5. Finetuning iron oxides: A (not so) rusty approach to combat harmful algal blooms

Iron oxide, or rust, is a rather common sight in our everyday life. But diving deep into its structure, right to the scale of individual atoms, allows for some remarkable transformation of its characteristics. Characteristics that allow it to efficiently remove phosphate at very low concentrations and combat harmful algal blooms.

Carlo Belloni*: "It's pretty exciting to work at such a scale, where the electronic properties of atoms can be modified, and check how this affects the phosphate adsorption properties of the overall iron oxide."*

Your research on P adsorption is quite different from the other phosphate projects. That's because you work with very dilute streams of P unlike concentrated streams in the other projects. This means the P recovery would not be as much. So, what is the main motivation for your research?

Carlo: When it comes to the research on P adsorption, the main drive is not about recovering the P. It is about stopping harmful algal blooms. In a conventional wastewater treatment plant, most of the P, usually 90 % or more is removed by the time the wastewater effluent is discharged. But this remaining concentration of P, even as low as 100 µg P/L, is enough to cause eutrophication because P is a limiting nutrient for the algae. The resulting harmful algal blooms have massive economic and environmental implications. Apart from damaging the ecosystem, it leads to huge economic losses for several industries like fishing, tourism, real estate to name a few. Hence there is an urgent need to stop this pollution and that is the main drive for the research on P adsorption. So, we use adsorption as a polishing step to reduce the P in the effluent stream to ultra-low concentrations.

Having said that, it is possible to reverse the adsorption and reuse the material used, which also allows the P to be recovered. But the amount of P recovered would be minimal, and this is more a bonus to the main purpose.

The material you use for adsorption is something we come across often in daily life, rust. But obviously, there is much more to rust than meets the eye, because your research is focused on improving this rust. Can you tell us what are you looking to improve?

Rust is a common name for iron oxides (FeO). When I say iron oxides, it also covers the iron hydroxides, and there are about 16 different types in total. We use these as our adsorbents, meaning they are the materials that adsorb phosphate. The iron oxides can be used as such, or they can be incorporated in backbones like ion exchange resins.

When you look at this process in the real-life, we pack the adsorbents in a column. This adsorption column is then exposed to the wastewater polluted with phosphate. Now how well the column performs depends on some key factors; like how much P can be removed by the adsorbent, how fast

can it be removed, how selectively does it bind P as compared to other ions, and to what extent can the process be reversed allowing the column to be reused and the P to be recovered.

But to enhance and improve these properties, these iron oxide-based adsorbents need to be modified. This can be done at different scales, which could be something from a few millimeters, and go down all the way to several hundred picometers **(Figure 1).** For my research, the focus is more on modifying the properties at the smaller scales.
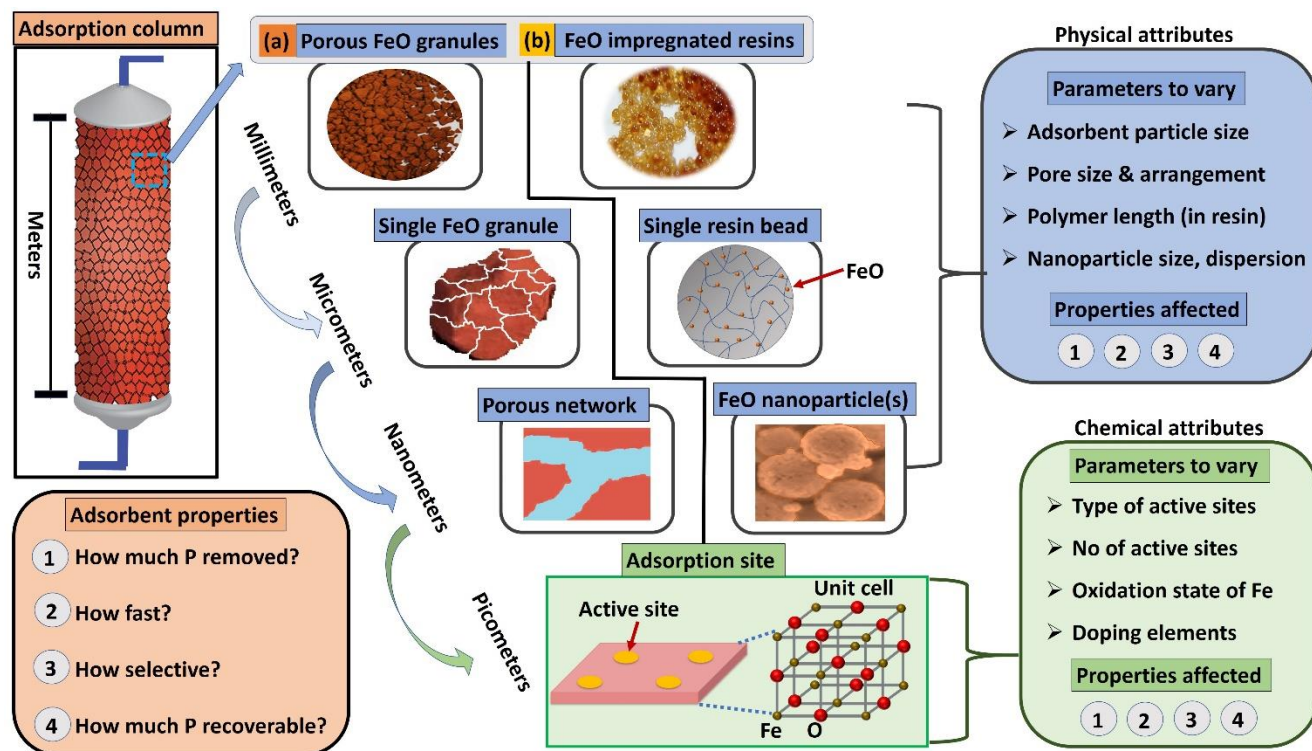

