

# Real-World vs Simulation - A Study Towards the Development of a Phosphate Ion Selective Electrode (P-ISE)

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**Abstract** - Phosphorus is a scarce and finite resource on the planet, and its non-gaseous environmental cycle makes access to non-mining means unavailable. At the same time, it is also one of the three most important (N, P, K) phytonutrients. It is added to agricultural soil by applying chemical fertilizer and spraying manure. However, when not completely consumed by crops and plants, it can be mobilized under reduced conditions and enter groundwater and surface water as leachate and / or runoff. To reduce the impact on this issue, research in this area is primarily focused on finding more optimal application rates (manure and chemical fertilizers) and efficient ways to recycle phosphorus. Accurate quantification of phosphate recovery can be achieved by performing a number of real-time, high spatial resolution soil measurements. However, there are currently no commercially available sensors that can measure soil phosphorus in real time on the go. The research described in this white paper is a preliminary attempt to solve this challenge.

**Index Terms** – Phosphorus, phosphate fertilizers, manure, phosphate ion selective electrode (ISE), potentiometry, cobalt rod, proximal soil sensing, precision agriculture.

## INTRODUCTION

Phosphorus is one among the three most essential (N, P, K) crop nutrients. Although phosphorus is referred to be very immobile, many cases of cyanobacteria and algae boom on Canadian surface water bodies has revealed a rising concern and researchers have confirmed that it is caused by agriculture based non-point source pollutants such as phosphates and nitrates [1]. Phosphorus is added to agriculture soils by applying chemical fertilizers and by applying manure

and if not completely consumed by crops and plants, can mobilize in reduced conditions and end up in ground water and on surface waters due to leaching and/or runoff respectively [2]. On the other hand according to some researchers, earth's phosphorus is going to reach its peak production by 2030 and the reserves are expected to be completely depleted in 50–100 years. Peak phosphorus is the point in time at which the maximum global phosphorus production rate is reached. Phosphorus is a scarce finite resource on earth and due to its non-gaseous environmental cycle has resulted in alternative means other than mining being unavailable [3, 4].

To reduce the impact on this problem, the research in this domain primarily focuses on discovering more optimal application rates (manure and chemical fertilizers) and efficient methods of recycling the phosphorus [5]. Accurate quantification of phosphate application rates can be done by taking large number of real-time ground measurements over a high spatial resolution. But currently there is no commercial sensor available which is capable to measure soil phosphorus in real-time and on-the-go

According to [6], experiments were conducted by adding cobalt oxide to soil/water solutions containing various concentrations of phosphates. Cobalt oxide has proven to be an efficient phosphate adsorbing agent, and therefore can be used to remove access phosphates from recycled water usage [7]. According to [2,8-11], it has been demonstrated (in lab) that cobalt oxide can be used as a phosphate ion specific electrode (P-ISE). There are more or less discrepancies about the mechanism, and therefore it is not very clear if such an (P-ISE) can be used as a real-

time sensor to measure phosphates in soil solutions and water samples on the go [12-15].

To address this issue, the first objective of the study discussed in this paper is to conduct some experiments of measuring the cobalt electrode response to various P concentrations, in presence and absence of other anions. Here, it is assumed that the mechanism is somewhat of an adsorption type, where  $H_2PO_4^-$  anions are adsorbed on the cobalt oxide surface generating a slightly negative potential w.r.t the reference electrode. The second objective is to replicate the results using simulations of the phosphate adsorption experiments similar to conducted in [6]. In addition to this, the author has also considered the presence of other anions and has tried to discuss the effects on phosphate adsorption due to increased ionic strength and therefore a decreased phosphate ion activity.

## MATERIALS AND METHODS



Figure 1: Real-time soil phosphate ion measurement setup

The setup used to conduct real-time experiments is illustrated using figure 1. The setup consists of an in house developed cobalt rod based phosphate ion detection electrode. It was accompanied with a standard glass pH electrode as well as a reference electrode. A standard ion meter was used to measure the responses from all three aforementioned electrodes. In simulation, the adsorption mechanism discussed in this paper is done using MS-Excel using the Freundlich Adsorption Isotherm equations. All the values and parameters used in the equation are taken from literature [6] as it is. The process is simulated in

6 steps using the equations and sample calculations as listed below. Results from sample calculations are shown in figures as followed.

