Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Hall, Dorrit , Zvipriel, Oren, Yoram and Soffer, Abraham(1987) 'Purification of Aqueous Suspensions from Colloidal Particles by Electro-Adsorption on Porous Carbon Electrodes', Separation Science and Technology, 22: 2, 1017 — 1027
To link to this Article: DOI: 10.1080/01496398708068996
URL: http://dx.doi.org/10.1080/01496398708068996

SEPARATION SCIENCE AND TECHNOLOGY, 22(2&3), pp. 1017-1027, 1987

Purification of Aqueous Suspensions from Colloidal Particles by Electro-Adsorption on Porous Carbon Electrodes

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ABSTRACT

The electrically induced adsorption of carboxylated colloidal particles from aqueous suspension on a carbon electrode was studied. Due to high colloid to electrode charge density ratio, adsorption is effected only to a small extent when the electrode potential is varied within the double layer potential range. At extreme potentials where water is involved in Faradaic reactions, colloid adsorption occurs due to pH variations. The process may be attractive for purification of suspensions from fine particles since no chemicals have to be added in order to induce adsorption or desorption of the colloid.

INTRODUCTION

The adsorption of colloidal particles onto solid surfaces has attracted the attention of numerous investigators. The main motivation for this line of research is the search for an efficient filtration bed for very fine particles. The conventional mesh type filtration beds fail to function in these cases since clogging problems appear soon after the beginning of the process. On the other hand, removal of suspended particles by deep bed type filters is effected via adsorption of the particles on a porous matrix throughout the filter depth rather than by entrapping them on the outer surface. These filters are composed of fibrous materials which carry high specific surface area for adsorption together with a good solution permeability. Thus, unlike conventional filters, relatively low pressure drops are required when the filtration of very fine particles is considered.

The process of adsorption of small colloidal particles onto large surfaces is termed "heterocoagulation" and has been studied by Hull and Kitchner (1), Vincent, Young and Tadros(2), Tamai et al. (3-6) and others. Tamai et al. discussed the influence of pH and solution concentration on the rate of deposition and the amount deposited of polystyrene lattices on synthetic fibers such as polyamide, polyester and polyacrilonitrile. It was found that the pH is of prime importance in determining the adsorption characteristics since it controls surface charge and thus the zeta potential of both the latex particles and the fibers. A maximum in the rate of adsorption was found to occur near the isoelectric point of the latex rather than in the expected region of zeta potentials of opposite signs. These systems were treated via the heterocoagulation theory of Hogg, Healy and Fuerstenau(HHF)(7). It was also suggested that particle-particle(PP) interactions have to be considered in addition to particle-fiber(PF) interactions, a point which was also discussed by Vincent et al.(2).

High surface area carbons and graphites can be excellent candidates for deep bed filtration for several reasons: since they are electric conductors they can be adjusted to carry a charge which is opposite in sign to that of the colloidal particles. Thus, the particles can be removed from the suspension due to attractive electrostatic interactions between the two double layers. Moreover, upon charging carbon and graphite electrodes to the proper potential range, water decomposition or redox reactions involving surface groups(8) can occur according to the following scheme(9) :

In the cathodic range

$$2e + 2H_2O \rightarrow H_2 + 2OH^-$$

$$S| + e + H_2O \rightarrow S|H + OH^-$$

In the anodic range

$$H_2O \rightarrow 2H^+ + 1/2\ O_2 + 2e$$

$$S| + H_2O \rightarrow S|O + 2H^+ + 2e$$

$S|$ symbolizes a surface group

Due to the high surface area of these materials these reactions can change the pH of the bulk suspension and consequently, the surface charge of the colloidal particles. This, according to Tamai et al, (3) may change the adsorption rate and amount adsorbed on the carbon bed.

It was deduced (10) that among the large variety of carbon and graphite forms, the fibrous structure is the most promising as an electrode bed for electrochemical filtration due to its high surface area and high liquid permeability. It was also found (11) that bacteria, which can be considered as colloids, can be removed from aqueous buffered solutions by forcing the solution through a charged graphite felt. The process is based on electrostatic interactions between the charged outer bacteria membrane and the oppositely charged electrode. Upon reversing the electrode charge, part of the adsorbed bacteria could be returned to the solution.

