



STUDY OF ADSORPTION KINETICS AND ZETA POTENTIAL OF PHOSPHATE AND NITRATE IONS ON A CELLULOSIC MEMBRANE

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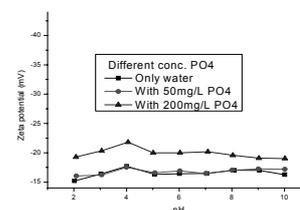
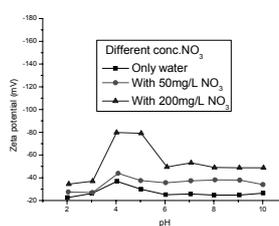
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In the context of process industries, membrane cleaning is one of the most important concerns from both economical and scientific points of view. The characterisation of membrane surface by using zeta potential technique provides a more appropriate tool to study the cleaning performance and membrane integrity. The effects of concentration, temperature and pH on zeta potential were also investigated. Kinetic studies were made using Langmuir and Freundlich isotherm model. The result of this study demonstrated the potential use of cellulosic membranes for nitrate and phosphate anions removal from potable water.



INTRODUCTION

Nitrate is one of the most common groundwater contaminants in rural areas and can create serious problems, such as eutrophication and outbreaks of infectious disease, when released into the environment.^{1,2} Contamination of drinking water by nitrates can cause potential hazards to human health. Excess nitrate in drinking water may cause blue-baby syndrome, which results from the conversion of hemoglobin into methemoglobin, a compound that cannot transport oxygen. Phosphorus occurs in natural waters and in wastewaters almost solely as phosphates. These are classified as orthophosphates, condensed phosphates

(pyro-, meta- and other polyphosphates) and organically bound phosphates. They occur in solution, in particles or detritus, or in the bodies of aquatic organisms.^{3,4} These forms of phosphate arise from a variety of sources. Small amounts of orthophosphate or certain condensed phosphates are added to some water supplies during treatment. Larger quantities of the same compounds may be added when the water is used for laundering or other cleaning, because these materials are major constituents of many commercial cleaning preparations. Phosphates are used extensively in the treatment of boiler waters. Orthophosphates applied to agricultural or residential cultivated land as fertilizers are carried into surface waters with

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storm runoff and to a lesser extent with melting snow. Organic phosphates are formed primarily by biological processes. They are contributed to sewage by body wastes and food residues, and also may be formed from orthophosphates in biological treatment processes or by receiving water biota. Phosphorus is essential to the growth of organisms and can be the nutrient that limits the primary productivity of a body of water. In instances where phosphate is a growth-limiting nutrient, the discharge of raw or treated wastewater, agricultural drainage, or certain industrial wastes to that water may stimulate the growth of photosynthetic aquatic micro- and macroorganisms in nuisance quantities. Phosphates also occur in bottom sediments and in biological sludges, both as precipitated inorganic forms and incorporated into organic compounds.

Filtration through a 0.20 μ m pore diameter membrane filter separates dissolved from suspended forms of phosphorus. No claim is made that filtration through 0.20 μ m filters is a true separation of suspended and dissolved forms of phosphorus; it is merely a convenient and replicable analytical technique designed to make a gross separation.

This technique to characterize the cleaning effect on membrane surfaces has very little precedence in literature.

According to the classical theory of electrokinetics whenever a solid is in contact with a liquid, preferential absorption of electric charge occurs at the surface of the solid. This will cause the solid phase to be charged electrically and the formation of a diffused layer of charges of opposite signs in the liquid next to the solid surface. The result is an electric double-layer and an electric potential across the layer called "zeta (ζ) potential". The magnitude of ζ potential reflects the quantity of charges absorbed by the solid.⁴⁻⁷ When an electric field is applied across an electrolyte solution, charged particles suspended in the solution are attracted towards the electrode of opposite polarity. Viscous forces acting upon the particle tend to oppose the motion and an equilibrium is rapidly established between the attraction and the viscous drag with the result that the particle moves with constant velocity.

