

**PHOSPHATE ADSORPTION ON MANGANESE AND IRON  
OXIDES AND ACID - LEACHED SEDIMENTS FROM THE  
CONTINENTAL SHELF OF EGYPT.**

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**ABSTRACT**

Experiments were designed to ascertain the respective role of the three sediment components: iron oxide, manganese oxide and other mineral constituents on phosphate ion removal from sea water under different conditions. The results showed that the adsorption capacity of  $Fe_2O_3$  is 1.5 to 4.0 times that of the acid treated sediments. Manganese dioxide adsorbs 2.0 to 4.5 times the amount absorbed by acid leached sediments. Several factors affect the adsorption process of phosphate on both oxides and other sediment constituents.

The hydrogen ion concentration seems to be the most important factor. Maximum adsorption occurs at pH range between 6 and 8; it ceases to occur below pH 2 and above pH 11. Concentration of phosphate ion in solution also affects the rate of reaction. Salinity variations within the range of 27‰ to 39‰ do not affect the adsorption of phosphate by  $Fe_2O_3$ ,  $MnO_2$  or other mineral constituents to any notable degree. It is suggested that most of phosphate ions are removed from the Nile waters before it reaches the sea. Areal steady state equilibrium between phosphate ions in solution and phosphate ions adsorbed on both  $Fe_2O_3$  and  $MnO_2$  is not reached in a short time intervals, but requires probably several hundreds of days.

**INTRODUCTION**

The Nile outflow was the major supply of fresh water and nutrients to the Eastern Mediterranean Basin before the construction of the new Aswan High Dam. The river outflow carried annually about  $5 \times 10^3$  tons of phosphate -P (Halim, 1960); the greater part of which was controlled by reactions taking place between the dissolved species and the particulate suspended matter. Halim and Morcos (1966) suggested that nutrients are adsorbed onto the suspended particulate matter in the river, desorption takes place in the sea until a new equilibrium is reached between dissolved and adsorbed phosphate ions. Berner (1973) pointed out the importance of iron oxide in removal of phosphorus from sea water. Chemical analysis

of ferro-manganese oxides from different environments indicate the presence of high concentrations of phosphorus in association with these oxides (Manheim, 1965; Mero, 1969). Sedimentary particles of the Nile are invariably stained with a reddish tint, mainly due to iron oxide coating. Beltagy et al. (1983) studied the distribution of non-detrital iron, manganese and phosphorus in the sediments off the Nile Delta. They found that phosphorus in the sediments is in excess of what is assumed to be in association with iron and manganese, and suggested that phosphorus may be associated with organic constituents.

Buljan (1957) had carried out some experiments on the artificial fertilization of natural waters with phosphate, and examined the behaviour of phosphate ions in these waters. Jitts (1959) investigated the effect of pH, particle size, iron and organic matter on the adsorption of phosphate by estuarine sediments and found the adsorption to be directly related to the ratio of iron to organic matter.

The present work was designed to study the respective role of iron oxide, manganese dioxide and other sediment components in the removal of phosphate ions from sea water under different conditions. It is hoped that the results obtained would be of some value for problems related to the role of sediments in transport and removal of pollutants in the area.

## MATERIAL AND METHODS

### a- Preparation of Sediment Samples

About 20 g. of the original untreated samples were washed until chloride free, dried at 95°C, ground gently in an agate mortar and sieved to pass 125 standard mesh size sieve.

Three grams of each chloride free, oven dried sediment samples were leached for 24 hours with 50 ml of 2% HCl, filtered, washed, then dried at 95°C for 6 hours and kept for the adsorption experiments. The hydrochloric acid extract of each sample was made up to a standard volume to be used later for the determination of PO<sub>4</sub>-P, Fe and Mn. Table 1 gives the characteristics of the sediment samples used in the present study, also locations of these samples are given in Fig. 1.

### b- Preparation of Fe<sub>2</sub>O<sub>3</sub>

Ten grams of ferric chloride were dissolved in 100 ml acidified distilled water. Ammonium hydroxide was added until no further precipitation occurred. The precipitate was filtered washed, dried and heated vigorously in a nickel crucible for 5 hours. The oxide obtained was then ground in an agate mortar to pass 125 standard mesh sieve. It was also examined under the microscope to insure uniformity.