The possibility of inducing adsorption or desorption of colloidal particles in aqueous suspensions by varying the electric potential (or charge) of an electrode has not to our knowledge, been proposed as a mean for controlling filtration. The ease of controlling the electrode potential by means of an external power supply, the low pressure drop required to drive the suspension when fibrous carbons are used, and the fact that the addition of chemicals (e.g., for pH control) is unnecessary are the most prominent advantages of this process.

In the present article, a study of the electrically induced adsorption of colloidal particles upon a fibrous graphite electrode is presented. The electrode potential is varied in a wide range to allow the study of colloidal adsorption characteristics when the double layer charging as well as water electrolysis occur.

EXPERIMENTAL

The adsorption cell is shown in figure 1 and the flow system is shown in figure 2. The cell is made of PVC and divided into two identical compartments by a cation exchange membrane. The space within each compartment is completely filled with 1.15 gr. of graphite felt (RVG 2000 produced by Le Carbon Lorraine, France) discs, 5 cm in diameter and 3 mm thick. One compartment serves for the working electrode and the other, for the auxiliary electrode. A two-way peristaltic pump was used to force independently, different solutions through each one of the compartments. The suspension containing 1 to 10 ppm inital concentration of the colloidal particles and 0.1 to 0.001M of NaCl was driven through the working electrode compartment. Solutions with the same NaCl concentrations but without the colloid were passed through the auxiliary electrode compartment. The solutions were pushed in a radial manner through the electrodes i.e., from its center to the circumference and were collected around it. In most experiments, the solution volume circulated through the working electrode was 60 ml. An Ag/AgCl couple dipped in the suspension as close as possible to the working electrode served as a reference electrode. The experiments were run in a potentiostatic mode with an H.B. Thompson & Asso. Ministat potentiostat.

Colloid concentration was monitored with a scattered light detector consisting of a small volume cell isolated from the surrounding light and connected to the outlet of the working electrode compartment. The suspension within the cell was illuminated with a He-Ne laser and the scattered light was detected by a Hamamatsu R1193U photodetector which was mounted perpendicular to the laser beam.

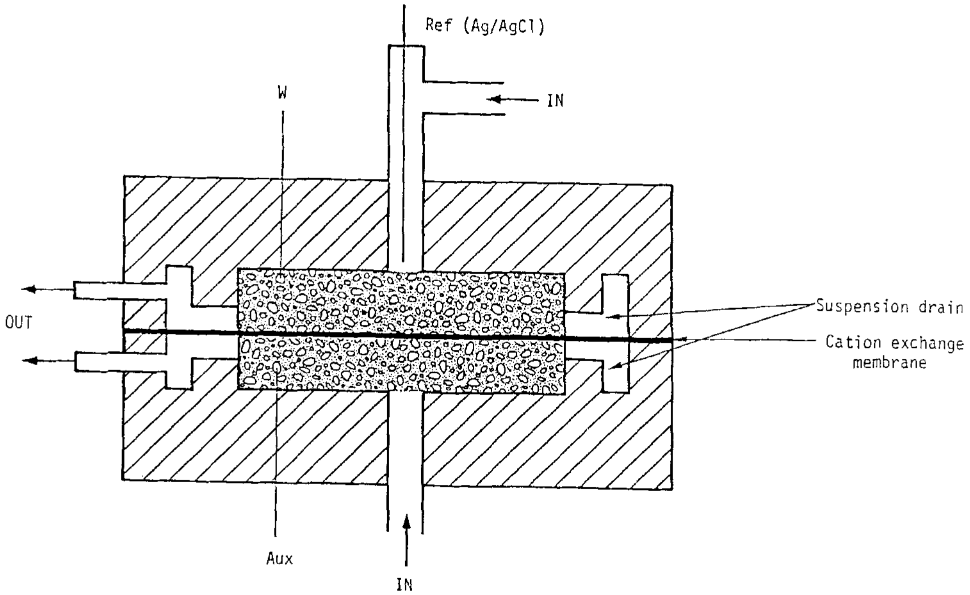

Fig. 1. Schematic representation of the adsorption cell. W- working electrode; Aux-auxiliary electrodes.

Monodispersed carboxylated polystyrene latex particles supplied by Polysciences were used. Their diameter was 0.15 ± 0.01μm Since the graphite felt fibers are about 10μm in diameter, they can be considered flat with respect to the particles. According to the manufacturer the particles carry 0.92 milliequivalents -COOH groups per gram. This is equivalent to a surface charge of approximately 240μCoul/cm^2. A glass electrode dipped in the solution outside the cell served for pH monitoring.