The velocity is dependent upon the electric field strength or voltage gradient, the dielectric constant and viscosity of the medium and the zeta potential of the particle. The particle's velocity under unit electric field is referred to as its electrophoretic mobility. It is established that the higher the

absolute value of zeta potential, the more stable the system will be and therefore it will be able to withstand better the additions of salts (which might otherwise destabilized it). It will also usually show a lower viscosity. In our study we used NaCl (0.1 M) as ionic strength regulator.⁸⁻¹⁰

The aim of this study is to investigate the effect of zeta potential on the removal of nitrate and phosphate anions and the application on the removal of these anions from potable water.

MATERIAL AND METHODS

1. Materials and apparatus

Absorbance measurements was performed using a PerkinElmer Lambda 650 spectrophotometer. The pH value was measured on a Jenway pH meter 370 (portable pH meter). All reagents used in this study (NaH₂PO₄, KNO₃) were purchased from Sigma Aldrich (Munich, Germany).

Cellulose membrane was purchased from Merck (Darmstadt, Germany) with a pore size of 0.2 μ m. The cellulose acetate membrane is made of a blend of cellulose diacetate no other details about her synthesis were given by the manufacturer. It was supplied as dry flat sheet and was stored dry at room temperature.

The zeta potential measurements were performed on Mark II apparatus produced by Rank Brothers Co. (Cambridgeshire,UK).

2. Methods

Synthetic solutions were prepared using the phosphate salt NaH₂PO₄ and KNO₃ for nitrates respectively. Synthetic solutions (phosphate and nitrates) were filtered through cellulose membrane of 0.2 μ m and the concentration was determined spectrophotometrically.

2.1. Determination of Nitrate Anion

Determination of nitrate anions content was performed spectrophotometrically using 1N HCl and absorbance reads at a wavelength of 220nm. Measurement of UV absorption at 220 nm enables rapid determination of NO₃⁻, because dissolved organic matter also may absorb 220 nm and NO₃⁻ does not absorb at 275 nm and measurement made at 275 nm may be used to correct the NO₃⁻ value. The nitrate calibration curve follows Beer's law up

to 11 mg/L NO_3^- . This method is suitable only for screening of samples that have low organic matter contents *i.e.* uncontaminated natural waters and potable water supplies.

2.2 Determination of Phosphate Anion

The procedure for phosphate involves the addition of a mixed reagent (sulphuric acid, ammonium molybdate, ascorbic acid, antimony potassium tartrate) to a known volume of sample, diluting to volume, shaking and leaving for 10 min. A blue phosphomolybdenum complex is produced and the absorbance is measured at 880 nm. The concentration is calculated using a predetermined calibration graph derived from standard solution treated in the same way.

RESULTS AND DISCUSSION

1. Kinetic study

Kinetic study was conducted at three different temperatures 293K, 303K and 313K and pH 5.50 ± 0.02 and a period between 0-48h. Experimental results are shown in Fig. 1 for nitrate and in Fig. 2 for phosphate ion respectively.

Study on the kinetics adsorption process for nitrate and phosphate anion on cellulose membrane followed: (i) influence of ambient temperature on the kinetics; (ii) influence of concentration; (iii) pH of adsorption solutions.

The anion concentration in solid phase (membrane) is the difference between the mass of

initial anions obtained, present in solution and mass anions in solution at a time reported when introduced in system a membrane:

$$Uptake = \frac{V \cdot (C_i - C_c)}{m} \quad (1)$$

Uptake – adsorption capacity at time t, the amount of anions retained per unit mass of membrane [meq/g];

V – volume of solution containing anions [L]

C_i and C_c – is the initial concentration of the anion and current concentration in the system [meq/g];

m – membrane mass, introduced in system [g].

Maximum adsorption capacity (uptake) for nitrate ion is about 2.17 meq/g and for the phosphate ion is about 0.87 meq/g. Cellulose membrane has a much higher adsorption capacity for nitrate ion compared to the phosphate ion. The isotherms of Langmuir and Freundlich model were used to characterize the equilibrium of adsorption of both anions.

