# STUDIES ON ACTIVE CARBON

# Part II. Ionic Adsorption by Active Carbon

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### Adsorption of Strong Electrolytes

The phenomenon of the adsorption of strong electrolytes by solid adsorbents, such as the zeolites, kaolin, fullers-earth and charcoal, is attended by a number of striking peculiarities. These cannot be explained by the usual consideration of Gibb's adsorption-formula or of a thick compressed layer. It has been found necessary to incorporate postulates of electrical or ionic adsorption in developing a theory for electrolyte-adsorption.

Cases of ionic adsorption are common. The adsorption of constituent ions by freshly formed precipitates (*e.g.*, the adsorption of chloride ions by silver chloride) has been observed in analytical work. Similarly, we have the adsorption of potassium chloride, potassium sulphate, sulphuric acid, hydrochloric acid and acidic and basic dyes on a variety of adsorbents, like silicic acid, fullers-earth, kaolin, active charcoal, fibres, filter-paper, quartz, glass, etc.

As in the case of non-electrolytes the adsorption-isothermal equation of Freundlich is valid for electrolytes over a limited range but the slope of the isothermal is smaller in the case of electrolytes. The most striking difference between the adsorption of electrolytes and that of non-electrolytes is that in most cases the former is "non-equivalent". That is to say, anions and cations are taken up not in equivalent amounts, but more of one and less of the other is adsorbed. Indeed, in some cases there is almost quantitative adsorption of one of the ions and none of the other, as in the adsorption of methylene blue by kaolin where the chloride ions are left behind wholly unadsorbed in the decolorised solution.

This preferential adsorption of one of the component ions of an electrolyte gave rise to speculation as to the state of its partner ion which is left behind in the solution. To explain this, it was

suggested that the unadsorbed ion was neutralised by a H<sup>-</sup>- or OH'ion resulting from a hydrolytic decomposition of water. Such fission adsorption, however, occurs only rarely (if at all), as was shown later by Michaelis and Rona (Biochem. Z., 1919, 97, 57) and by Freundlich and Neumann (Z. physikal. Chem., 1909, 67, 538). These authors found that in almost all cases an exchange adsorption takes place; that is, the ion that is adsorbed sets free from the surface of the adsorbent another ion of the same sign, thereby maintaining the ionic equilibrium in the solution. It is obvious that this would happen when the adsorbent is either an electrolyte by itself or contains electrolytes as impurities. For example, in the case of the adsorption of a cation by kaolin, the calcium ion of the latter goes into solution in exchange for the cation adsorbed. Thus, as Michaelis and Rona (Biochem. Z., 1920, 102, 268) have pointed out. adsorption from solution can be either polar or apolar, or both. As instances of "apolar adsorption", the adsorption of non-electrolytes and of weak electrolytes by various substances may be quoted. The term "polar adsorption", on the other hand, covers the adsorption of polar molecules by polar adsorbents. It includes, therefore, the adsorption of acid substances by basic adsorbents and vice versa, and also exchange adsorption, as in the case of adsorption by zeolites. Hydrolytic adsorption where, as in the adsorption of methylene blue by charcoal, hydrolysis of the adsorbate takes place in solution, is also a case of polar adsorption. It is to be noted that in polar adsorption both the adsorbent and the adsorbed substance are electrolytic in character, and so this has often led to the expression, "electrical adsorption". This, unfortunately, leads one to the erroneous idea that the forces at work in polar adsorption are wholly different from those involved in apolar adsorption. The exact nature of polar adsorbents has been the subject of some speculation, and it is generally held that such an adsorbent is composed of a fixed and a mobile group of ions or ion-complexes (Freundlich, Colloid and Capillary Chemistry, London, 1926, p. 207). The fixed group constitutes the skeleton of the solid while the mobile ion is free to leave the solid in exchange for an ion of like polarity adsorbed by the solid. Alternatively, a non-polar adsorbent might have such a strong tendency to adsorb ions that these, although firmly held by

the surface, would still behave as mobile ions. Lastly, polar impurities might also give rise to polar adsorption by normally nonpolar adsorbents. Thus, an essential feature of all polar adsorbents is the presence of a mobile and a fixed group of ions. It is important to remember that the activity of a polar adsorbent depends not only on the lability of the exchangeable ion but also on the activity of fixed ion-skeleton.

