were characterized by absorbance measurement of decolourised potassium permanganate ($KMnO_4$) solution [2] The specific surface areas of the activated carbons were determined by adsorption of paranitrophenol. In another study activated carbon produced from palm kernel shell was found to be effective in removal of colour from an effluent[3]. Mkayula and Matumbo produced activated carbon from different agrowastes using both physical and chemical activation methods. The activated carbons were characterized using both iodine and methylene blue number. The B.E.T specific surface area of the carbons were determined from Nitrogen physical adsorption data at 77.4K[4]. In another study, Adediran and Nwosu determined the Freundlich adsorption parameters of activated carbons produced from local materials including used tyres, unripe plantain peel, cow hair and hoof [5].

The purpose of this study is to produce activated carbon from cheap and abundant local raw materials and to characterize same. The waste materials include coconut shell, used tyre, maize cob, guinea corn stem and orange peels. Chemical activation method was employed and the samples obtained were characterized by observing their ability to decolourise standard solutions of methylene blue, methyl red and potassium permanganate. The surface area of each sample was determined from Langmuir adsorption isotherm data[6].

EXPERIMENTAL

Carbonisation and chemical activation:

Carbonisation was carried out in a specially constructed burning chamber which allows limited air supply. Each sample weighing 100 g was first dried in the oven at 100°C for one hour. The sample was

then introduced into the burning chamber for charring. The charred product was allowed to cool down to room temperature, ground to a workable size with a mortar and pestle and screened to obtain samples of four different particle size ranges (i.e. 0.112-0,125 mm, 0.125-0.25 mm, 0.25-0.5 mm and 0.5-0.8 mm). The next step involved purification of the sample in 0.5M hydrochloric acid solution followed by rinsing with distilled water to remove the excess acid. The sample was then dried in the oven at 100°C for one hour [6,13].

Activation of samples was carried out in a muffle furnace using orthophosphoric acid (H_3PO_4); potassium hydroxide (KOH), and zinc chloride ($ZnCl_2$) separately as activating reagents. A carefully weighed 25.0 g sample was put in a beaker containing 500 cm^3 of 1.0 M solution of activating reagent. The content of the beaker was thoroughly mixed and heated until it formed a paste. The paste was then transferred to a crucible, the crucible was placed in the furnace, and the furnace was fired at 500°C for two to three hours. After allowing the activated sample to cool down to room temperature, it was washed with distilled water and then dried in the oven at 100°C for several hours. The final product was kept in an air-tight vial ready for use[13].

Characterization of samples

Ash content and percentage fixed carbon:

The carbon content was determined by igniting a carefully weighed 2.0 g sample of the activated carbon in a Bunsen burner flame and cooling in a desiccator. The crucible with its content was then heated in a muffle furnace at 900°C for three hours. It was allowed to cool down to room temperature and weighed. The cycle of heating in the furnace, cooling and weighing was repeated several times[5,13]. The percent fixed carbon was deduced from the ash content following literature method[2,9].

Adsorption Experiments:

Adsorption experiments were carried out by contacting coloured standard solutions with known amounts of activated carbon and measuring the absorbance of the solutions at previously determined wavelength of maximum absorbance (λ_m) for the solution. This afforded the determination of the quantity of solute removed from the solution[2]. In a typical experiment, 0.1 g of activated carbon was weighed carefully and added to 100 cm^3 of solution containing 100 mg/dm^3 of solute (that is, methylene blue, methyl red or potassium permanganate) in a stoppered conical flask. The mixture was shaken vigorously on a mechanical shaker for one hour. The mixture was then filtered and the absorbance of the filtrate measured at the predetermined wavelength, λ_{max} (630 nm, 535 nm and 605 nm for methylene blue, methyl red and potassium permanganate solutions respectively) using the Spectronic 20 spectrophotometer. This procedure was followed for each particle size range of each activated carbon sample and for each of the coloured solutions. The Langmuir adsorption isotherm data were obtained as follows: Different quantities (between 100 mg and 1000 mg) of activated carbon of the same particle size range were each contacted with 100 cm^3 of coloured solution (e.g methylene blue) containing 250 mg/dm^3 in a stoppered flask. The flask with its content was placed on a mechanical shaker for continuous vigorous shaking for one hour. The mixture was then filtered as described earlier, to afford determination of the residual concentration of the filtrate after adsorption [6,7,13].