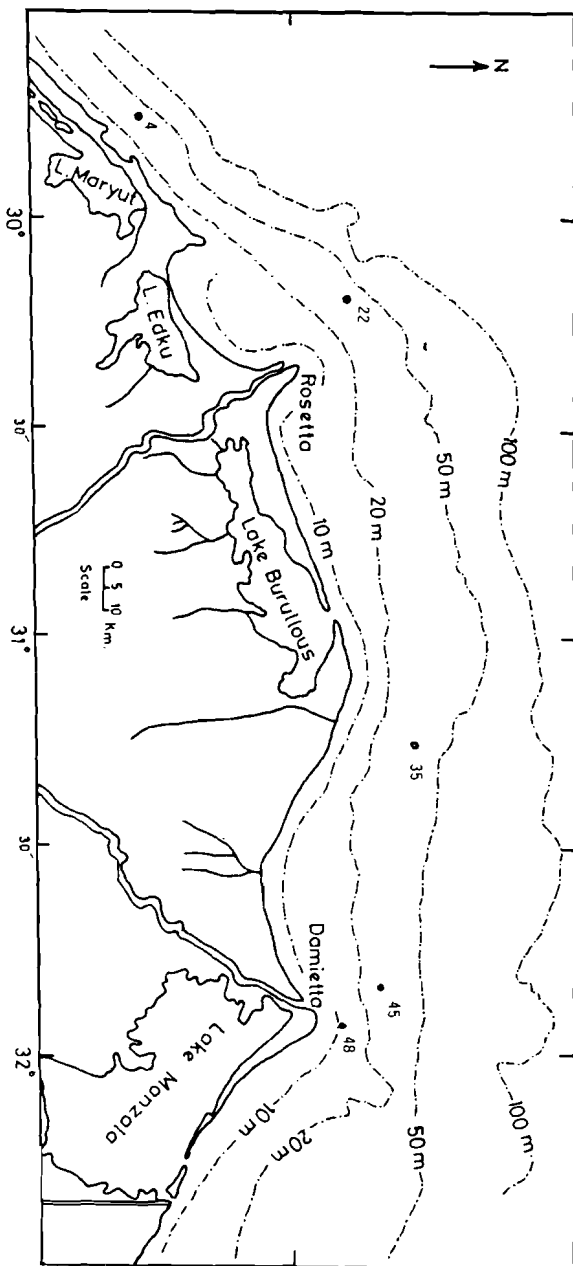


Fig. (1)  
Locations of sediment samples used in the present study.

#### **c- Preparation of MnO<sub>2</sub>**

Ten grams of potassium permanganate were dissolved in 100 ml distilled water, filtered and the solution was reduced with excess H<sub>2</sub>O<sub>2</sub>. The precipitated MnO<sub>2</sub> was filtered, washed, dried and then ground to pass 125 standard mesh sieve.

#### **d- Preparation of Trace Metal Free Sea Water**

Forty liters of sea water were filtered, the pH was adjusted to 11 using 30% NaOH solution. Calcium and magnesium hydroxides were precipitated scavenging with them most of the trace elements. The supernatant solution was filtered, adjusted to pH 8 using dilute HCl. The salinity was adjusted to 38.5‰ using A.R. sodium chloride.

#### **e- Adsorption Experiments**

Experiments on the effect of varying pH, ion concentration, weight of solid material in suspension and salinity were conducted. All experiments were performed for a duration of one hour as a constant time, at pH 8 and salinity 38.5‰, except for these carried out with varying times, pH and salinity. The pH was adjusted using an electronic pH meter and salinity was adjusted using an induction salinometer. A constant weight of 20 mg of each of Fe<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub> were used in every experiment, except those experiments carried out with varying weight.

Experiments involving acid leached sediments were carried out as follows: i) 40 mg for experiments involving time effect; ii) 40 mg from samples 4 and 22, 24 mg from samples 45 and 48, and 30 mg from samples 35 for all other experiments.

Experiments were carried out in 100 ml stoppered acid washed cylinders vigorously shaken every five minutes. Adsorbed phosphate ions was measured as the difference between the original and final phosphate concentration in solution.

## **RESULTS**

### **A- Phosphate Adsorption On Iron and Manganese Oxides**

#### **1- Rate of Phosphate Ion Removal**

The adsorption isotherms for ferric oxide and manganese dioxide at different concentrations within time intervals from 5 to 4320 minutes are shown in Fig. 2.

A higher rate of adsorption is observed in the first 300 minutes. The onset of equilibrium depends on the original concentration of phosphate in solution, the higher the concentration the shorter the time needed. No true equilibrium was attained however, particularly, at lower concentrations. This may be due to the change in the type of adsorption process between the respective oxide and phosphate ions (see for ex. Olson and Watenable, 1957).