Langmuir equation characterized very well the experimental data for both nitrate and phosphate anion. Because R^2 has values above 0.9869 can be considered satisfactory for Langmuir equation for adsorption of nitrate (Fig. 2). Since the regression coefficient values are around the values 0.9869 to 0.9640 for nitrate and for phosphate respectively indicating that this equation characterizes very well the adsorption for the nitrate ion while the adsorption of the phosphate ion is not a specific (Fig. 3).

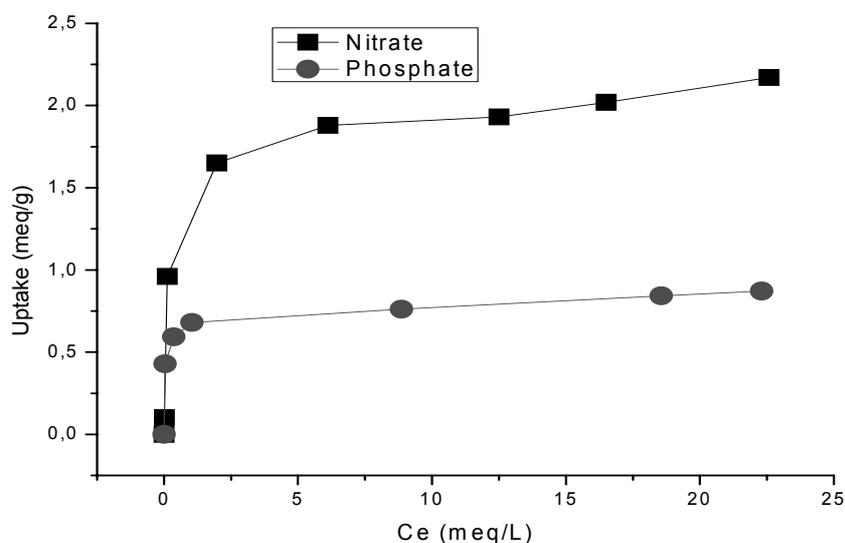


Fig. 1 – Adsorption isotherms for phosphate and nitrate anions.

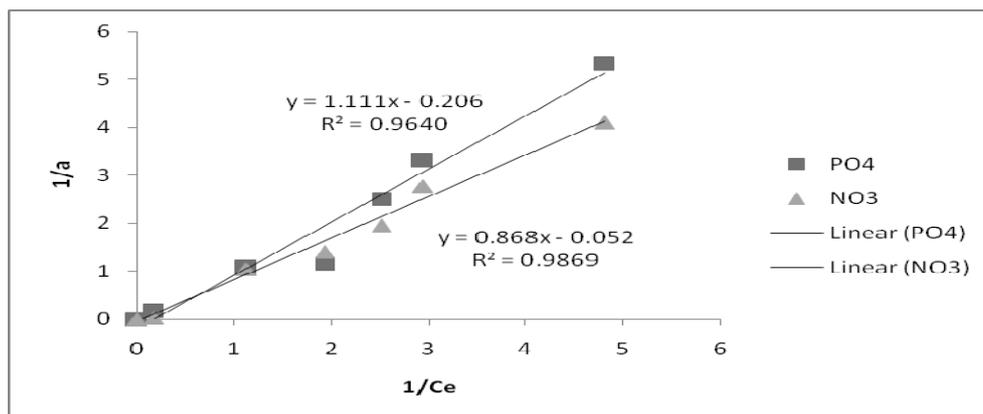


Fig. 2 – Linearized Langmuir equations.