All relevant experimental data were collected also for a sample of commercial activated carbon (May & Baker) in powder form following the above procedure.

Treatment of data:

For each activated carbon sample the adsorption capacity (i.e. the amount of solute adsorbed per gram of the adsorbent) was calculated from the absorbance data under different experimental conditions. The percentage of different solute adsorbed by the activated carbon samples from the coloured solutions were also calculated. The linearised form of the Langmuir isotherm equation is given by [11-13]

$$\frac{1}{X} = \frac{1}{X_m K}\cdot\frac{1}{C} + \frac{1}{X_m}$$

where X = amount of solute adsorbed per unit mass of adsorbent,

X_m = limiting amount of solute (adsorbate) adsorbed per unit mass of adsorbent (i.e monolayer capacity)

K = a constant, and

C = concentration of the solute in the solution that is in equilibrium with the adsorbent.

A least-square linear regression analysis of the experimental data was carried out, and the experimental data were fitted to the Langmuir isotherm to obtain a linear graph from which the monolayer coverage, X_m was determined [1,3]. The specific surface area, S, of each sample was also calculated from the value of X_m by using the equation [6,7,13]:

$$S = X_m \times N \times a$$

where N = Avogadro 's constant (6.02×10^{23} mol^{-1}),

a = the area of the adsorbate molecule (for methylene blue, a = 120 A [2,7,13]).

RESULTS AND DISCUSSION

The percentage yield of carbonised product, percent ash and percent fixed carbon are presented in table 1 for all the activated carbon samples prepared. Used tyre gave the highest yield of carbonised product while orange peels gave the lowest. The results for all the samples fall within the range of published data [4,5]. The values of percent ash and percent fixed carbon for activated carbon prepared from coconut shell (samples CSP, CSZ and CSK) agree with those for the commercial activated carbon (CAC). Again, samples from orange peels (OPP, OPZ and OPK) have the lowest percent fixed carbon and the highest ash content. A correlation has been shown to exist between percent fixed carbon and adsorption capacity. Samples with high adsorption capacities are found to have high percentage fixed carbon [2].

The adsoption capacities and the percent solute adsorbed by the samples in methylene blue, methyl red and potassium permanganate solutions are given in tables 2 and 3. The data in table 2 are presented as bar charts in figures 1, 2 and 3 for adsorption from solutions of methylene blue, methyl red and potassium permanganate respectively. The data show that the factors which may influence the magnitude of the adsorption capacity of activated carbon include

a. the raw material from which the carbon is prepared,

b. the activating reagent used, and

c. the nature of the solute material being adsorbed (i.e the adsorbate or dye solution).

Activated carbons prepared from coconut shell (CSP, CSZ and CSK) and used tyre (UTP, UTZ and UTK) have adsorption capacities that are comparable with that of the commercial activated carbon (CAC) in all the three dye solutions. On the other hand, activated carbons from maize cob (MCP, MCZ and MCK), guinea corn stem (GCP, GCZ and GCK) and orange peels (OPP, OPZ and OPK) consistently have lower values (Table 2, Figs. 1- 3). The reason for this trend may be found in the percent fixed carbon content of the samples[2, 4, 14].