### Equations [2]:

$$\text{Fraction } H_2PO_4^- \text{ (MF)} = \frac{1}{\frac{10^{-19.55}}{[H^+]^2} + 10^{2.5} \times [H^+] + 1 + \frac{10^{-7.2}}{[H^+]}}$$

Eq. No. (1)

$$\text{Concentration (C)} = F \times \text{Molarity} \quad \text{Eq. No. (2)}$$

$$\text{Ionic strength (I)} = \frac{1}{2} \sum_i C_i Z_i^2 \quad \text{Eq. No. (3)}$$

$$\text{Activity co-efficient } (\gamma) = 10^{-(AZ_i^2 \left( \frac{\sqrt{I}}{1+\sqrt{I}} \right) - 0.3I)} \quad \text{Eq. No. (4)}$$

$$\text{Activity} = \gamma \times C \quad \text{Eq. No. (5)}$$

$$\text{Freundlich equation: } \log_{10} \text{ sorbed}^* = \log_{10} K + b \times \log_{10} \text{ sorbent}^{**} \quad \text{Eq. No. (6)}$$

Sorbed\*: The quantity is as concentration in mol g<sup>-1</sup>

Sorbent\*\*: The quantity is as concentration and activity in mol L<sup>-1</sup>

### Sample calculations [2]:

Consider a soil solution (10 ml @ pH 4.0) containing, 0.1M, Na<sub>2</sub>SO<sub>4</sub>, 0.1M KCl, 1mM PO<sub>4</sub> and 0.1g of Co

- Using equation (1) above, the molar fraction of  $H_2PO_4^- = 0.985$
- Using equation (2) above, the concentration of  $H_2PO_4^-$  is 9.85E-04 M
- Using equation (3) above, the total ionic strength can be calculated as: Total-IS = IS(0.1M Na<sub>2</sub>SO<sub>4</sub>) + IS (0.1M KCl) + IS(0.000985 M  $H_2PO_4^-$ ) + IS(0.001M H<sup>+</sup>) = 0.35.
- Using equation (4) above, the activity co-efficient for  $H_2PO_4^-$  is calculated as 0.74
- Using equation (5) above, the activity is calculated as 7.32E-04 M
- Using the parameters from table (1), all above calculated values and inserting them in equation (6) above the amount of  $H_2PO_4^-$  adsorbed can be calculated as  $\text{Log}_{10} (H_2PO_4^- \text{-sorbed}) = -0.653 \text{ mol g}^{-1}$

## RESULTS AND DISCUSSION

The cobalt, pH electrode responses are shown in figure 2 & 3. (please refer to table 1 and figure 4 for the parameters and the data fitting curve respectively). Depending on the pH of solutions, phosphate generally occur in 4 different ionic forms such as

$H_3PO_4$ ,  $H_2PO_4^-$ ,  $HPO_4^{2-}$ ,  $PO_4^{3-}$ , where with increasing pH, each of these forms go de-Protonation at pKa values of 2.12, 7.21 and 12.67 respectively. In a range of pH 4 to 8,  $H_2PO_4^-$ , is generally the most dominant form and therefore in all the simulations it is considered that only the  $H_2PO_4^-$  ion will be involved in the adsorption mechanism. At any given pH of a certain  $PO_4$  molar concentration, the author has calculated the fraction curve using equation (1) above and then calculated the molar fraction using the equation (2) above, for various concentration. Figure 5 depicts a typical  $PO_4$  fractionation curve and figure 6 depicts the curves of various  $H_2PO_4^-$  fractional concentrations.

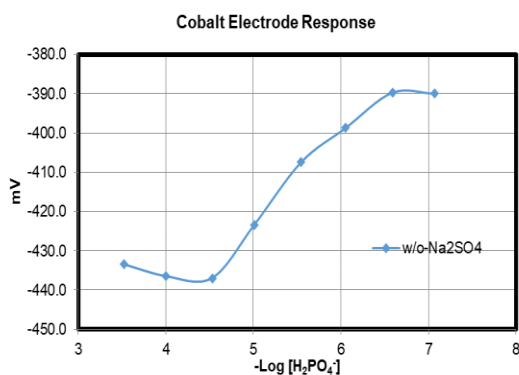


Figure 2: Cobalt Electrode Response to various ppm concentrations (in absence of interfering ions)