Although exchange-adsorption of electrolytes on polar adsorbents resembles compound-formation in that the principal valencies play a greater part than in the case of ordinary adsorption, there is, however, one significant difference. In the formation of an ordinary chemical compound, the valence forces of the two reactant molecules are wholly engaged, whereas in the case of polar adsorption only *part* of the principal valencies of the adsorbent are involved and the remainder maintains the structure of the adsorbent.

Polar adsorbents can also be regarded as amorphous solid electrolytes, possessing a tendency to dissociate electrolytically in aqueous media. The mobile ion, which is only loosely held by the solid, tends to disperse ionically in water, leaving the solid oppositely charged. This is manifested by the migration of the solid particles in cataphoresis, the charge determining the direction in which the solid particles move. The conception of "electrical charge" on polar adsorbents is further exemplified by the selective adsorption of electrolyte-dyes, *viz.*, the so-called acidic and basic dyes. Generally, these dissociate strongly in aqueous solution. Some of them are more or less colloidally dissolved, but still are almost identical with ordinary electrolytes. In general, a positive adsorbent (*e.g.*, kaolin) tends to take up an acidic dye in preference, while a negative adsorbent (*e.g.*, ferric oxide) prefers a basic dye.

Adsorbent charcoal is also known to behave as a polar adsorbent in several instances and adsorption of electrolytes by charcoal is in most cases non-equivalent. It is also influenced to a remarkable extent by the pH of the solution and by the presence of other ions. However, adsorption of electrolytes by charcoal has never been found to be entirely polar, since apolar adsorption occurs simultaneously. While the apolar part of the phenomenon was believed to reflect the true character of the charcoal, the polar part was ascribed to impurities present in the adsorbent. While there is no doubt that impurities, which are extremely difficult to exclude, have been responsible to a large extent for the observed polar effect of charcoal, evidence has steadily accumulated in recent years to show that even pure charcoal is capable of polar adsorption.

The view that polar adsorption by charcoal is due entirely to the presence of ash-forming impurities rested mainly on the tacit assump tion that the structure of adsorbent charcoal consisted purely of carbon atoms and also on the basis of earlier experimental results which appeared to indicate that the adsorption of electrolytes by "de-ashed" charcoal was non-hydrolytic and equivalent (Rona and Michaelis, *Biochem. Z.*, 1919, 97, 94; Freundlich and Losev, *Z. physikal. Chem.*, 1907, **59**, 284).

#### THE CONSTITUTION OF ACTIVE CARBON

Purity of charcoal, as ordinarily mentioned, refers only to its freedom from mineral impurities. It has, however, been established that even the purest specimens of active charcoal contain traces of oxygen and hydrogen as impurities, both the gases being firmly held by the carbon atoms.

The formation of complex oxides on the surface of activated carbon has been established principally by two lines of investigation, namely, (1) measurement of the heat of adsorption of oxygen on carbon, and (2) examination of the gas obtained by the degassing of activated charcoal. It was found that the gas collected by evacuation of active carbon depended not only on the temperature of desorption but also on two other factors, namely, (1) the amount of oxygen adsorbed, and (2) the temperature at which the gas was adsorbed. Dewar (Proc. Roy. Soc., 1905, 74, 122, 127) found that when oxygen was adsorbed at the temperature of liquid-air, the heat evolved per gram molecule of gas adsorbed was about 3,000 calories. This heat was of the same order as that produced with inert gases like helium, argon or nitrogen. He found moreover that the gas adsorbed on charcoal at such low temperatures could be pumped off unchanged and that no chemical combination took place between hydrogen and oxygen, or between oxygen and carbon monoxide adsorbed on the surface. Thus the adsorption of oxygen, as that

of any other gas, on charcoal at liquid-air temperature was a fully reversible process unattended by any chemical phenomena.