For all the samples studied and the three activating reagents used orthopliosphoric acid appears as the most effective in activating the samples (Tables 2 & 3, Figs. 1-3). All the samples activated with orthophosphoric acid have higher adsorption capacities than similar samples activated with either zinc chlo-

TABLE 1: Percent ash and percent fixed carbon of activated carbon

Raw Material	Activating agent	Abbreviation for Activated carbon sample	Percentage yield of carbonised product	Percentage ash ±0.01	Percentage fixed carbon ±0.01
Used tyre	H_3PO_4	UTP	40.79	6.74	93.26
Used tyre	$ZnCl_2$	UTZ	40.79	6.84	93.16
Used tyre	KOH	UTK	40.79	6.08	93.92
Maize cob	H_3PO_4	MCP	30.50	25.22	74.78
Maize cob	$ZnCl_2$	MCZ	30.50	25.36	74.64
Maize cob	KOH	MCK	30.50	25.44	74.56
Coconut shell	H_3PO_4	CSP	33.69	11.60	88.40
Coconut shell	$ZnCl_2$	CSZ	33.69	11.40	88.46
Coconut shell	KOH	CSK	33.69	11.48	88.52
Guinea corn stem	H_3PO_4	GCP	23.30	32.70	67.30
Guinea corn stem	$ZnCl_2$	GCZ	23.30	31.16	68.84
Guinea corn stem	KOH	GCK	23.30	33.01	66.99
Orange peels	H_3PO_4	OPP	25.11	43.45	56.55
Orange peels	$ZnCl_2$	OPZ	25.11	43.43	56.57
Orange peels	KOH	OPK	25.11	43.48	56.52
Commercial activated carbon		CAC		11.69	88.31

TABLE 2: The adsorption capacities of activated carbon

Sample	Quantity of solute adsorbed (mg)		
	Methylene Blue solution (MB)	Methyl Red solution (MR)	Potassium Permanganate solution (PP)
UTP	6.8	5.10	3.6
UTZ	6.6	4.55	2.7
UTK	6.7	4.80	3.1
MCP	5.6	4.20	2.1
MCZ	5.2	4.00	1.5
MCK	5.0	3.40	1.2
CSP	7.6	5.70	4.8
CSZ	6.0	4.50	2.6
CSK	6.8	5.25	4.4
GCP	5.1	3.60	1.3
GCZ	4.9	3.30	1.2
GCK	4.0	3.10	1.0
OPP	3.2	2.80	0.8
OPZ	2.2	2.20	0.4
OPK	2.8	2.50	0.7
CAC	7.0	5.50	4.6

TABLE 3; Percentage of different solute adsorbed from their solutions

Sample	Quantity of solute adsorbed (mg)		
	Methylene Blue solution (MB)	Methyl Red solution (MR)	Potassium Permanganate solution (PP
UTP	68.0	51.0	36.0
UTZ	66.0	45.5	27.0
UTK	67.0	48.0	31.0
MCP	56.0	42.0	21.0
MCZ	52.0	40.0	15.0
MCK	50.0	34.0	12.0
CSP	76.0	57.0	48.0
CSZ	60.0	45.0	26.0
CSK	68.0	52.5	44.0
GCP	51.0	36.0	13.0
GCZ	49.0	33.0	12.0
GCK	40.0	31.0	10.0
OPP	32.0	28.0	8.0
OPZ	22.0	22.0	4.0
OPK	28.0	25.0	7.0
CAC	70.0	55.0	46.0

TABLE 4: Adsorption isotherm experimental data for CSK sample in methylene blue (MB) solution

Mass of activated carbon	[MB] after adsorption C x 10 (mg/dm³)	Final mass of MB after adsorption x 10 mg	Mass of MB adsorbed x 10 mg	Mass of MB per unit mass of activated carbon	1/X	1/C x 10¹ dm³/mg
10	4.00	0.400	2.100	0.210	4.8	0.25
15	2.10	0.210	2.290	0.150	6.6	0.48
25	1.00	0.100	2.400	0.090	11.1	1.0
35	0.80	0.080	2.420	0.069	14.5	1.25
45	0.60	0.060	2.440	0.054	18.5	1.70
50	0.55	0.055	2.445	0.049	20.4	1.80
70	0.36	0.036	2.464	0.035	28.4	2.80
100	0.25	0.025	2.475	0.025	40.5	4.00

TABLE 5: Langmuir constant X_m and specific surface are data for samples of activated carbon