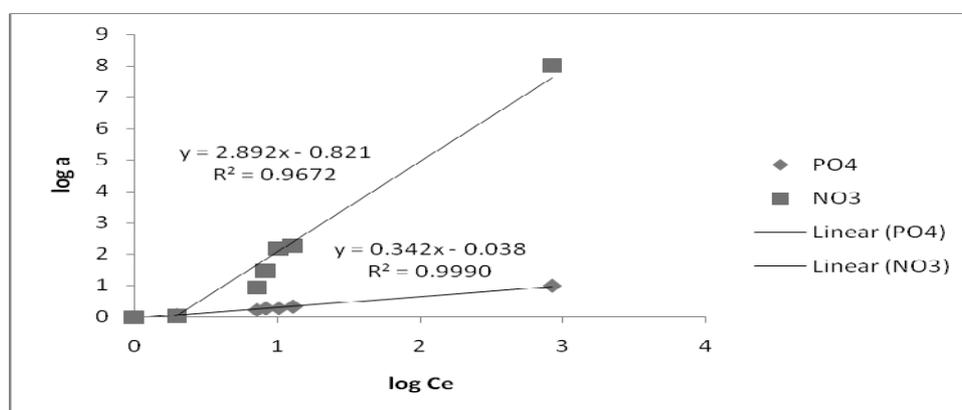


Fig. 3 – Linearized Freundlich equations.

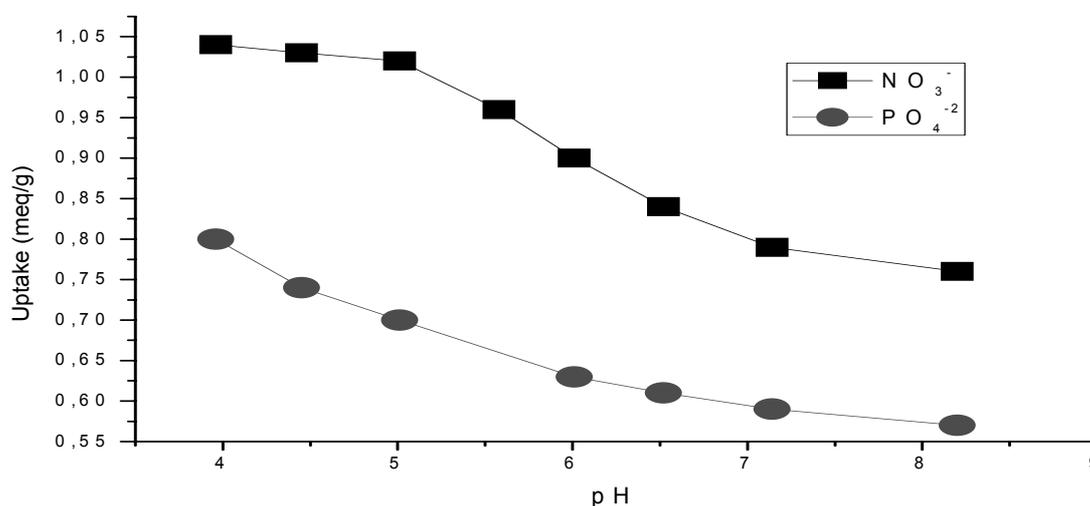


Fig. 4 – Variation of pH versus adsorption capacity for the nitrate and phosphate anions.

Freundlich equation characterized very well the phosphate adsorption on cellulosic membrane, because the regression coefficient is 0.9990 for phosphate anion.

The pH influences the adsorption process: as pH increases the adsorption capacity (uptake) decreases (Fig. 4).

Figs. 5 and 6 show that as the temperature increases the adsorption rate increases so that the time to achieve concentration equilibrium at a temperature of 293K is 1300 minutes, at a temperature of 303K, the necessary time to reach equilibrium is about 950 minutes and a temperature of 313K time to reach equilibrium is about 550 minutes.