At higher temperatures, however, the adsorption of oxygen is accompanied by far greater heat evolution. On desorption, very little oxvgen is recoverable by evacuation, the gas removed consisting largely of carbon monoxide and carbon dioxide (Lowry and Hulett, J. Amer. Chem. Soc., 1920, 42, 1417; Garner and McKie, J. Chem. Soc., 1927, 2450; Shah, ibid., 1929, 2661, 2676). Under these conditions, the heat of adsorption has been found to vary with the amount of oxygen adsorbed. Keyes and Marshall (J. Amer. Chem. Soc., 1927, 49, 156), Ward and Rideal (J. Chem. Soc., 1927, 3117) and Garner McKie (loc. cit.) have observed that the heaf evolved was abnormally high for the initial amounts of oxygen adsorbed. For example, Garner and McKie found that the heat of adsorption was at a maximum when the amount of oxygen adsorbed was  $1.5 \times 10^{-5}$ g.-mols./g. At higher concentrations the heat of adsorption steadily decreased until a constant value of 4.000 calories was finally The maximum heat of adsorption was found obtained. to increase with temperature. Thus, from a value of 70,000 calories at 18°, the molar heat of adsorption of oxygen rises to 115,000 calories between 100° and 200° and to 224,000 calories at 450°. It is significant that the heat of adsorption measured just above 100° is approximately equal to the sum of the heat of combustion of carbon to carbon dioxide and the heat of adsorption of the latter gas on charcoal.

It is clear that the irreversibility of the adsorption of oxygen on carbon at the ordinary and higher temperatures and the abnormal heat evolution accompanying such adsorption cannot be fully explained by the classical physical concepts of adsorption. The important distinction between the adsorption of oxygen at low and at elevated temperatures suggest, naturally, the occurrence of chemical phenomena at the higher temperatures. The term "chemisorption" (or "chemosorption") refers to those special cases of adsorption where chemical interaction occurs between the adsorbent and the adsorbate.

Valuable data regarding the interaction of carbon with oxygen were obtained in a series of investigations on the combustion of carbon carried out by Wheeler and his co-workers and by Shah (Rhead and Wheeler, J. Chem. Soc., 1912, 101, 846; 1913, 103. 461, 1210; Wheeler, ibid., 1918, 113, 945: Tideswell and Wheeler. ibid., 1919, 115, 895; 1920, 117, 794; Francis and Wheeler, ibid., 1925, 127, 112, 2238; 1926, 1410; 1927, 2958; Shah, loc. cit.). The experiments of Rhead and Wheeler show that carbon, at all temperatures up to 900° and probably also above that temperature. has the power of retaining oxygen tenaciously. This oxygen cannot be removed by exhaustion alone, but also requires heating of the carbon during exhaustion. When quickly released in this manner it appears, not as oxygen, but as carbon dioxide and carbon monoxide. The proportions in which it appears in these two oxides when completely removed depend on the temperature at which the carbon has been heated during oxygen-fixation. Shah (loc. cit.) found that nitrous oxide, carbon monoxide, carbon dioxide and nitrogen were adsorbed by carbon and could be removed completely by evacuation at 0°. When oxygen and nitric oxide were adsorbed, only part of these gases could be desorbed as such at 0°. By raising the temperature, varying amounts of carbon monoxide and dioxide were obtained, thus providing strong evidence for the view that the oxygen is "fixed" on carbon by surface-combination rather than by pure adsorption.

There has been much speculation regarding the state of this "fixed oxygen" on the surface of carbon, and physical, physicochemical and chemical theories have been put forward. Keyes and Marshall (*loc. cit.*) concluded, on the basis of heat of adsorption data, that the adsorbed oxygen molecules or atoms can be regarded as being in a special state of valency such as would enable this first layer to adsorb a second layer of molecules of the same or of a different species. Shah (*loc. cit.*) also holds practically the same view. Adopting the suggestions of Brodie (*Annalen*, 1873, 169, 270), Berthelot (*Bull. Soc. Chim.*, 1876, 26, 102) and Armstrong (*J. Soc. Chem. Ind.*, 1905, 24, 473), Wheeler and his co-workers (*loc. cit.*) postulated that the first step in the oxidation of carbon is the formation, on the surface, of "a loosely formed physico-chemical complex which can be regarded as an unstable compound of carbon and oxygen of an at present unknown formula,  $C_xO_r$ " which is