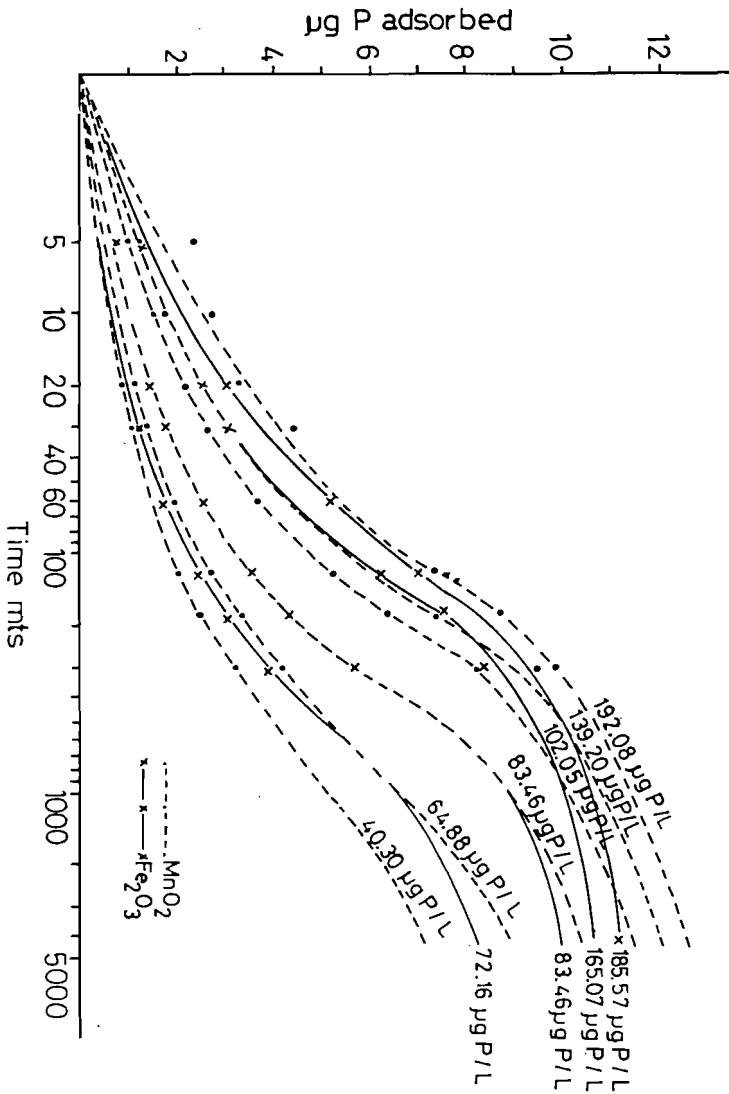


Fig. (2)  
 Rate of phosphate adsorption from sea water by Mn O<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>  
 at different phosphate concentrations.

After 4320 minutes the observed values of adsorbed phosphate on iron oxide and manganese dioxide were 11.19 and 12.55 mg P/g respectively. The maximum rate of adsorption was within the first 5 minutes, where 12.99% and 12.39% of the total phosphate ion in solution were adsorbed by iron oxide and manganese dioxide respectively. At the same concentration levels, 60.38% and 65.35% of phosphate ions in solution were removed after 4320 minutes by the two oxides.

The adsorption isotherms within the given limits of concentrations may be represented by the formula:

$$Y = at^{\frac{1}{2}}$$

where: Y = total phosphate removed from solution, t = time in minutes and a is constant depending on the original phosphate concentration. Plotting a against concentration results in a straight line relationship (Fig. 3) which can be fitted by the equation  $a = kC$  where C = original concentration, and k is constant. Thus, before equilibrium, the total amount of phosphate adsorbed may be obtained from the relationship:

$$Y = kC \cdot t^{\frac{1}{2}}$$

### 2- Effect of Varying the Suspension Load

The proportional increase of the available surface area within the amount of oxide in suspension depends on the particle size and the homogeneity of the oxide in suspension. The microscopic examination of the particles revealed that they are homogenous without noticeable difference in the particle size.

Within an hour, 5 mg of each of the iron oxide, and the manganese dioxide adsorbed 6.93% and 6.77% of the phosphate present. 37.73% and 32.84% of the phosphate were removed by 25 mg of each of the oxides. The relationship between the amount of adsorbed phosphate and the weight of suspended oxide can be represented by the equation:

$$y_w = k_w \cdot W$$

where:  $y_w$  = amount of phosphate adsorbed, W = weight of the oxide in suspension and  $k_w$  is constant. This relationship is presented graphically in Fig. 4.

### 3- Effect of Phosphate Ion Concentration

For a constant time interval of one hour, a straight line relationship exists between phosphate adsorbed and phosphate ion concentration in solution (Fig. 5). However, it appears from the present study that the original phosphate concentration affects both the rate of adsorption and the amount of phosphate adsorbed. Thus, at any concentration the relationship may be represented by the equation;

$$Y_c = K_c \cdot C,$$

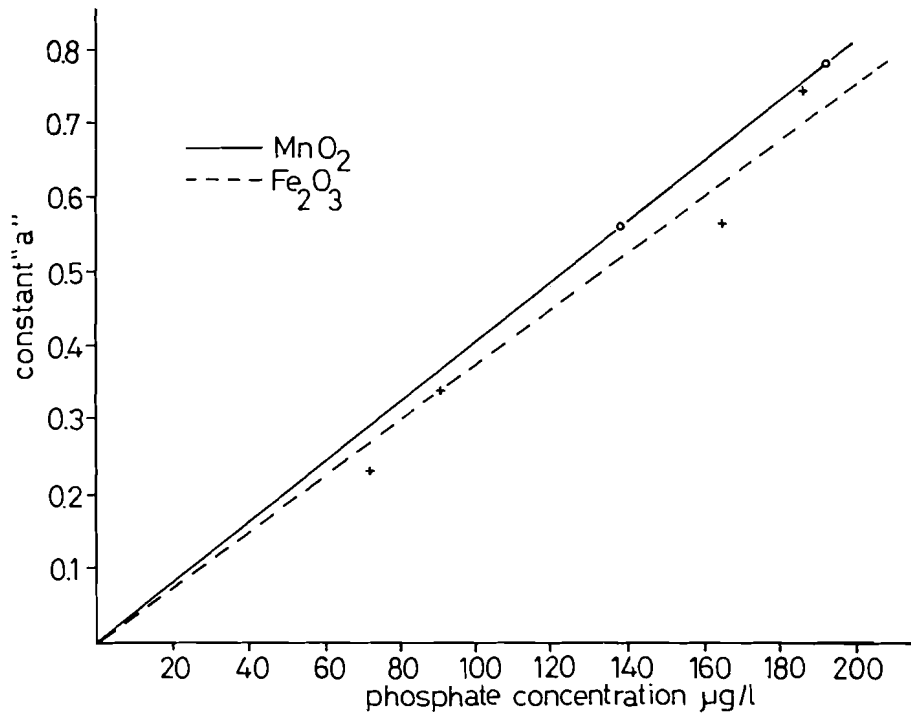


Fig. (3)  
The rate of phosphate adsorption by MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> in relation to phosphate concentration.

where:  $Y_c$  = the amount of phosphate adsorbed,  $K_c$  = constant, specific for each concentration and  $C$  is the concentration of phosphate ion in solution.