Figure 1: Importance of studying the adsorbent at the atomic level - Two iron-based adsorbents (a) Porous granular FeO (b) Hybrid anion exchange resins are inspected from the millimeter scale all the way down to the picometer scale. The parameters that can be varied and the adsorbent properties affected are subsequently shown for the different scales.

Could you give a few examples of what could be modified at different scales? And why are you more interested in looking at the smaller scales?

When you look at the scale of a few millimeters, you could think about varying a parameter like the particle size. For instance, if you make the adsorbent particles smaller, for a non-porous material, it would result in a significant increase in specific surface area, which in turn would result in more P removal. If it were a porous material, reducing the particle size would mean shorter path lengths for diffusion, and it would improve the speed of adsorption.

At the level of micrometers and nanometers, parameters like pore size and polymer length can be varied. If you consider a hybrid anion exchange resin (HAIX), this has iron oxide nanoparticles impregnated in a polymer backbone to give higher mechanical strength to the overall composite. By varying the length of the polymer used, the extent of cross-linking between the polymers can be varied.

Having a lower degree of crosslinking would allow for more swelling of the resin and the phosphate can diffuse faster. This would improve the overall adsorption speed, although it would decrease the available surface for adsorption. Varying the size of pores can also help in excluding large competing molecules and improve the selectivity for P adsorption.

But when you start looking at the level of unit cells and individual atoms, you will see that it is where you can finetune parameters that affect important chemical properties of the adsorbent. This includes properties like the binding strength and affinity for P adsorption. For instance, changing something like the oxidation state of Fe can result in the formation of a completely different iron oxide. The different iron oxides have varying crystal structures, which in turn affects the active sites, i.e., the sites where P adsorbs on the adsorbent. This affects the P binding strength which would affect the selectivity as well as the reversibility of the process.

The adsorption properties can thus be varied both at the physical and chemical level. But the chemical attributes dictate the innate or intrinsic interactions, and the physical attributes function as an auxiliary to facilitate these interactions.

Would you say there is also a lot of possibilities to finetune parameters at the smaller scales?

Definitely. It's pretty exciting to work at such a scale, where the electronic properties of atoms can be modified, and check how this affects the phosphate adsorption properties of the overall iron oxide.

Another example along this line is how doping elements onto the iron oxide structure could affect the adsorption. To understand this effect, let me explain the mechanism of P adsorption first. The active sites on the iron oxides are the hydroxyl groups attached to their surface. When a phosphate solution is brought into contact with the iron oxide, the phosphate ions exchange with these surface hydroxyl groups **(figure 2).** The phosphate forms a chemical bond with the iron atom and hydroxide ions are released. This reaction can be reversed by bringing the iron oxide in contact with an alkaline solution that has a high concentration of hydroxide ions.