In a typical experiment the suspension was at first circulated through the bypass and the scattered light detector in order to determine the initial colloid concentration and its stability. Then, it was forced through the working electrode which was charged to a predetermined potential, for adsorption studies. The working electrode potential was varied as required throughout the experiment.

RESULTS AND DISCUSSION

Titration Curves for the Carboxylated Colloid

In figure 3 the degree of dissociation of the carboxylic groups carried by the colloidal particles is shown as a function of the pH

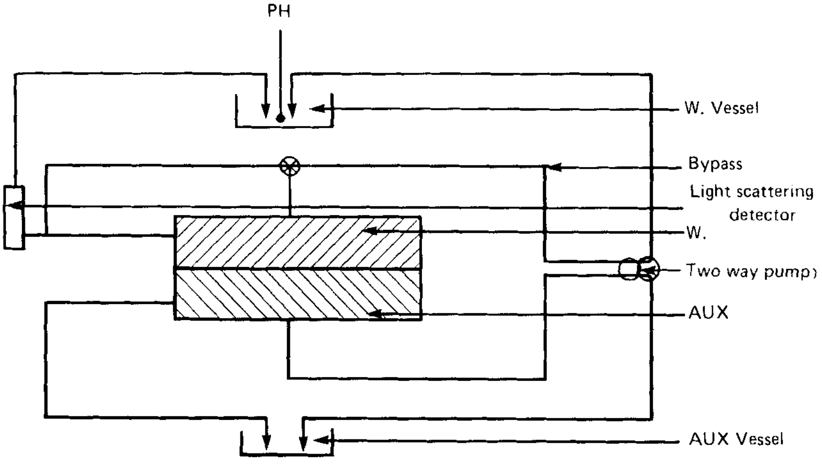

Fig. 2. Solution flow diagram. PH - pH electrode.

of the suspension. The curves were obtained by titration with NaOH followed by back titration with HCl while NaCl was kept constant at 10^{-3}M. During the titration, a slow response of the pH to the added alliquots of the hydroxide or the acid was observed. This indicates that a significant fraction of the carboxylic groups is located at the interior bulk of the colloidal particle and impose slow dissociation processes. The slow processes may also be a reason for the fact that the forward and the backward titration curves do not coincide. Nevertheless, these curves provide the means for the determination of the surface charge on the particles as a function of pH, which is necessary for estimation of PP and PF electrostatic interactions.

It is evident from figure 3 that below pH 7-8 the degree of dissociation changes slowly with pH while at higher pH values the curves are very steep and at pH 9.5 about 50% of the surface groups are dissociated. It is worth mentioning that during the titration, no mutual coagulation was observed even at pH values as low as 4.

Dependence of adsorption on pH

In this series of experiments the suspension was forced through the working electrode at open circuit conditions. Variations in pH were achieved by the addition of the proper amounts of NaOH or phosphate buffer. The results are shown in figure 4 where the amount of the adsorbed colloid is given as a function of its equilibrium concentration in the suspension and pH. It is evident that there