#### 4- Effect of pH

The effect of pH on the adsorption of phosphate ions by iron oxide and manganese dioxide is shown in Fig. 6. Maximum adsorption for ferric oxide and manganese dioxide takes place in a narrow pH range between 6 and 8. No adsorption occurs below pH 5 or above pH 11 with iron oxide, not does it occur below pH 2 or above pH 10 with manganese dioxide.

#### 5- Effect of Salinity

It appears from Fig. 7, that phosphate adsorption is completely independent of salinity in the range between 22% and 39%.

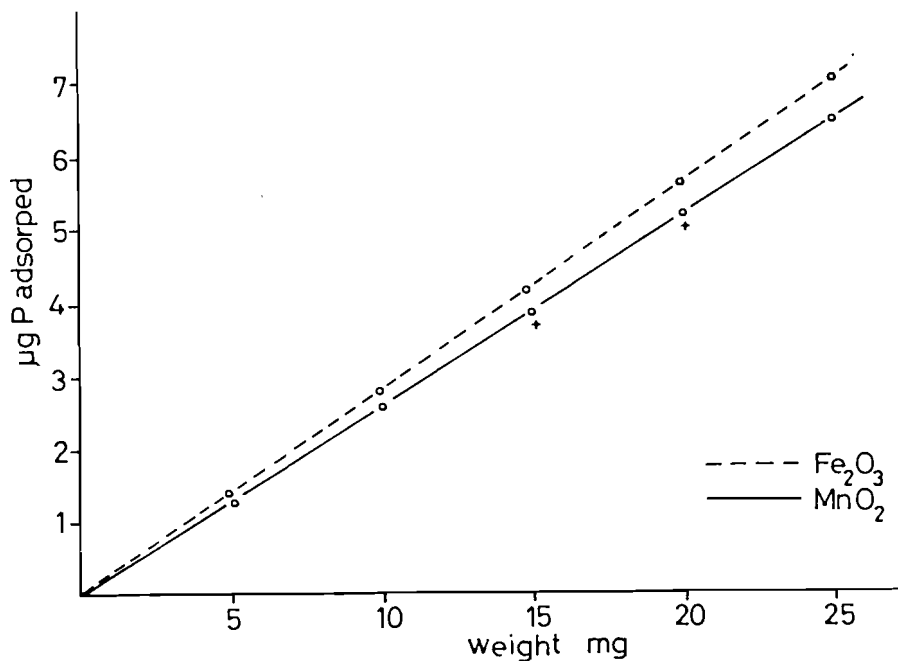


Fig. (4)  
Effect of weight of Fe<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub> in suspension of phosphate adsorption from sea water.

## B- Phosphate Adsorption on Acid Treated Sediments

### 1- Rate of Phosphate Ion Removal

The adsorption isotherms of the five sediment samples (Table. 1), within time intervals varying from 5 to 900 minutes at a constant phosphate concentration of 187.7 ug PO<sub>4</sub>-P/l are shown in Fig. 8.

For all samples examined, the first segment of the isotherms is characterized by its steepness, which is followed by a plateau. This indicates a higher rate of adsorption in the first few minutes. The equilibrium is reached after variable time intervals for different samples. Sediment 35 which is a sandy-silt-clay sample, adsorbed small amount of phosphate compared with other samples, particularly samples 45 and 48 that are mainly silt. It appears however, that the state of equilibrium is approached within 30 to 60 minutes, and in all cases it was reached in a less than 900 minutes.



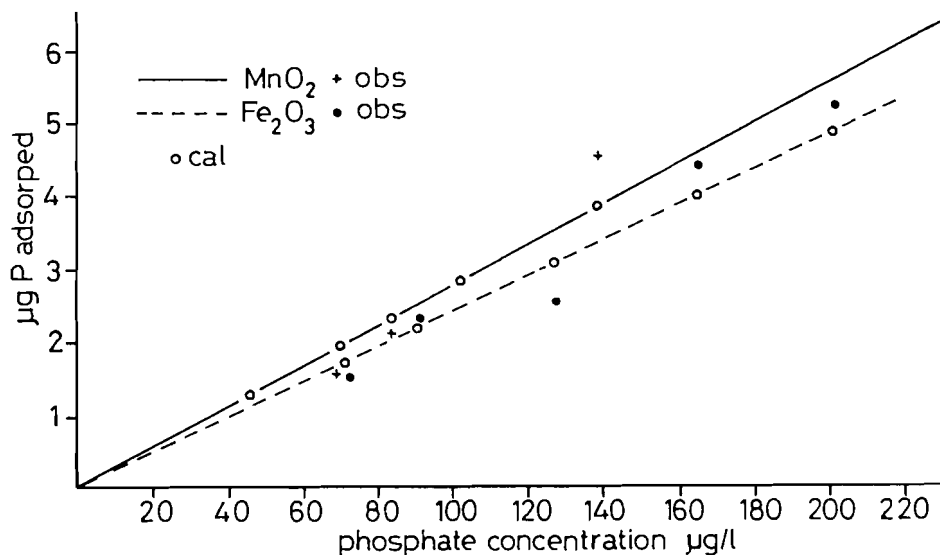


Fig. (5)  
Effect of phosphate concentration on adsorption from sea water by  
 $MnO_2$  and  $Fe_2O_3$ .