While the surface hydroxyl groups provide the active sites for adsorption, the adsorbent also has a surface charge that aids in adsorption. The wastewater effluent usually has a pH of around 7, and the phosphate ions are negatively charged at this pH. Depending on its chemical composition, the adsorbent can either have a positive or negative charge at this pH. Having a positive surface charge is favorable to attract the phosphate ions towards the active sites of the adsorbent. Doping the adsorbent with a positively charged metal ion could help in making the surface more positive, which would improve the adsorption performance. It could also improve the stability and strength of binding.
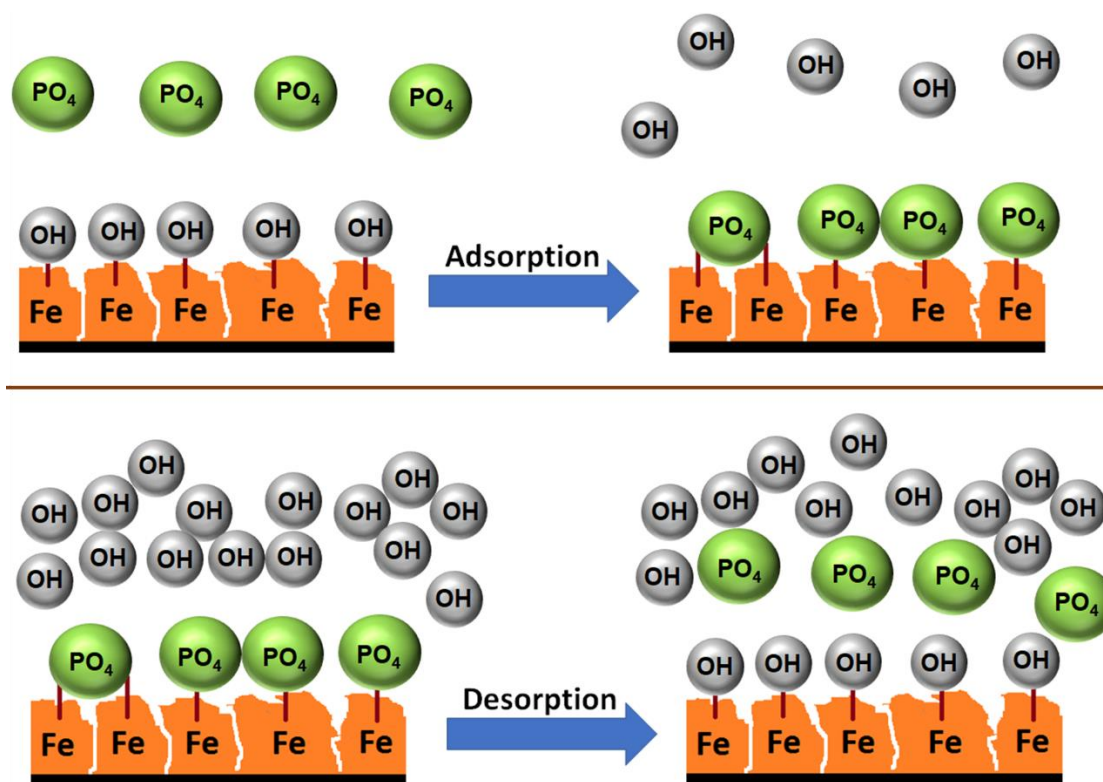
Figure 2: Mechanism of phosphate adsorption on iron oxide surface - (Top) Phosphate adsorption happens via ligand exchange with surface hydroxyl group; (Bottom) To reverse the reaction, a high concentration of hydroxide ions is required to provide enough driving force. Note that this illustration does not show the charges involved. Depending on the solution pH, the ions, as well as the adsorbent, will have a charge which will also influence the adsorption.

But when you make changes to your adsorbent at the atomic scale, you would need an equally sensitive technique to detect such changes. And it seems you do have such a tool in your arsenal. Could you please explain the technique and its specialty?

Indeed, we use a special spectroscopic technique called Mössbauer spectroscopy. In fact, the technique is so vital and useful for our analysis, that the core of our research in varying the iron oxide properties is built around this. It is the main analysis tool in the project.

To briefly describe it, the technique uses a gamma ray active source, made of cobalt (^{57}Co) which irradiates the sample **(figure 3)**. Then, each iron nucleus in the sample will absorb this radiation, in a way that strongly depends on the surrounding electronic environment (how electrons are disposed around the nucleus). As a result, we obtain an adsorption spectrum, a sort of picture from which we can retrieve much fine, yet fundamental information.

This technique studies interactions at the nuclear level and displays an energy resolution of 10^{-12}. It can detect the slightest difference in the iron oxide atomic environment. It can thus sense the oxidation state, the level of crystallinity, and the magnetic behavior of the sample and hence determine the type of iron oxide. This would work for any type of iron oxide, whether it is amorphous or crystalline. Thus,

unlike techniques like X-ray diffraction which can only characterize crystalline samples, Mössbauer spectroscopy can be used even for amorphous samples.