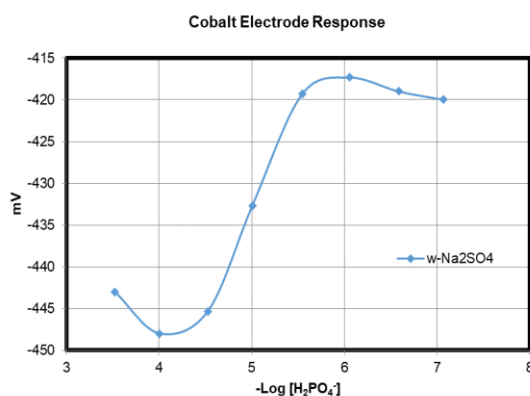


Figure 3: Cobalt Electrode Response to various ppm concentrations (in presence of interfering ions)

Table 1: Parameters (Freundlich Isotherm)

Freundlich Isotherm			
$[H_2PO_4^-]$	b	Log Kd	L/S
1.00E-01	0.589	-2.5	1000
No	pH	(-)Log Ce	(-)Log Ae
0	4	0	2.50

1	4	1	3.09
2	4	2	3.68
3	4	3	4.27
4	4	4	4.86
5	4	5	5.45
6	4	6	6.03
7	4	7	6.62
8	4	8	7.21

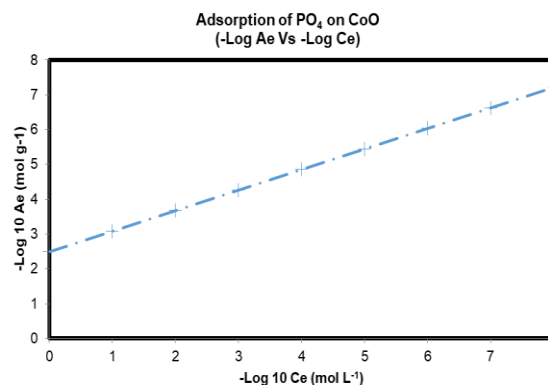


Figure 4: Data fit (a)

Later an activity of  $H_2PO_4^-$ , was calculated at each pH for all simulated molar fractions. These activities were calculated using equation (5) above. Prior to calculate the  $H_2PO_4^-$  activity, the activity coefficient and the ionic strength of the solution was calculated using equation (3) and equation (4), where  $Na^{2+}$ ,  $K^+$ ,  $SO_4^{2-}$  and  $Cl^-$  exhibited as fixed activities while  $H^+$  and  $H_2PO_4^-$  as varying activities. The total ionic strength was then calculated by adding ionic strength of all anions and cations present in the solution at different pH.

All above simulated data was fitted to a Freundlich adsorption isotherm, as given in equation (6) and various curves were plotted in function of pH. Figure 7 depicts a curve showing the difference between molar fractions of concentration and activity of  $1\mu M$   $H_2PO_4^-$ , where not much significant difference is observed. Later figures 8-10, depict the curves for adsorption of  $H_2PO_4^-$  on cobalt a surface, when concentrations of  $H_2PO_4^-$  varied from 0.1 M to  $1\mu M$  of  $H_2PO_4^-$ . All the data is plotted for adsorption of  $H_2PO_4^-$  in presence and in absence of other ions in the solution between the pH range of (4-8) it is observed that the activity of  $H_2PO_4^-$  reduces by about 26-27 % and so as its adsorption by about 2-12% in presence of other ions as compared to the absence of other ions.