Sample	Langmuir constant, X_m x $(355.9)^{-1}$ mole g^{-1}	Specific surface area, S (m^2g^{-1})
UTP	0.442	899
UTZ	0.392	796
UTK	0.439	891
MCP	0.325	659
MCZ	0.276	561
MCK	0.244	495
CSP	0.455	923
CSZ	0.412	836
CSK	0.444	903
GCP	0.256	519
GCZ	0.251	509
GCK	0.199	404
OPP	0.174	353
OPZ	0.155	315
OPK	0.163	330
CAC	0.446	907

ride or potassium hydroxide. The trend is the same in all the three dye solutions investigated. The reason for this is not immediately obvious, but may be partly due to the fact that orthophosphoric acid is both a strong acid and an oxidising agent. Thus, it may be able to open up and enlarge pores in the carbonised samples better than either potassium hydroxide or zinc chloride.

The effect of the nature of the dye (solute material) on the adsorption capacities of activated carbon and percent solute adsorbed can be seen clearly by comparing data in columns 2, 3 and 4 of tables 2 and 3. The data show that for all the samples both the adsorption capacity and percent solute adsorbed decreased in the order:

Methylene blue > methyl red > potassium permanganate.

This shows that activated carbon (adsorbent) ha greater affinity for methylene blue adsorption tha either methyl red or potassium permangana (adsorbates). This has been suggested to be due to th fact that activated carbon being an organic adsorbe adsorbs organic substances more readily than it ac sorbs electrolytes from solution[1,8]. The report o Schulinger and Erskine also agree with this[15]. Thu methylene blue ($C_{16}H_{18}N_3SCl.2H_2O$), a cationic o ganic dye stuff[10], and methyl red ($C_{15}H_{15}N_3O$ also an organic dye stuff, are expected to be bett adsorbed by activated carbon than potassium pe manganate (an inorganic compound), as shown b our results. As to the greater adsorption of methyler blue than methyl red by activated carbon, it has bee

shown that activated charcoal adsorbs more of organic dyes in aqueous solution than when dissolved in ethanol[16]. This has been explained as being due to the relative polarity of ethanol and water. In our study methyl red was dissolved in ethanol because it is not soluble in water while methylene blue was dissolved in water[13].

The data in table 4 and figure 4 are for the adsorption isotherm of activated carbon (derived from coconut shell and using potassium hydroxide as activating agent) in methylene blue solution. The linear plot, which is representative of the results for the other samples, shows that the adsorption isotherm is in agreement with the Langmuir adsorption isotherm. The Langmuir constant (X_m) and the specific surface area(S) determined from the isotherms are summarised in table 5 for all the samples. The data in Table 5 show that activated carbons derived from used tyre and coconut shell compare favourably with commercial activated carbon in specific surface area. By comparison, the activated carbons prepared from maize cob, guinea corn stem and orange peels have lower specific surface areas compared with the commercial activated carbon. Comparison of the data in table 5 with those in tables 2 and 3 shows that our results confirm the expected correlation between specific surface area of adsorbent and the adsorption capacity. The larger the surface area the larger the quantity of solute adsorbed[1-5].

The specific surface areas reported for our samples in this study are in the same range with those reported by Mkayula and Matumbo for activated carbons prepared from similar and related raw materials [4]. Moreover, the surface areas of our samples are in close agreement with the mean specific surface area of 708 m^2g^{-1} of activated charcoal distributed by Fisher Scientific Company and the American Norit Commercial samples with specific surface area of between 600 -1000 m^2g^{-1}[6].

Our results show that activated carbon produced from coconut shell, used tyre and maize cob can serve as useful alternatives to the imported commercial activated carbon. Orthophosphoric acid was found to be the best activating agent in our study. However, in view of its high cost, there is the need to do further investigation to identify other chemical reagents, especially wastes from chemical industry, which can be used as activating agents. This may result in savings of scarce foreign exchange.