## 2- Effect of Varying Phosphate Concentration

Figure 9 shows the phosphate uptake by different sediment samples. It appears that sediment samples No. 35, 45 and 48 behave similarly. Phosphate adsorbed increases with increasing phosphate concentration in solution up to a concentration of 290  $\mu\text{g P/l}$ . Samples No. 4 and 22 however, ceased to adsorb phosphate ions at much lower concentration (120  $\mu\text{g P/l}$ ).

## 3- Effect of varying the sediment load in suspension

The adsorption isotherms of different sediment samples are given in Fig. 10. As was observed for iron and manganese oxides, phosphate adsorbed by the sediments showed proportional increase with the weight of sediment in suspension. However, at the same phosphate ion concentration of 187.7  $\mu\text{g P/l}$ , the constant of proportionality is different, being lowest for sample No. 35 and highest for samples No 45 and 48.

## 4- Effect of pH

The effect of varying pH on phosphate ion adsorption by different type of sediments is shown in Fig. 11. The five curves are also dome shaped with maximum adsorption at a critical pH range of 6 to 8. For each sediment however, the peak falls within a narrow range. No appreciable adsorption was observed below pH 4 or above pH 10.

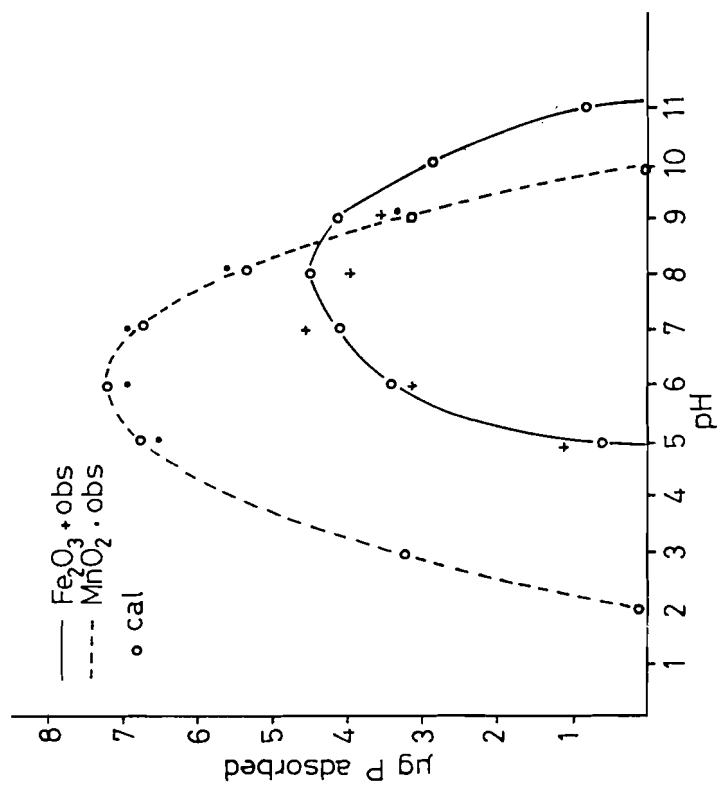


Fig. (6)  
Effect of pH on phosphate adsorption by Iron and Manganese oxides.

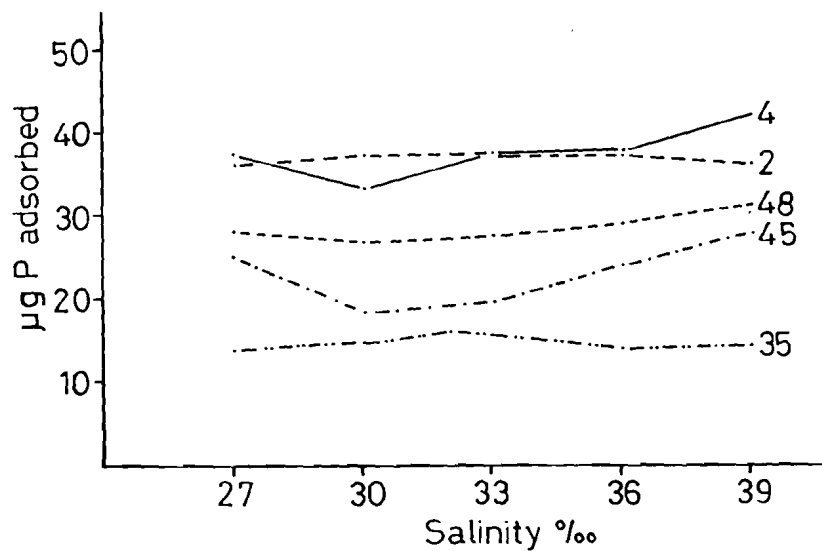


Fig. (7)  
Effect of salinity on phosphate adsorption from sea water  
by different types of sediments.

TABLE (1)  
Type and characteristics of the sediment samples.