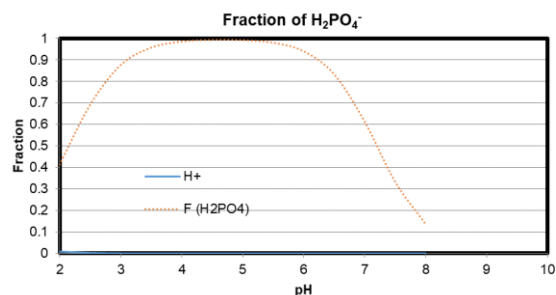


Figure 5: Fraction of  $H_2PO_4^-$  as a function of pH

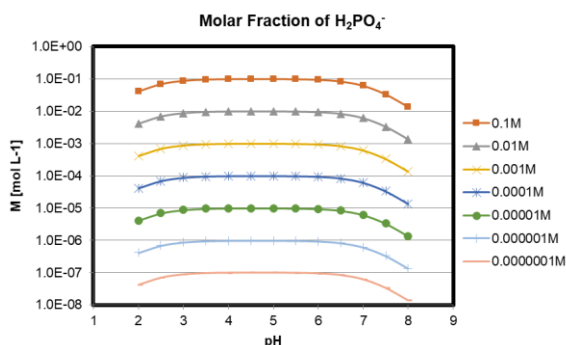


Figure 6: Molar fraction of  $H_2PO_4^-$

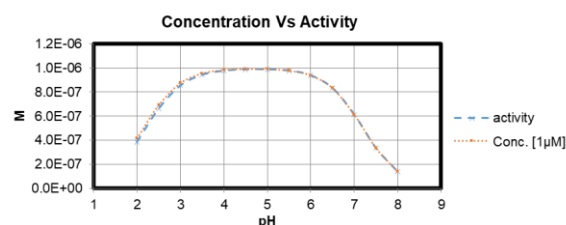


Figure 7:  $H_2PO_4^-$ , Concentration Vs Activity as a function of pH

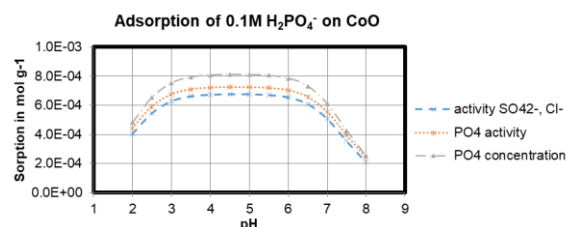


Figure 8: Difference in adsorption due to phosphate and other anion activities (a)

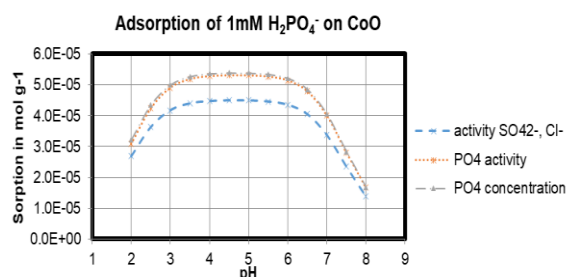


Figure 9: Difference in adsorption due to phosphate and other anion activities (b)

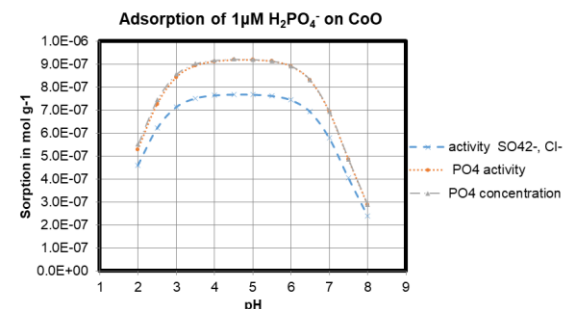


Figure 10: Difference in adsorption due to phosphate and other anion activities (c)

Later the simulated data for pH 4.0 was chosen for all scenarios as shown in table-2 and plotted as shown in figure 11. Where not much significance difference in the adsorption of  $H_2PO_4^-$  can be observed. By using the Freundlich adsorption isotherm equation one can only calculate the amount of material adsorbed in presence of its ionic solution (single ion), while in real life situations, there would be many other ions present, and therefore they would try to adsorb, and perhaps reduce the effective adsorption of the material of interest.

When applied this concept to our cobalt electrode, we can observe comparing results such as by decreasing  $H_2PO_4^-$  ions in solution less amount of  $H_2PO_4^-$  ions get adsorbed on the cobalt surface and similarly less negative potential is observed on the electrode and vice versa, but the presence of other ions that can potentially adsorb on cobalt surface, would still generate some electrode potential and therefore would give false response. Thus there would be need to investigate the adsorption mechanism, by applying extended Freundlich's adsorption isotherm which take into account the presence of other competing ions and then the results may be compared to the electrode potential for the same case and therefore the author of this report would like to propose of conducting more experiments and simultaneous simulations from which it might be possible to find strong relationships between the adsorption mechanism and the electrode potentials. (i.e. a general relationship between the Nernst Equation and Extended Freundlich Adsorption Isotherm for  $H_2PO_4^-$  on cobalt oxide, in presence of other competing ions.)