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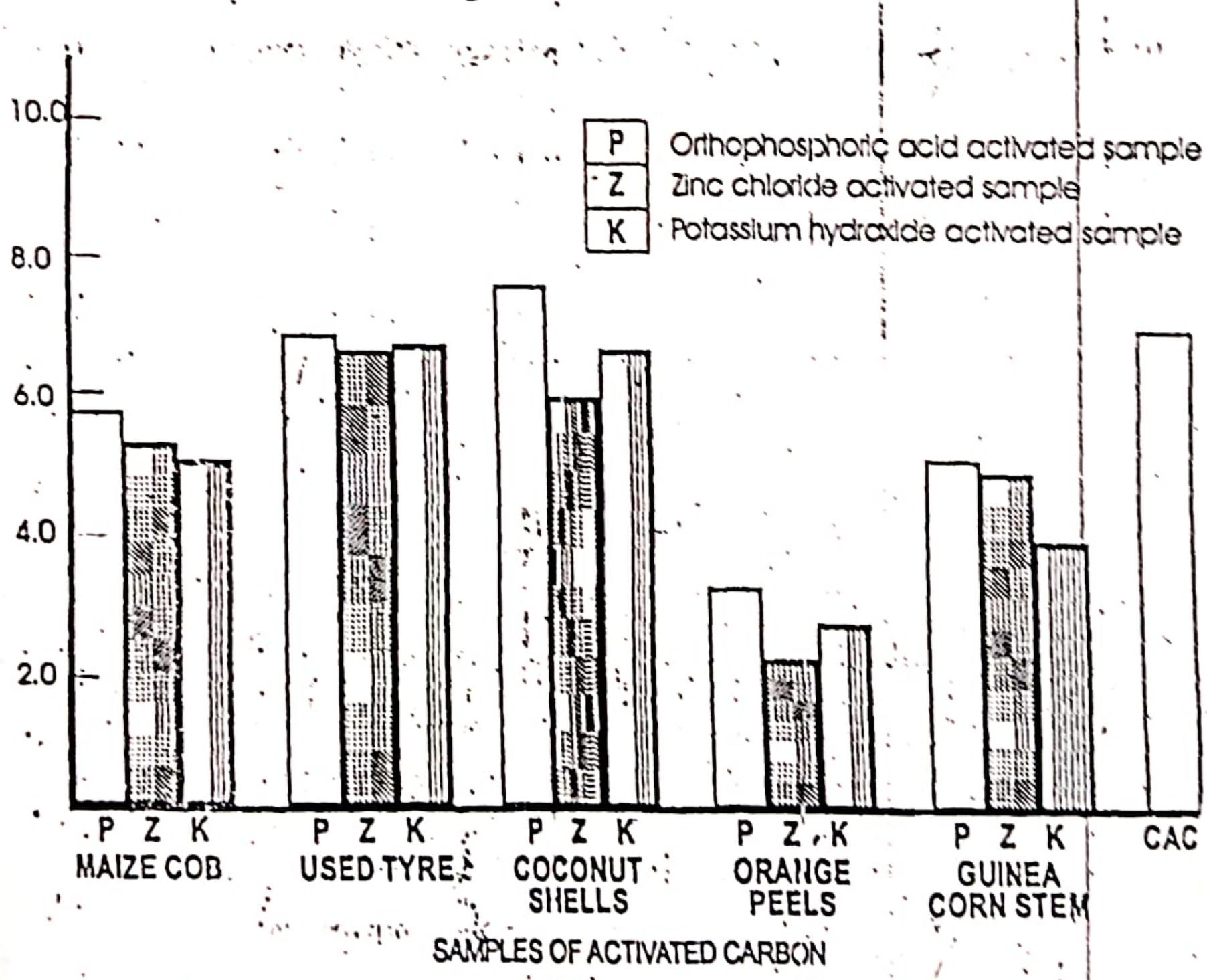


Fig. 1: Adsorption capacity of activated carbon based on decolourisation of methylene blue solution.