Also, if an iron-based sample is doped, or if a phosphate molecule strongly binds to our adsorbent, the Mössbauer spectrum of the system changes. This gives information about the type of bonding and any changes in the interaction due to the doping element.
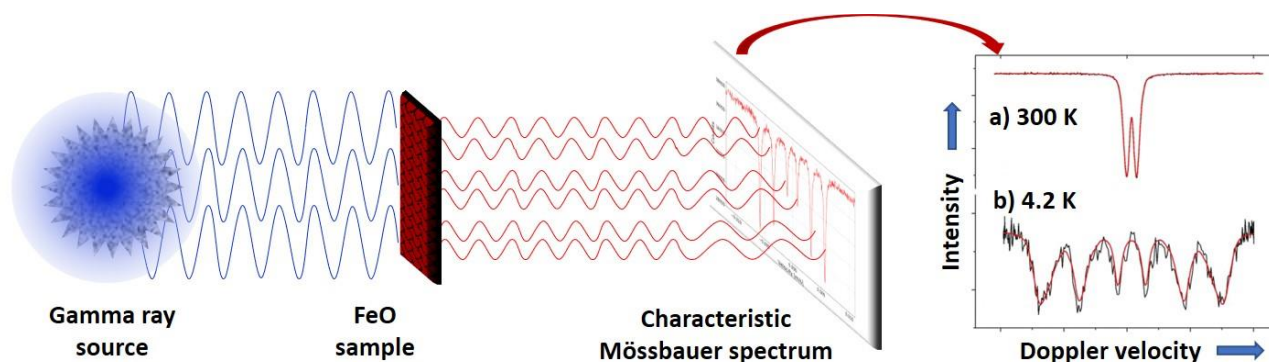

Figure 3: Mössbauer spectroscopy: An extremely high-resolution nuclear technique - The iron oxide sample is bombarded with gamma rays and the signal is a collective response, from every single atom in the sample, for this reason, there is no need for the sample to have an ordered crystalline structure. The Mössbauer spectrum shown here was recorded at two temperatures, room temperature (300 K) and that of liquid helium (4.2 K), which provided additional information. This enabled to characterize the sample as ferrihydrite, a highly amorphous iron oxide.

This seems to be such a powerful technique. Are there any limitations to this technique?

This technique only works with few elements, depending on if the radioactive source (element) and the irradiated sample (element) satisfy certain conditions. Fortunately, iron is one of them and is the most widely studied using this technique. Besides that, to have the best possible signal of Fe and P interaction on the adsorbent surface, the adsorbent particles should be small enough, to increase the signal coming from the surface sites, compared to that of the bulk. So, I typically perform my experiments on iron oxide nanoparticles.

But for practical applications, one wouldn't expect to use nanoparticles as such because it can be very difficult to handle and recover them. So how representative are your studies involving nanoparticles for real-scale applications?

The overall adsorption is a combination of physical effects, like pore diffusion inside the adsorbent, and chemical effects, like the type of interaction at the active site. I use nanoparticles to isolate and study the chemical interactions involved in P adsorption, as well as those provided by the dopants. However, it should be possible to include these nanoparticles as such in larger composite particles, like impregnating them inside an anion exchange resin. This way, the chemical properties of the iron oxide would still be representative when they are applied on a real scale.

Since your technology is meant as a polishing step, one could say that you work with relatively cleaner solutions. This could mean a less challenging matrix, where you have lower concentrations of

contaminants and competing ions compared to processes upstream of the WWTP. So, what are the challenges you face in your project?

The fact I work with dilute streams already possess an important challenge. Since the concentration of phosphate is so low, the overall amount of phosphate removed by the adsorbent is also significantly low. So, the treatment becomes very expensive, unless you find a way to reuse the adsorbent. This is done through a process called adsorbent regeneration, which is not well studied but is an extremely crucial aspect. Studying the chemical interactions between Fe and P would be useful to understand how reversible the adsorption is.

Besides that, when it comes to finetuning the adsorbent, there are so many variables to choose from regarding the type of material and how to modify it. Thus, which parameter to choose or select can also be challenging. It is interesting to search for solutions in different topics; for example, similar adsorbent modifications are done in research groups that work with adsorption or catalysis involving gases. But this might bring other challenges since doping an adsorbent with a specific element might have a different effect in the gas phase as compared to liquid phase adsorption.

Thus, there are challenges aplenty, but it's important to realize that this is the nature of research, and it's the same attribute that makes it exciting.