Table 2: Freundlich Isotherm (modified data)

N	p	c	[(sorp	activt	[(sorp	activ	[(sorp) +
o	H	o	)	y(w/o	)	ity(w	activity
		n	conc]	)	actv]	)	ions]
		c					
1	4	1	3.09	1.09	3.14	1.14	3.17
3	4	3	4.27	3.02	4.28	3.14	4.35
6	4	6	6.03	6.01	6.04	6.14	6.12
8	4	8	7.21	8.01	7.22	8.14	7.29

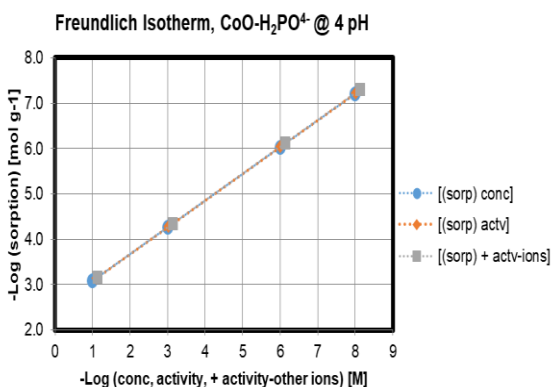


Figure 11: Data fit (b)

Finally, after applying Nernst equation [1] as shown in eq. No. 7, the cobalt electrode potential were estimated. As illustrated in figures 12 and 13, the simulated values and the real-time values for cobalt electrode potential showed a similar trend.

$$E = E' + 0.0591 / n \times \text{Log}_{10} [\text{H}_2\text{PO}_4^- \text{Sorb}] \text{Eq. No. (7)}$$

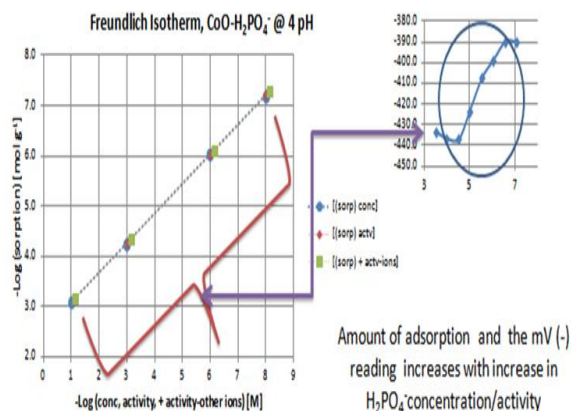


Figure 12: Simulation data fit in comparisons to real-time measurement using the setup(c)

## Applying the Nernst Equation

[(sorp) + actv-ions]	[(sorp) actv]	E
3.171505	3.142	-0.458
4.349297	4.277	-0.434
6.116292	6.040	-0.400
7.294292	7.218	-0.376

$$E = E' + 0.0591/n * \text{Log}_{10} [\text{H}_2\text{PO}_4^- \text{Sorb}]$$



Figure 13: Data fit after applying Nernst equation (d)

## FUTURE WORK

The current adsorption isotherm discussed in this paper takes into account only for concentrations of  $\text{H}_2\text{PO}_4^-$  where as soil solutions usually contain many other anions, such as  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  etc, which would compete with  $\text{H}_2\text{PO}_4^-$  in this adsorption mechanism. Therefore the author would like to propose for conduction of more experiments to estimate the extended Freundlich adsorption isotherm parameters. Later the author would also like investigate more on the relationships between the extended Freundlich adsorption mechanism and the electrode potential response, in presence of fixed activities of other anions.

## CONCLUSION

Adsorption of  $\text{H}_2\text{PO}_4^-$  ions on the cobalt oxide surface might be responsible for the increasing net (-ve charge) on the cobalt surface. Less adsorption takes place at lower  $\text{H}_2\text{PO}_4^-$  concentrations which perhaps explains a lesser (-ve reading) Increase in ionic strength of the solution reduces the  $\text{H}_2\text{PO}_4^-$  ion activity in solution but this has not shown any significant reduction on its adsorption in this case. Probably more investigations by applying extended Freundlich adsorption isotherm, might help to understand the mechanism in a more better way.

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