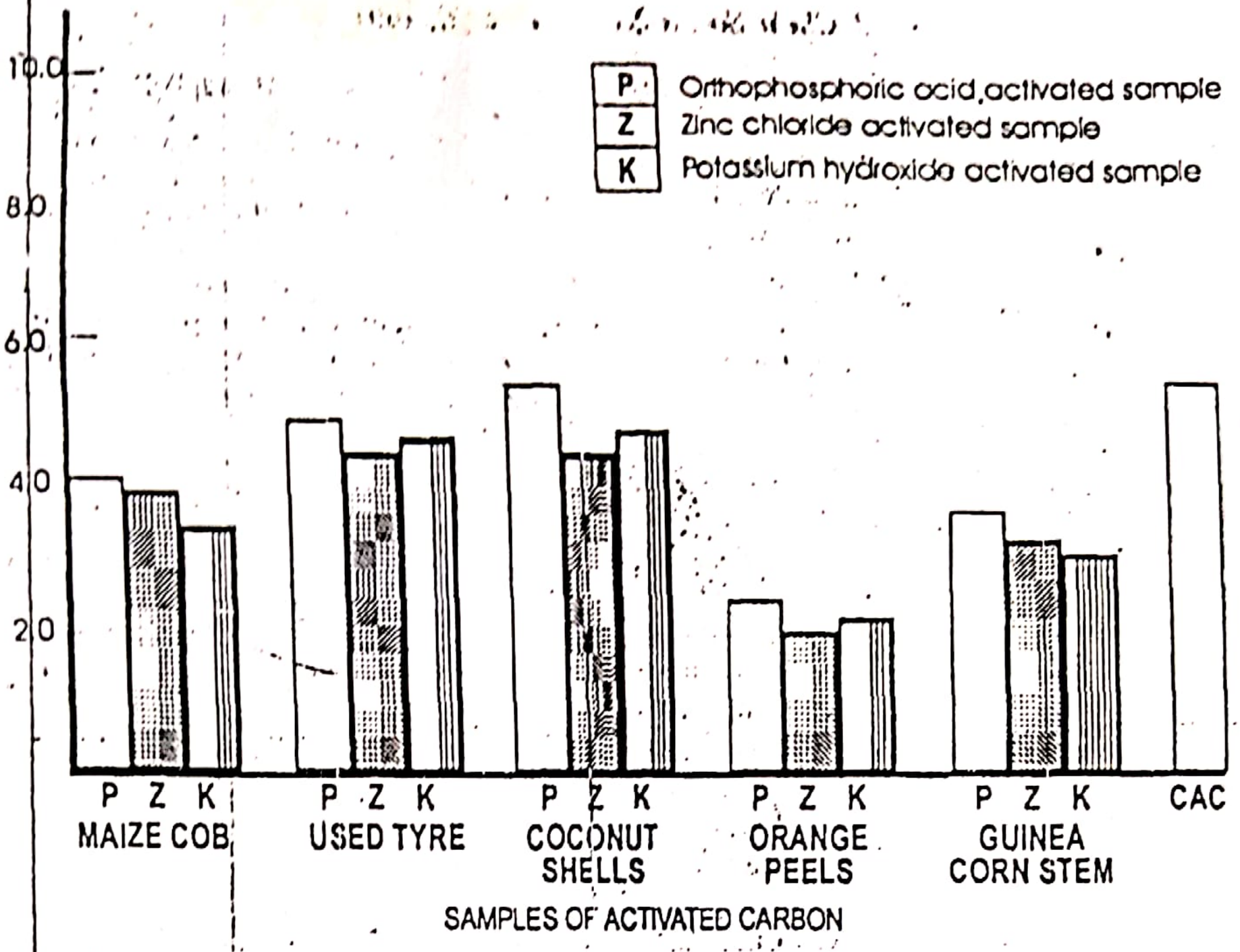


Fig. 2: Adsorption capacity of activated carbon based on decolourisation of methyl red solution.