Sample	Depth	Type of	Wt. %			
			Carbonate	Iron	Manganese	Phosphorus
4	37	Sandy silt	13.9	0.79	0.04	0.05
22	30	Silty sand	6.9	0.94	0.07	0.065
35	27	sandy silt clay	8.3	0.78	0.03	0.06
45	22	silt	20.7	0.64	0.06	0.04
48	10	silt	6.6	0.90	0.06	0.05

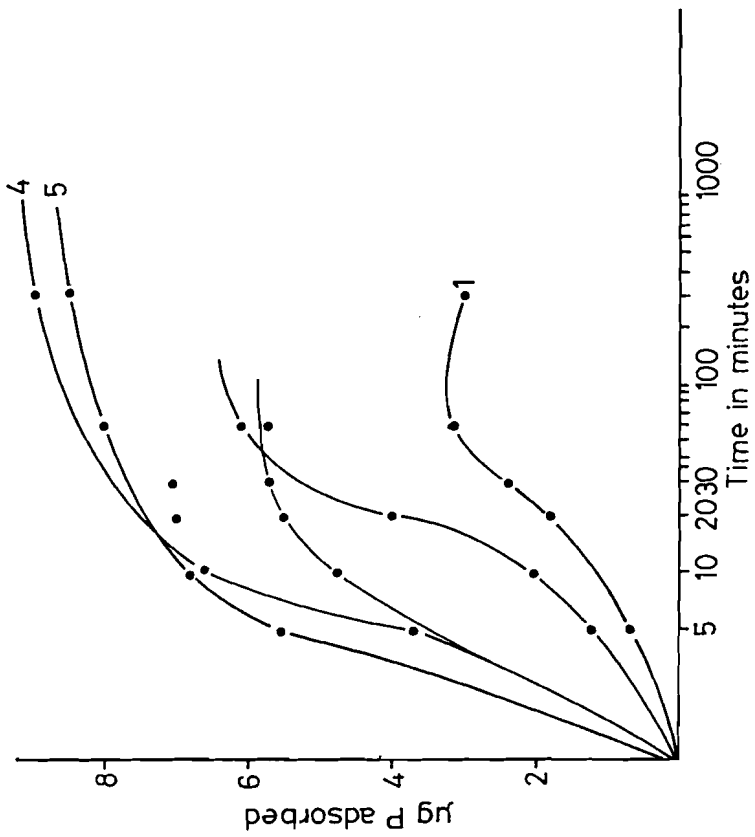


Fig. (8)  
Rate of phosphate adsorption by different types of sediments.

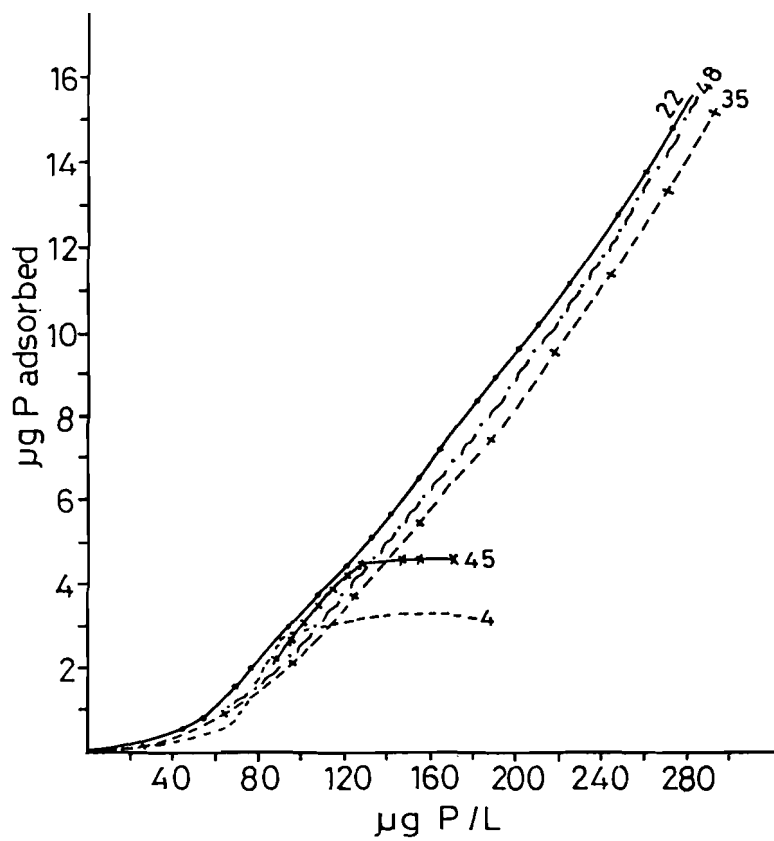


Fig. (9)  
Effect of phosphate concentration on phosphate adsorption  
from sea water by different types of sediments.