decomposed by heat into carbon monoxide and carbon dioxide. A similar view is held by Lowry and Hulett (loc. cit.), who consider that the carbon-oxygen complexes formed at ordinary temperatures are stable solid oxides which on heating disintegrate into carbon monoxide and dioxide. Langmuir (J. Amer. Chem. Soc., 1915, 37, 1154) studied the reactions between carbon and oxygen by heating a highly graphitised filament of very pure carbon and obtained evidence of a firmly held layer of oxygen on the filament. The great stability of this adsorption layer supports the view that it consists of oxygen atoms chemically combined with the carbon atoms. Garner and McKie suggest that at very low temperatures adsorption of oxygen on charcoal is a purely physical phenomenon; but at ordinary and higher temperatures the formation of oxides takes place on the surface. Rideal and Wright (J. Chem. Soc., 1925, 127, 1347) postulate the occurrence of at least three types of surface oxides: one, removable only at high temperature (ca. 1000°); a second, removable as carbon dioxide on evacuation, or as carbonate on fusion with alkali; and a third, removable at low temperature as oxygen.

The presence of chemisorbed oxygen on the surface of charcoal follows also from the marked chemical activity of activated charcoal, quite apart from general adsorptive properties. It is known that at ordinary and higher temperatures the adsorbed oxygen has remarkable catalytic properties, in contrast with Dewar's experience at liquid-air temperature. It was shown by Calvert (J. Chem. Soc., 1867, 20, 293) that between 0° and 150° this oxygen could oxidise ethyl alcohol to acetic acid and ethylene to carbon dioxide. Feigl (Z. anorg. allgem. Chem., 1921, 119, 305) noted the catalytic oxidation of sulphides, iodides, chromites, sulphites, stannite, mercurous salts and oxalic acid in solution. King (J. Chem. Soc., 1937, 1489) has made an intensive study of the catalytic activity of ash-free activated sugar-charcoal in many reactions in the solution-phase such as the oxidation of ferro-cyanide, arsenite, nitrite and quinol and the decomposition of hydrogen peroxide.

Kruyt and de Kadt (Kolloid Z., 1929, 47, 44; Kolloid Beih., 1931, 32, 249) and Kolthoff (J. Amer. Chem. Soc., 1932, 54, 4473) found that active charcoal, heated for some time in a stream of oxygen, acquired the property of removing alkali from solution. thereby suggesting the formation, on the charcoal, of a "definite chemical compound with acid character". King (J. Chem. Soc., 1933. 842) actually isolated a crystalline acid (probably oxalic acid) from the aqueous extract of ash-free sugar-charcoal which had been previously exposed to air or oxygen at room-temperature. The amount of acid formed on the carbon did not diminish even with ten successive exposures of the sample to air or oxygen. This again proved that the acid obtained by extraction was not an impurity priginally present in the charcoal, but was actually formed each time on exposure to air. The acid was formed when the specimen was exposed to oxygen and nitric oxide, but not with nitrous oxide. nitrogen and carbon dioxide. Treatment of air-exposed sugarcharcoal with dilute sulphuric acid resulted in the formation of small amounts of hydrogen peroxide, thus confirming the previous observation of Lamb and Elder (J. Amer. Chem. Soc., 1931, 53. 157).

King suggested that oxalic acid as well as hydrogen peroxide was derived from the surface-oxide complexes. Lamb and Elder considered that a "peroxide complex" was present on the carbon. Another significant observation made by King (*J. Chem. Soc.*, 1934, 22) was that the presence of a small minimal amount of water (*ca.* 5%) in the air or oxygen was essential for the formation of oxalic acid or hydrogen peroxide. King (*ibid.*) also noted that the amount of oxalic acid or hydrogen peroxide produced from a certain quantity of charcoal corresponded to only about 0.5 per cent. of the total amount of oxygen adsorbed by it. This agrees with the estimate given by Rideal and Wright (*loc. cit.*) for the fraction of charcoal-surface that is chemically reactive.

King has carried out a systematic investigation of the properties of "pure" sugar-charcoal activated by heating in a current of moist air, oxygen or carbon dioxide. In particular, the temperature of activation was found to affect seriously the adsorptive and catalytic properties of charcoal. Activation at about  $450^{\circ}$  yielded specimens with maximum base-sorbing and minimum acid-sorbing properties, while charcoal activated at higher temperatures (*ca.*  $850^{\circ}$ ) adsorbed the maximum of acid, but little of base

(King, J. Chem. Soc., 1937, 1489). It was also found (*ibid.*, 1936, 1688) that in many oxidation reactions the maximum catalytic activity was shown by charcoal activated at 450°, whereas for the decomposition of hydrogen peroxide activation at 850° produced the most active carbon. It was thus established that the specimens activated at the lower temperature were markedly different from those produced at the higher temperature. Indeed, so intimate was the relation between the activation-temperature and the activity of the specimen that a specimen first activated at 850°, acquired upon re-activation at 450°, the adsorptive and catalytic properties characteristic of the lower temperature, and vice versa. These results were explained by postulating the existence of two specific oxides on the surface of active carbon: one, predominantly acidic in character and formed at an optimum temperature of 450° and the other, a basic oxide produced at higher temperatures like 850°.