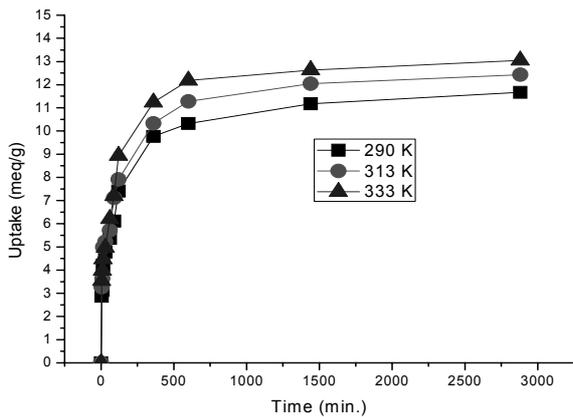


Fig. 5 – Variation of concentration of anions nitrate adsorbed on cellulose membrane, with time at different temperatures.

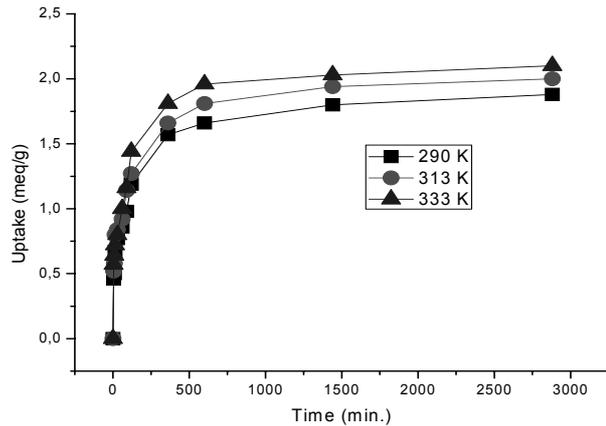


Fig. 6 – Variation of concentration of anions phosphate adsorbed on cellulose membrane with time at different temperatures.

For nitrate and phosphate at different temperatures: 293K, 303K and 313K it can be concluded that the stage determining the internal diffusion rate is due to pore diffusion constant values which are about ten times smaller than constant values diffusion in the film.

2. Zeta potential measurements

ζ -Potential measurements were carried out with a Microelectrophoretic zeta potential analyzer at 295-301K. In order to reduce the effect of concentration polarization and prevent any change in pH, the direction of the electric field was reversed several times in each measurement and the average value of electroosmotic flow was used for calculating the zeta potential. The pH was checked before and after each experiment to ensure that no change had occurred.

The electrophoretic mobility of the dispersion transferred into the microelectrophoretic cell was measured. The ζ potential was calculated using the Smoluchovski equation:

$$\zeta = \frac{4\pi\eta U}{\varepsilon} \quad (2)$$

ε = dielectric constant;

η = viscosity;

U= electrophoretic mobility;

In water at 298K, the relationship between electrophoretic mobility and zeta potential reduces to:

$$\zeta = \frac{93.09}{Time} \quad (3)$$

The interaction of colloidal particles with membrane surfaces in aqueous media is dependent

on, among other variables, the zeta (electrokinetic) potentials of the membrane surface and suspended particles. These, in turn, are controlled by the surface chemistry of the membranes and colloidal particles, as well as by the chemistry of the solution. Hence, the determination of zeta potential of cellulosic membranes at various solution chemistries is of paramount importance.

When brought into contact with an aqueous electrolyte solution, cellulosic membrane surfaces acquire an electric surface charge through several mechanisms. These mechanisms include dissociation (ionization) of surface functional groups, adsorption of ions from solution and adsorption of polyelectrolytes, ionic surfactants and charged macromolecules.

The zeta potential is a measurable parameter, related to the charge and electric double layer of surfaces in aqueous solutions. For macroscopic surfaces, as in the case of cellulosic membranes, the zeta potential can be determined by the streaming potential technique.

It is shown that solution chemistry plays an important role in controlling the zeta potential of cellulosic membranes.

The zeta potential studies of nitrate from water on cellulosic membrane were conducted in the following conditions: 50 and 200mg/L initial concentration of anion and 0.1M NaCl electrolyte solution.

It was noticed that the zeta potential decreased when we put an electrolyte (0.1M NaCl) (Figs. 7-8). This was due to the decrease in the effective thickness of the diffused layer as the ionic strength increases. The increase in ionic strength leads to a compression of the diffuse layer.