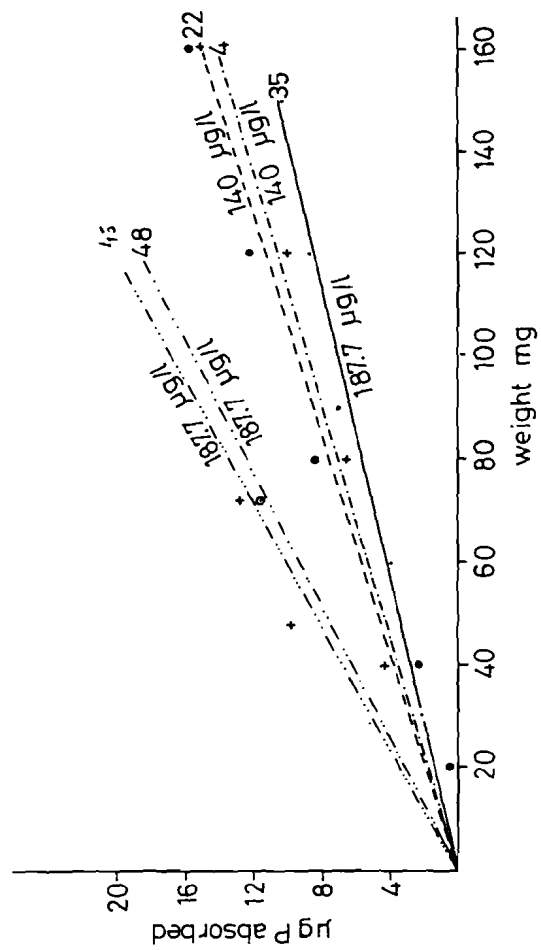


Fig. (10)  
Effect of weight of sediments in suspension on phosphate adsorption from sea water.

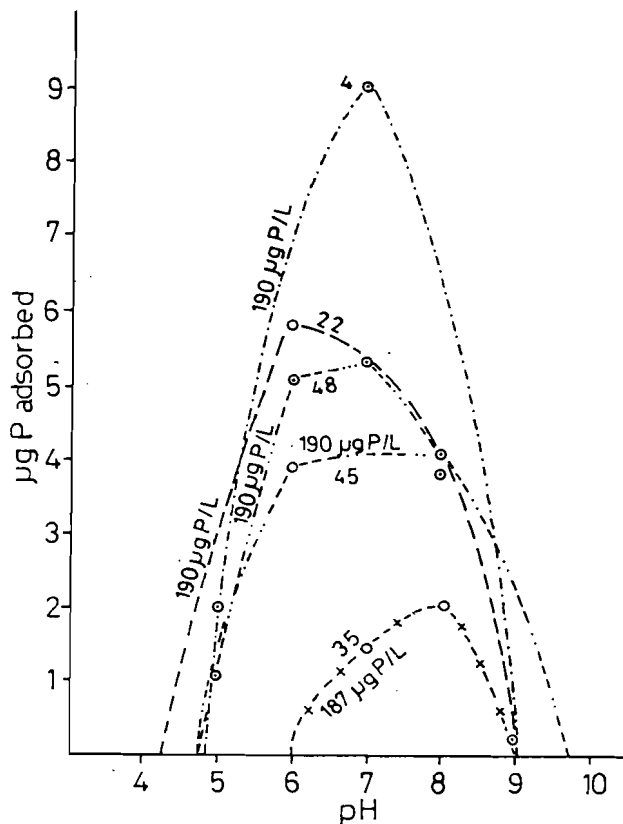


Fig. (11)  
Effect of pH on phosphate adsorption from sea water by different types of sediments.

**5- Effect of Salinity**

salinity variations seem to have no effect on the process of phosphate ion adsorption from sea water in the range of salinity between 27% and 39% (Fig. 12).

**DISCUSSION**

Solutes tend to accumulate at interfaces if surface tension is thereby lowered, and this process is called adsorption. In sea water, finely divided organic and inorganic particles are present and adsorption of soluble species on particles is the major means of interaction between solid and solution

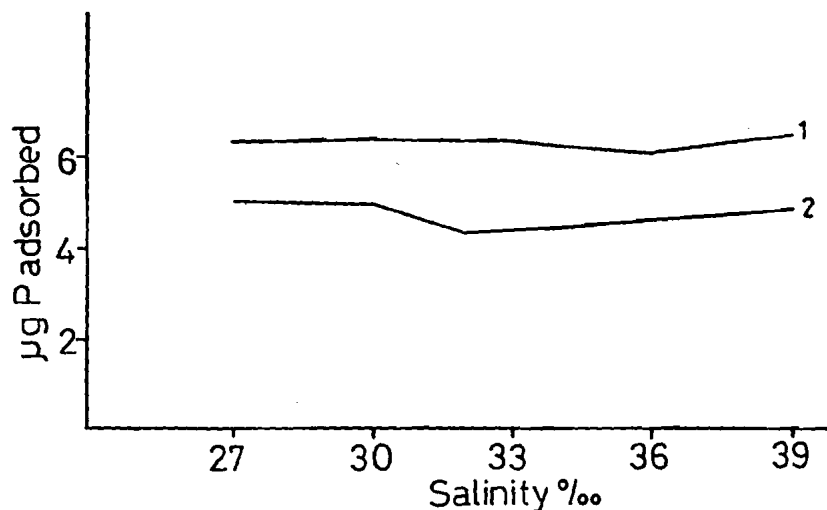


Fig. (12)  
Effect of salinity on phosphate adsorption  
from sea water by MnO<sub>2</sub> (1) and Fe<sub>2</sub>O<sub>3</sub> (2).

phases. Three types of adsorption mechanisms were recognized: i) mechanical or physical adsorption; ii) ion-exchange adsorption; and iii) chemical adsorption. The third type is irreversible and ions adsorbed can be removed only by the destruction or structural modification of the parent material (Subramanean et al., 1974).