Although many suggestions have been put forward concerning the structure of the surface-oxide film on active carbon, it is still premature to consider definite formulæ for the complexes formed on the surface. King (J. Chem. Soc., 1933, 842) recognises two mechanisms for the chemisorption of oxygen on carbon: (1) according to the Heitler-London mechanism, resulting in a complex with an unsaturated valency as represented by the scheme:

$$C + O_2 \rightarrow C - O - O - -;$$

and (2) the formation of a loose valency-structure as shown below:

$$-C = C - + 0 = 0 \rightarrow C - C$$

$$1 \qquad 1 \qquad 0 \qquad 0$$

King suggests that both types of oxides are produced on the charcoalsurface at least in the initial stages of activation. Both the above structures explain the formation of oxalic acid and hydrogen peroxide from active carbon, but the complex of the first type has a free valency to facilitate further adsorption on the oxide-layer. These remarks apply, however, only to charcoal containing a trace of moisture. On the other hand, specimens prepared under thoroughly dry conditions are much less active (King, J. Chem. Soc., **1934**, 22). They desorb at much higher temperatures than the normal "moist" specimens and there is a preponderance of carbon monoxide in the gas removed. It follows, therefore, that in the dry specimen of active charcoal the forces binding the chemisorbed oxygen are much stronger than those suggested by the two structures given above. The structure originally proposed by Langmuir (*loc. cit.*) is more suitable:



Schilov and his co-workers (Z. physikal. Chem., A, 1930, 148, 233; *ibid.*, 1930, 149, 211; Kolloid Z., 1930, 52, 107) investigated the adsorption of acids and alkalis by thoroughly out-gassed charcoal under varying pressures of oxygen and explained their observations by proposing the existence of three surface-oxides: A and B are basic oxides formed at moderate temperatures, while C is an acidic oxide formed from B between 300° and 850°. A is formed from B in vacuum.



ACTIVE CARBON AS A POLAR ADSORBENT

Recent studies with activated charcoal have established that the chemisorbed oxygen on carbon, which accounted for the catalytic activity of the adsorbent and the selective adsorption of acids and bases, also enables the carbon, even when free from ash, to behave as a polar adsorbent in aqueous systems. Thus, it has been shown that ash-free carbon migrates in cataphoresis, alters the pH of water and adsorbs electrolytes "non-equivalently".

The concept of "electrical charge" on carbon particles, that is, their electro-kinetic potential with respect to the dispersing medium, dates back to the researches of Perrin (*Jour. Chim. physique*, 1904, 2, 60) who, from the results of electrosmosis through carbon-filters and suspensions of carbon-particles, concluded that the particles of carbon were electropositive in acid and electronegative in alkaline solutions. Between the two extremes there must naturally be a particular value of pH (not necessarily 7) at which the carbon should be electrically neutral with respect to the surrounding medium. This value of the pH, known as the "iso-electric point", is a very important constant for a decolorising charcoal.

Perrin's work was followed by similar investigations carried out by Gyemont (Kolloid Z., 1921, 28, 103) and Umetsu (Biochem. Z., 1923, 135, 442). The results of osmosis were further confirmed by observations on the electrophoresis of carbon-particles in aqueous suspension. The earliest of these was that of Goldberg (Kolloid Z., 1922, 30, 230) who, using colloidal carbon, studied the influence of various factors on the cataphoretic velocities of carbonparticles. The colloidal suspension, obtained by the action of sulphuric acid on sugar, followed by dialysis, was very stable and the particles were negatively charged in both acid and alkaline solutions. Kruvt and de Kadt (loc. cit.) showed both by cataphoresis and by electrolyte-coagulation that the particles of charcoal are negatively charged in water. They further found that the same charcoal heated at 1000° either in vacuum or in carbon dioxide, became positively charged in water and that the negative charge was restored by heating again at 400° in oxygen.