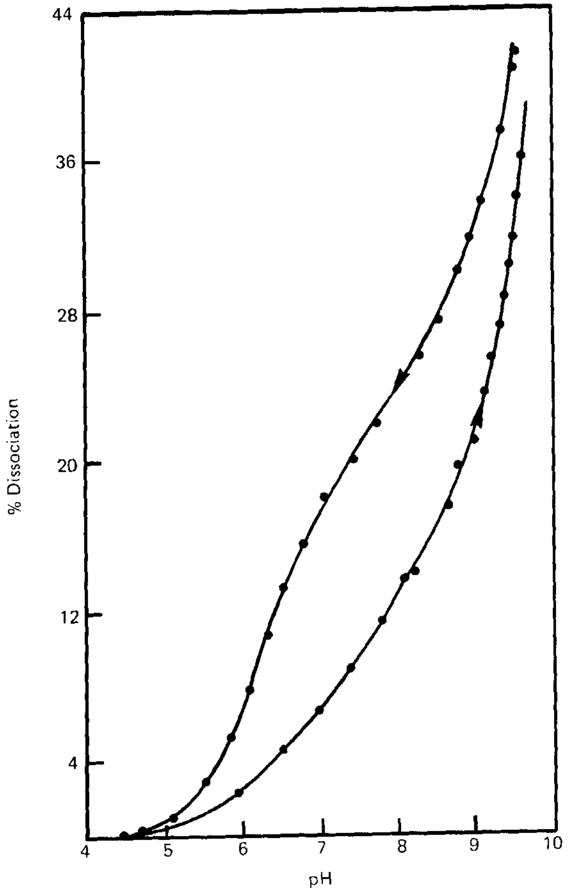

Fig. 3. Dissociation degree of carboxylated latex as a function of pH

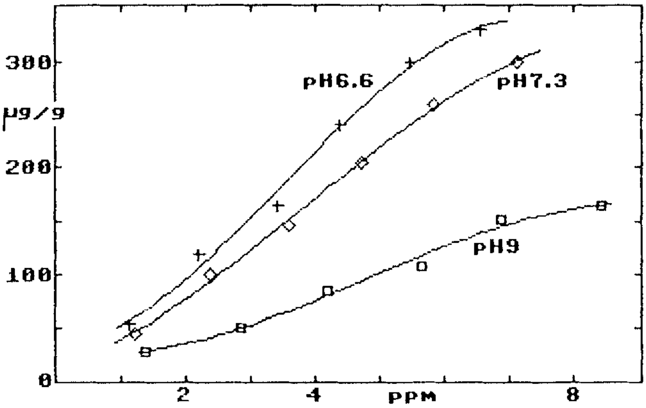

Fig. 4. Amount of colloid adsorbed (in μgr per gr electrode) as a function of suspension concentration and pH

is a significant effect of pH on the adsorption of the colloid namely, the amount adsorbed decreases as the pH increases. This effect may be attributed to the increasing of PP electrostatic repulsions as more surface groups dissociate when pH increases. Generally, repulsions between particles become more pronounced as they approach the electrode since while doing this, interparticle distances decrease.

Electrically induced adsorption of colloids

*As mentioned earlier, adsorption of colloids as a result of the application of electric charge to the electrode was investigated at high potentials where water electrolysis (and thus, pH changes) occur. At lower potentials, water may be involved in changing the pH of the suspension via interactions with surface groups as described above. However, in the present case these processes are minor since the amount of surface groups present on graphite is minute(12). At the potential range where charging of the double layer is the main process taking place, no effect of potential variations on the extent of adsorption was observed. This is questionable in the light of previous works(1-6) where electrostatic repulsive or attractive forces (between similar or oppositely charged surfaces respectively) were clearly found to govern colloid adsorption. However, it should be noted that in the present case the graphite electrode can be charged at the most to a charge density of about 5μ Coul/cm^2 (12) which is 40 times lower than the charge density on the colloid at complete dissociation. Thus, in view of figure 3, the charge on the particles at pH 6-7 (which prevailed in the suspension during the double layer charging experiments) or higher is high when compared to that on the electrode. This may

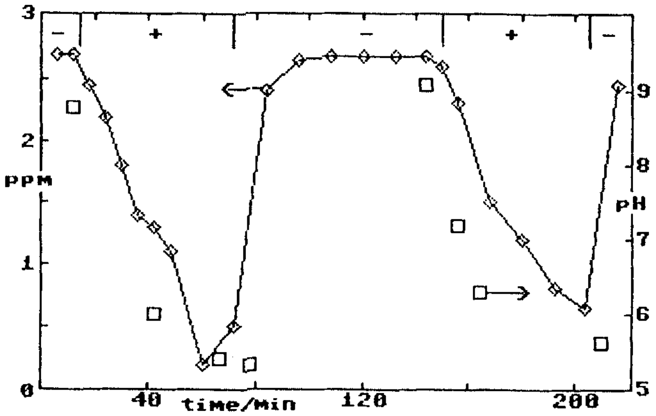

Fig. 5. Variations of colloid concentration (◇) and pH (□) in the suspension as a function of time. The working electrode potential ranges are indicated as: + = 500mV; - = -500mv.

result in strong PP repulsions with negligible influence of attraction or repulsion of the electrode when its potential is varied.

A typical pattern of adsorption of colloids as a result of electrochemically induced pH variations is depicted in figure 5. The concentration of the colloid in the solution and the pH are given in this figure as a function of time and potential variations of the working electrodes. When the potential is 500mV the pH decreases, followed by a decrease of the colloid concentration whereby when the potential is changed to -500mV the pH and the colloid concentration increases. It is evident that colloid adsorption responds to pH in accordance with the results shown in figure 4.