The results of the present study indicate that adsorption of phosphate ions on both iron oxide and manganese dioxide is not a simple reaction. Variation of the amount of phosphate adsorbed on these oxides with time, showed a stepwise pattern. This may indicate that the first layer of phosphate ions adsorbed on to the surface of these oxides can no longer stay at the adsorption sites on the surface of the compound, it rather get fixed in the solid phase and a form of complex similar to that suggested by Williams et al. (1976). The formation of the complex leads to the creation of new sites ready to adsorb more phosphate ions until quisequilibrium is reached, this equilibrium is a transition stage before the complex is formed and another adsorbed layer starts to develop. Thus, a true equilibrium may never be reached or it would a very long time to take place.

Amorphous hydrated ferric oxide has an isoelectric point of 8.5, and at pH values below IEP, can remove as much as 5% of its own weight of phosphorus in orthophosphoric formm solution (Stamm and Kohlstchutte,



1965). The formula of the resultant hydrous ferric oxide orthophosphate complex can be written as  $Fe_x(OH)_{3(x-y)}(PO_4)_y \cdot z(H_2O)$ . It might be possible, thus, that manganese dioxide gives similar complex with phosphate ions in solution. Release of phosphate ions from these complexes seem to be very difficult process and may need complete or partial destruction of the parent material. Such conditions is not likely to occur in the sea under normal conditions, and only when anoxic conditions in the water or suitable variation in the oxidation reduction potential in the sediments would occur, one expect that phosphate ions could be released. This may mean that adsorption on iron and manganese oxides form, under normal condition, a sink for phosphate, and may be other ions.

The effect of pH seem to agree with what proposed by Kester et al. (1975) where maximum adsorption occurs around the isoelectric point of the oxides.

Other parameters seem to affect only the rate of removal of ions from solution rather than the amount adsorbed at equilibrium when it is reached between the oxides and ions in solution.

Acid treated sediments exhibited physical and may be, ion exchange adsorption mechanism. This is shown by their adsorption isotherms (Fig. 8). A state of equilibrium is reached within time intervals varying between 10 and 60 minutes. The amount of phosphate ions removed from solution is proportional to the amount of suspended sediments. This is in accordance with the known Langmuir and Freundlich adsorption isotherms; since the amount of phosphate ions removed will be proportional to the surface area available. However, it is likely that ion-exchange adsorption occurs on clay constituents of the sediments, and may be humic substances. This is evidenced by the varying rates of reaction of different sediments which correspond almost to their particle size composition. Silty and silty clay sediments adsorbed more phosphate and required longer time to reach equilibrium than sand and sandy silt sediments. According to Beltagy (1973) and Beltagy et.al (1972) the mineralogy of a sediment can be related to the particle size composition of the sediment. Quartz and less degraded minerals are concentrated in the sand or coarser fraction, and clay minerals and highly degraded minerals are concentrated in the finer fractions. Sediments before the Nile Delta are mostly derived from suspended matter carried down by the River. This suspended material contains a relatively high concentrations of clay minerals. Like any tropical river, kaolinite, illite are dominant constituents of the suspended load. Compared with sediments rich in montmorillonite and highly degraded illite, it is expected that these deposits will have lower capacity for ion exchange adsorption.

However, sediments No. 33, 45 and 48 which are mainly river derived sediments have much higher capacity to absorb phosphate ions than sediments No. 22 and 4. Still sample No 22 which was sampled just west of the river estuary of Rashid, has higher adsorption capacity than sediment No. 4 collected from the west of Alexandria, opposite to Lake Maryut, with very little contribution from the river suspended load.

Phosphate ions removed on the acid leached sediments are directly related to the amount of sediment in suspension, with ion concentration being the governing factor of the rate of reaction. pH however, stands as the main factor that affects the adsorption process on sediment particles. Thus, at pH between 6 and 8 sediments adsorb phosphate from solution, below pH 4 and above pH 10 adsorption ceases to occur. Thus, slightly more phosphate ions are removed by the sediment at pH between 6 and 7, which is the pH of the Nile water near the estuary, than in sea water. Accordingly, it seems that with the negligible effect of salinity changes on the adsorption of phosphate, pH is the controlling factor to the adsorption or release of phosphate ion by sediment particles in this area. It remains, however, that iron and manganese oxides adsorb more phosphate ions than acid treated sediments. Because of the low concentrations of these compounds in the sediments off the Nile Delta (Beltagy et al, 1983), they play a limited role in the removal of phosphate ion from sea water. Removal of phosphate ions, and probably other ions, is mainly achieved by other mineral constituents and organic matter.

#### CONCLUSION

Adsorption of phosphate ions on both iron oxide and manganese dioxide is mainly chemical, with the formation of metal oxide-phosphate complex. Real equilibrium is not reached in a short time, and large quantities of phosphate ions are removed by these oxides before equilibrium is reached. The complexes formed are not easily destroyed, and phosphate ions are not released when minor changes in the environment occur. The pH is significant factor in affecting the adsorption of the ions on these oxides. On the other hand, adsorption of phosphate ions on acid leached sediments seem to be a mixed physical and ion-exchange modes of adsorption. Equilibrium is reached relatively fast. The reaction is still pH dependent. Salinity does not affect the removal of phosphate ions by sediments or the oxides in the range of 27%-39%. It is likely that phosphate ions are adsorbed in the river onto the suspended particles. In the sediments of the Nile Delta, iron and manganese are present in a small quantities to account for the total phosphate in the sediments, it is suggested that phosphate ions may be associated with sediment organic matter, besides other mineral phases.

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