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UTILIZATION OF MARBLE POWDER AND THE CLAY (GACCI MUTTI) AS THIN LAYER CHROMATOGRAPHY ADSORBENT

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Mixed marble powder and clay (Gacci Mutti) (19:1) was found satisfactory for separation of selected types of organic compounds. This was used as such without any treatment. Water was selected as the slurry liquid, about 10 ml water was sufficient for 20g mixed marble powder and Gacci Mutti. Ink pigments were sepearated by using solvent system, (i) ethanol, ammonia and water (8:1:1), (ii) n- butanol, ethanol, ammonia (2N) and water (6 :2:2:1). The separated ink spots on Marble powder and Gachi Mutti were clear, bright and consistent as compared with that on silica gel. 2,4-dinitrophenylhydrazones were separated in solvent system, (i) petrol fraction boiling range 40 - 120° and ether (39:10), (ii) petrol fraction boiling range 40 - 60° and ether (15:4:5). Due to inertness petrol fraction boiling range 40 - 60° is selected as separating solvent for 2,4- dinitrophenylhydrazones. The separation of amino acids were carried out by using the solvent system: ethanol, ammonia and water (8:1:1). The separated spots on silica gel faded rapidly on exposer to light while on marble powder and Gacci Mutti these were compact and unchanged for several months.

Key words: T.L.C adsorbent, Petrol distillate organic compound.

Introduction

Chromatography is the name given to a particular family of separation techniques. The original method was described by Tswett [1], who used it for the sepration of coloured substances and the name chromatography stems from this. However, the limitation to coloured compunds no longer obtains and most chromotographic separation are now-a-days performed on mixtures of colourless substances including gases. There are various kinds of chromatographic techniques such as (1) column chromatography [2] (2) paper chromatography [3] (3) electrophoresis [4] (4) gas chromatography and (5) thin-layer chromatography.

Thin-layer chromatography (T.L.C.) was first studied by Stahl [3]. This method has found application in the study of compound including terpenes, organic per-oxide, alkaloids, steroids, 2,4- dinitrophenylhydrazone, amino acids, inks and inorganic analysis. The most commonly used adsorbent in T.L.C. are silica gel, [5], alumina [6], kisselguhr [7], powdered cellulose [8], magnesium carbonate [9] and calcium carbonate [10].

Some of these adsorbent such as silica gel, alumina and magnesium sulphate are used in laboratories. These adsorbents are mostly imported from abroad. The quoted cost of silica gel is Rs. 450/Kg, alumina Rs. 460/Kg and magnesium sulphate Rs. 250/Kg. In order to save foreign exchange, there was a need to study such adsorbents which were cheaper and locally available. It appeared from the constituents of marble and clay (Gacci Mutti) that these materials could be used as adsorbents. Marble and clay are available in the domestic market and can be purchased at a price of Rs. 2/kg.

Similarly petroleum ether of various grades (b.p. 40-60, 60-80, 80-100°) finds wide use in chromatography. In the present work it is aimed to fractionally distilled the petrol and finds it usefulness for chromatography purpose.

Experimental

Sampling. Marble powder was purchased from Jamrud Gem Stone Factory, Peshawar. Marble is supplied to the factory from Dugger and Malagory in NWFP. Marble powder (180 mesh) used for the present work was from Malagory. Clay (Gacci Mutti) was purchased from the market in the form of lump, ground to fine powder, unless it passes through 180 mesh sieve. it was used as such without further treatment.

Preparation of thin layer plates. Marble powder and Gacci Mutti of particle size 180 mesh were mixed in the ratio 19:1 for 15 mins with water (10ml) in a morter with a pestle to obtain a slurry. A thin layer of slurry (0.25mm) was spread out on glass plate (5x10 cm) and dried at room temperature. That thin layer plate was activated in an oven at 110-120° for 20 mins. The sample was spotted on plate with help of capilllary tube. The solvent of the spotted sample was evaporated and the plate was developed in the developing solvent system. The various samples separated are: (1) ink pigments (2) 2,4-dinitrophenylhydrazones and (3) amino acids.

Result and Discussions

Gacci Mutti. It is a group of clay, the definition of which varies with different fields. Clay [11] as by geologist, is a size term refer to sedimentary rock particles of mechanical deposition having a diameter of 1/256 mm or smaller. Clay minerals are commonly platy in shape and one of its properties is as adsorbent in T.L.C.

Marble powder. Marble is a crystalline limestone which has granular structure. Its major constitutents are calcium carbonate and magnesium carbonate.

Consistent good results were obtained with thin layer of mixde Marble powder and Gacci Mutti. Slurry with water produced smooth surface so it was selected as slurry liquid. The selected activation temperature for thin-layer plate was of the order of 100-150°.

Separation of commercial inks. Ink is a mixture of colouring matter dispersed in a vehicle [13] or carrier, which form a fluid or paste which can be printed on a substrate and dried. The vehicle of the spotted ink on this layer plate was evaporated because in the presence of it the spot diffused when developed in solvent system. Studying various developing solvents it was found that an entirely non polar solvent (e.g. petrol distillate of different boiling range) had no effect on inks and that a system of polar solvent (mixed ethanol, ammonia and water) is necessary for a good separation of inks. Ink pigments (black, blue and red) were easily separated on silica gel by using solvent system containing ethanol, glacial acetic acid and water but that system destroyed thin-layer plate of Marble powder and Gacci Mutti. Water gave good separation but the pigment spots moved with solvent front. So it was necessary to use a mixture of solvent systmes contianing (i) ethanol, ammonia and water (ii) ethanol, butanol, ammonia (2N) and water.