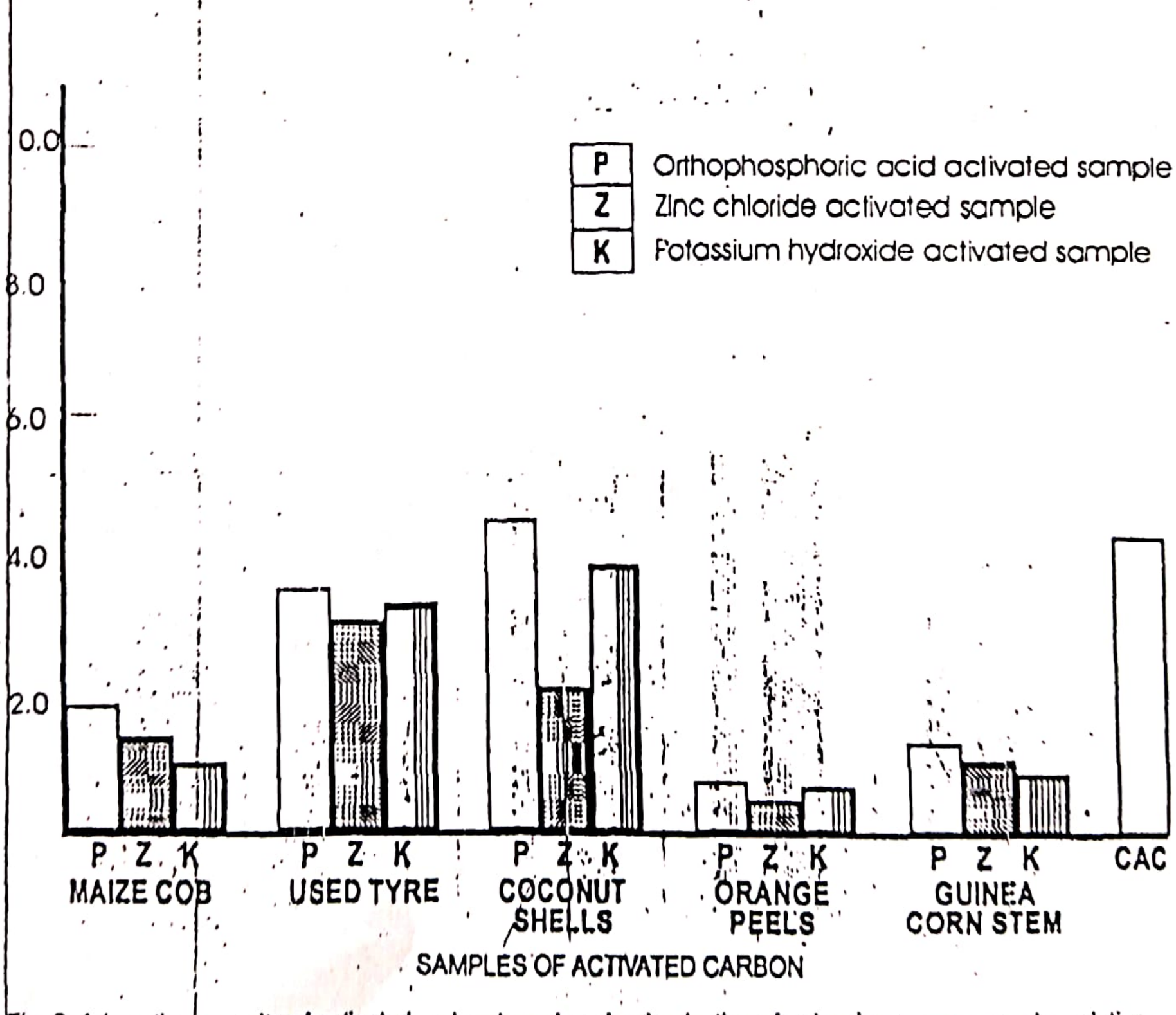


Fig. 3: Adsorption capacity of activated carbon based on decolourisation of potassium permanganate solution.