The differences in electro-kinetic charge on charcoals activated by different means were investigated by Ogawa (*Biochem. Z.*, 1925, 161, 275) who concluded that the electrical as well as the adsorptive properties were influenced by progressive activation. Olin, Lykins and Munro (*Ind. Eng. Chem.*, 1935, 27, 690) correlated the intrinsic adsorptive capacity of carbon, as determined by the conventional gas-adsorption method, with its electro-kinetic charge as given by its speed of migration in an aqueous medium of high pH. They further studied the variations in cataphoretic velocity brought about by changing the pH of the medium and found that the change of pH affected both the magnitude and the sign of the charge on the carbon-particles. Finally, Bennister and King (*J. Chem. Soc.*, 1938, 991) investigated the electrophoretic velocities in aqueous suspension of samples of pure sugar charcoal activated at various temperatures between 400° and 1000°. They found that the particles remained negative throughout this range of activation-temperatures and that a maximum velocity was noted for carbons activated at 850°. Bennister and King suggest that the charge on carbon-particles should be associated with the chemisorbed oxide layer, the nature of which varies with the temperature of activation and also determines the adsorptive and catalytic properties of the carbon. It is also possible that coupled with the presence of a chemisorbed oxide layer, there occurs a non-equivalent adsorption of ions when the adsorbent is suspended in electrolyte-media. This would account for the variation of the electro-kinetic charge with the pH of the medium and the alteration of pH by the addition of active carbon to water or to the solution of an electrolyte.

Frumkin (Kolloid Z., 1930, 51, 123) investigated the adsorption of electrolytes by ash-free sugar-charcoal, activated by heating at 1000° in a stream of carbon dioxide. When the carbon was thoroughly out-gassed it did not adsorb electrolytes, but its adsorptive power returned in presence of air. Under such conditions, the amount of hydrochloric acid adsorbed was equivalent to the oxygen content of the charcoal. The solution reacted alkaline and it was inferred that carbon containing oxygen behaved in the system as an "oxygen-electrode" and that hydroxyl ions were sent into solution from the adsorbed layer, according to the scheme:

$$C_x O + H_2 O \rightarrow C_x + 2 (+) + 2OH'$$

In this case the carbon-particles assumed a positive charge with reference to the solution. When, however, the carbon contained hydrogen and no oxygen, its behaviour towards electrolytes was entirely reversed. It adsorbed alkali to an extent determined by the hydrogen-content, but failed to take up acids. A suspension of the carbon containing hydrogen reacted acid. This was explained as follows:

$$C_x + H_2 \rightarrow C_x + 2 (-) + 2H^{-1}$$

According to this view, carbon behaves as a "hydrogen-electrode" in presence of hydrogen. Frumkin also found that a trace of platinum greatly enhanced the activity of carbon. Though the cause of the electrical charge on "pure" carbon is still obscure, its polar character has been established. It follows, therefore, that the adsorption of electrolytes by "pure" carbon is partly polar and partly apolar, and need not exclusively be the latter as was originally surmised. The extent and character of the polar adsorption by carbon will depend naturally upon the conditions of its preparation. Adsorbent charcoal as obtained in practice is seldom pure, and invariably the impurities are polar in character. The charcoal can, therefore, be regarded as a mixture of polar substances, the carbon itself being one of them. The impurities may either oppose or augment the effect of the carbon. The resultant depends on two principal factors: (1) the amount of impurity present in the specimen, and (2) the relative activities of the carbon and of the

Polar adsorption by charcoal is of considerable importance when the adsorbent is employed in the decolorisation of aqueous solutions because the equilibrium pH of the solution as well as the effect of this pH on the activity of the charcoal depend on this fundamental property of activated charcoal. Indeed, it has been pointed out that the polar behaviour of active carbon is almost as important as its adsorptive-capacity, and often determines the choice of the particular type of carbon employed.

various impurities as polar adsorbents.

#### Summary

1. The theories of adsorption of electrolytes by polar adsorbents are examined in the light of available experimental evidence.

2. The presence and state of oxygen chemisorbed on carbon are discussed.

3. The behaviour of ash-free carbon as a polar adsorbent under various conditions is presented in this paper.

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