The separated ink spots which were clear and bright at the end of development period remained unchanged during light and air exposition for several months. By comparing the R_f value (Tables 1, 2), separated on Marble powder and Gacci Mutti with that of silica gel indicates the effectiveness of the new adsorbent.

Separation of 2,4-dinitrophenylhydrazones. 2,4- Dinitrophenylhydrazones were prepared [14] from hydrazine, by reacting with acetone and benzaldehyde. 2,4-Dinitrophenylhydrazones were separated on the plates using various solvents. The petrol distillate fractions (boiling range 40-120, 40-60°) were found excellent developing solvent for the spotted plates. But petrol distillate having boiling range 40- 120° changed the colour of 2,4-dinitrophenylhydrazone on the plate while the fraction 40 - 60° had no effect on it. So the last fraction was selected as developing solvent for 2,4- dinitrophenylhydrazones (Table 3).

Separation of amino acid. Selected amino acids. glycine, L- cystine, β-alanine, α-amino butaric acids and α-alanine

TABLE 1. R_f VALUES OF INKS ON MARBLE POWDER AND GACCI MUTTI SOLVENT; ETHANOL-AMMONIA-WATER (1) (8:1:1), (III) (8:1:1) FOR I HR 45 MINS.

Inks		Components			
		a	b	c	d
Black	(i)	0.854	0.837	0.743	0.683
	(ii)	0.908	0.875	0.815	0.683
Blue	(i)	0.877	0.829	0.743	0.683
	(ii)	0.916	0.866	0.750	0.683
Red	(i)	0.871	0.828	-	-
	(ii)	0.891	0.866	-	-

Activated at 109° for 15 min.

TABLE 2. R_f VALUES OF INKS ON (I) MARBLE POWDER AND GACCI MUTTI (II) SILICA GEL UNDER THE SAME CONDITION. SOLVENT SYSTME: N-BUTENOL-AMMONIA-WATER (6: 2: 2: v/v).

Adsorbents	Inks	Components			
		a	b	c	d
Marble &	Black	0.90	0.811	0.34	
gacci mutti	Red	0.93	0.81	0.34	0.85
Silica gel	Black	0.58	0.56	0.509	
	Red	0.43	0.41	0.38	

Activated at 120° for 20 min.

TABLE 3. R_f VALUES OF 2,4-DINITROPHENYLHYDRAZONES ON MARBLE POWDER AND GACCI MUTTI IN SOLVENTS (I) PETROL FRACTION (40-120) ETHER (39-10 v/v), (I) PETROL FRACTION (40-60)-ETHER (15:4.5 v/v). (I) FOR 1 HR. 17 MIN (II) FOR 12 MIN.

2,4-Dinitrophenyl hydrazone of		Components	
		a	b
Benzaldehyde	(i)	0.87	
Acetone	(i)	0.97	
Mixed acetone & benzaldehyde	(i)	0.97	0.87
	(ii)	0.62	0.55

(i) Activated at 120° for 20 min. (ii) Activated at 109° for 20 min.

TABLE 4. R_f VALUES OF AMINO ACIDS SEPARATED ON (I) MARBLE POWDER AND GACCI MUTTI (II) SILICA GEL IN SOLVENT SYSTME; ETHANOL-AMMONIA WATER (6: 1: 1 v/v) FOR 2 HRS. 7 MIN. .

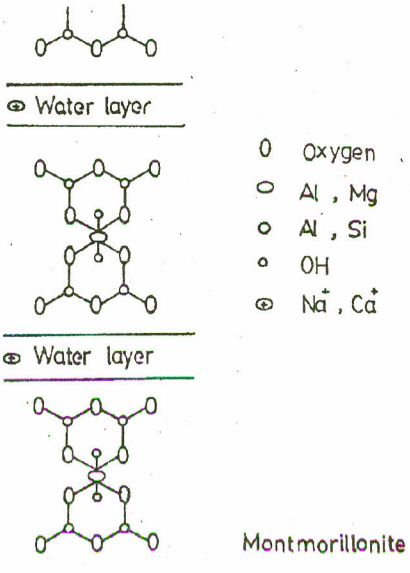
Amino acids		Components		
		a	b	c
1. Glycine	(i)	0.21		
	(ii)	0.68		
2. DL - α - amino	(i)	0.29		
N-butyric acid	(ii)	0.90		
3. DL - α - alanine	(i)	0.39		
	(ii)	0.72		
4. Mixed 1,2,3	(i)	0.39	0.29	0.20
	(ii)	0.74	0.88	0.63

Activated at 120° for 20 min.

were separated on activated plates using various solvent. Ethanol, ammonia and water (8:1:1) mixture was selected as the developing solvent system. The rate of flow of amino acids (Table 4) on thin layer of marble powder and Gacci Mutti was very slow and the separated spots were very close to each other. But these were compact and remain unchanged to air and light exposition for several months. While that separated on silica gel under the same condition faded rapidly (after 15 mins) on exposer to air and light.

Conclusion

We concluded from the properties of the clay (i.e. an acidic solvent destroy the thin layer) that Gacci Mutti is closely ralated to the mineral composition and structure of montmorillonite which has been used as adsorbent in column chromatography.



Ion exchange properties in montmorillonite [1] are compensated by cations K^+,Ca^+,Na^+) sorbed between the three layers clay mineral sandwich (I). These ions are relatively lose although stochiometrically held and give rise to major cation exchange properties of the montmorillonite. The acidic solvent destroyed the thin layer of marble powder and Gacci Mutti because H^+ ion leached away the base from the clay.

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