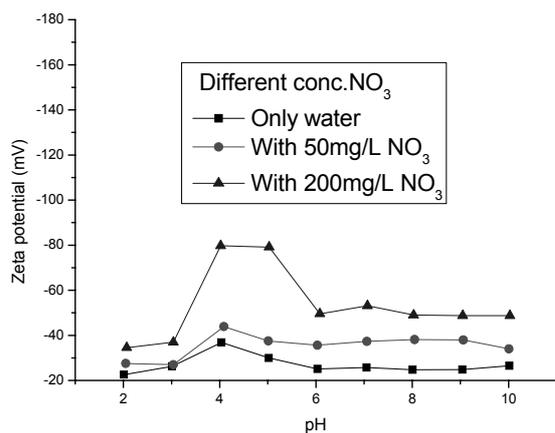


Fig. 7 – pH dependence versus zeta potential in the nitrate solution, with 0.1M NaCl electrolyte, on cellulosic membrane.

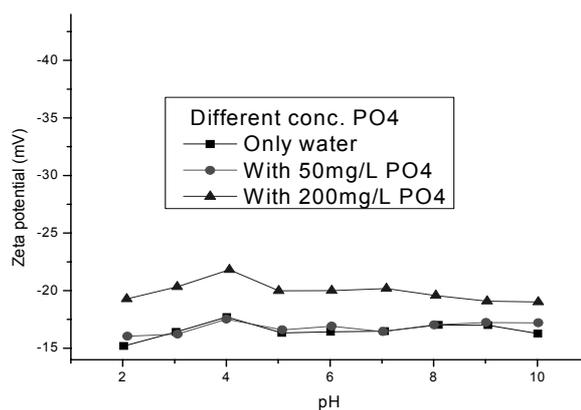


Fig. 8 – pH dependence versus zeta potential in the phosphate solution, with 0.1M NaCl electrolyte, on cellulosic membrane.

Based on these results, the following observations are made: (i) the zeta potential is negative at all pH values investigated; (ii) the zeta potential becomes more negative as the pH increases; (iii) for pH values greater than about 5, the zeta potential becomes more negative as the ionic strength increases.

CONCLUSIONS

The streaming potentials of cellulose membranes were studied with NaCl electrolyte solutions to investigate the influence of salt type and concentration on the zeta potential and kinetic surface charge density of the membranes. The zeta potentials decreased with increasing salt concentration, whereas the kinetic surface charge densities increased. The kinetic surface charge densities could be described by Freundlich isotherms, except in one case, indicating that the membranes had a neglectable surface charge. The kinetic surface charge density noticed was caused by adsorbed anions. Salt retention measurements showed different mechanisms for salt separation for the two investigated anions.

The temperature was not found to have any significant effect on membrane zeta potential; however, the effect of pH and concentration of different ions had pronounced effects on the surface charge and zeta potential.

Adsorption studies were performed according to two parameters: pH and concentration solutions. Langmuir equation characterized very well the experimental data for both nitrate and phosphate ions. Maximum adsorption capacity for nitrate ion

was higher compared to that of phosphate ion which means that cellulose membrane has a much higher adsorption capacity for nitrate ion than phosphate ion.

Maximum adsorption capacity for nitrate ion is about 2.17meq/g and for the phosphate anion is about 0.87meq/g, which means that the cellulose membrane has a much higher adsorption capacity for nitrate ion than phosphate ion. Langmuir equation characterized very well experimental data only for nitrate anion.

Since the regression coefficient values is around the values of 0.9990 to 0.9672 for phosphate and nitrate anion which means that Freundlich equation characterized very well the adsorption of phosphate anion than of nitrate anion. The pH influences the adsorption process: as pH increases the adsorption capacity decreases.

Temperature influences the time required to achieve equilibrium adsorption process, as temperature increases the time required to achieve equilibrium decreases for both anions. Cellulose membrane with a pore size of 0.2 μ m is suitable to be used for retaining nitrate and phosphate anions from potable water.

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