It should be noted that in most of the experiments in this series the time lapse between potential reversals was limited to 120 min since effects of H^+ ion penetration through the cation exchange membrane were detected afterwards. In some experiments dilute NaOH solution was added to the auxiliary electrode solution in order to eliminate H^+ ions formed there when the working electrode is highly negative.

Figure 6a shows the effect of solution flow rate on the electrochemically induced pH variations in the cell and figure 6b shows the corresponding effect on the adsorption of colloids. In both cases the data are presented as a function of the number of times the solution volume is passed through the working electrode compartment. The decrease in pH and the increase in the amount

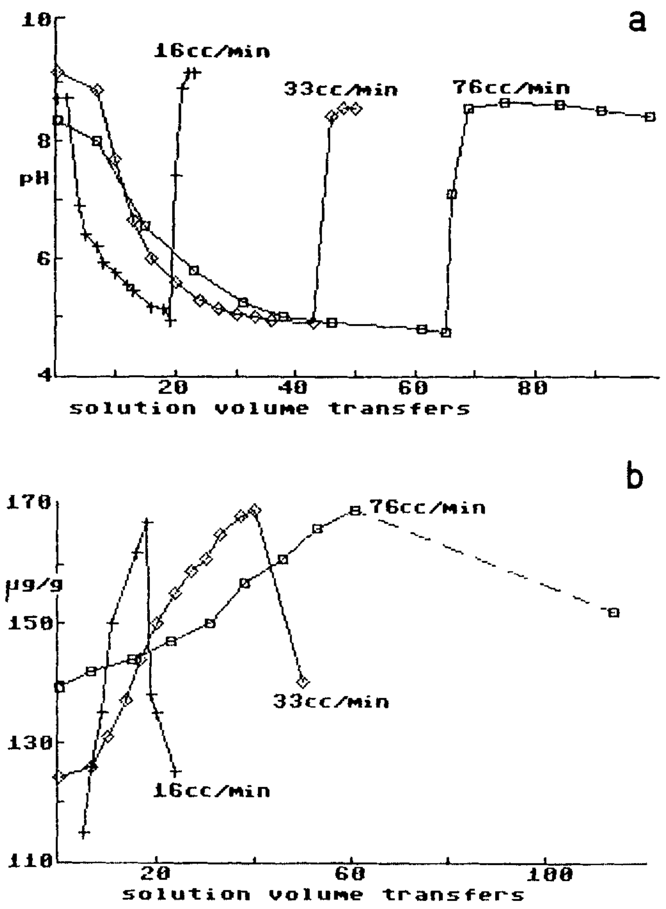

Fig. 6. a) pH; and b) amount of adsorbed colloid as a function of the number of suspension volume transfers through the working electrode and the flow rate.

of colloid adsorbed is a result of charging the electrode to 500mV while the sudden pH rise in each curve(and the decrease in the amount of adsorbed colloid) results from charging the electrode to -500mV. A striking feature in these figures is that pH variations are not affected by the solution flow rate while the rate of colloid adsorption is significantly affected, namely, it decreases as the flow rate increases. The insensitivity of pH to flow rate is not surprising. The measured pH variations in the bulk solution results from local pH variations near the surface of the electrode. The solution at the electrode interface, the pH of which in fact governs adsorption, is diluted with a large volume of the bulk solution,thus diminishing the effect of flow rate. However, reduction of local H^+ ion concentration by dilution with the bulk solution (a process which is accelerated as the flow rate increases) should bring about a decrease in the rate of adsorption as the local pH increases. Also, the effect of hydrodynamic shear forces imposed on the adsorbing particles by the flowing solution(13) should not be excluded. These forces become more pronounced as the flow rate increases, thus resulting in slowing down the adsorption process.

CONCLUSIONS

In the particular case studied, where experimental conditions force high particle to electrode charge density ratio, electrostatic effects on the adsorption characteristics of the particles on the electrode are not prominent. In the present case as well as in other cases where the charge on the particles is pH dependent (like e.g. in suspensions of metal oxides (14, 15)). adsorption or desorption can be induced by varying the pH of the suspension either manually or by electrochemical water decomposition at high potentials. The latter process is interesting from the practical point of view since it removes the necessity of adding chemicals to the suspension.

It is expected that in cases where the colloid is not so highly charged with respect to the electrode, adsorption and desorption could be induced by mutual interactions of the two double layers rather than by pH variations.

ACKNOWLEDGEMENT

This study was supported by the Applied Research Foundation of the Israel Academy of Sciences and Humanities.

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