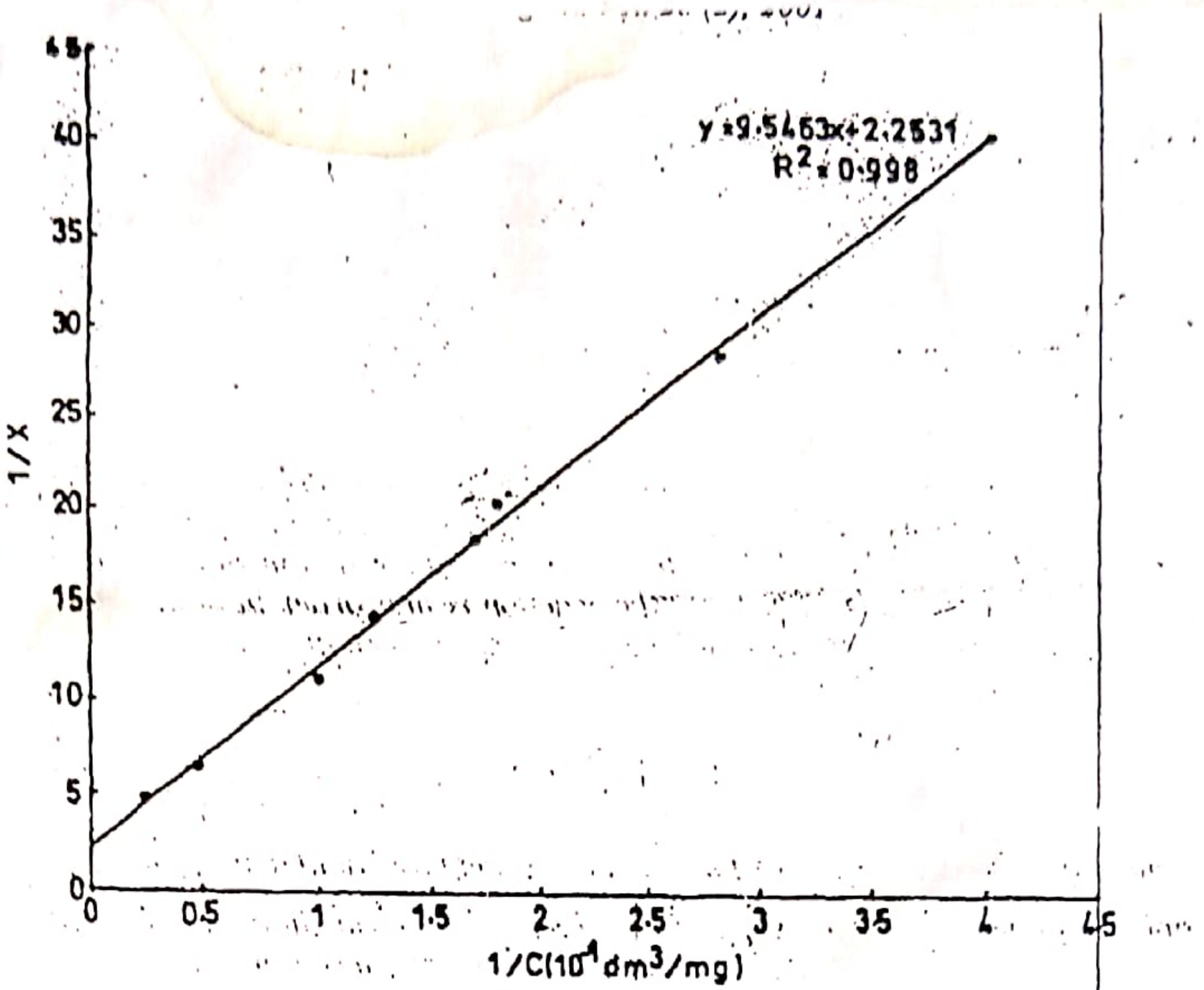


Fig. 10: Langmuir adsorption isotherm of CSK in methylene blue solution.

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