How Rusting Iron Can Clean Up Toxic Spills

Rusting iron could offer an environmentally friendly way to stop toxic chemical spills and make further clean-up safer, reveals Andrew Feitz.

Molecular-sized nanoparticles of iron rust extremely fast. In the process they produce powerful oxidants called hydroxyl radicals that are capable of breaking down almost all pesticides, industrial waste chemicals and other toxic organic compounds that are usually difficult to clean up.

Normally these incredibly powerful oxidants can only be produced in large quantities using a combination of hazardous chemicals or high energy ultraviolet light. But research we have conducted at the University of NSW in conjunction with the University of California, Berkeley, has revealed a way to make the same oxidants by simply exposing nanoparticles of iron to air.

Even more surprising is that these very same oxidants are raging inside our bodies.

Rusty Nanoparticles

Iron naturally rusts in the presence of air and water. In the classic corrosion process, metallic iron releases electrons as it oxidises to soluble ferrous iron (Fe^{2+}). The electrons can travel through the metallic iron and react with oxygen and water droplets at the surface of the iron. The oxygen and water accept the electrons and form hydroxyl ions (OH^-), which then react with Fe^{2+} to form a ferrous hydroxide precipitate. Rust is produced by oxidation of the precipitate (Fig. 1a).

But using particles 1000 times smaller than the width of a human hair greatly accelerates the process and results in the formation of an intermediate product, hydrogen peroxide (H_2O_2). Instead of electrons reacting with oxygen and water to produce hydroxyl ions, electrons appear to reduce oxygen directly to hydrogen peroxide (Fig. 1b).

The combined surface area of the nanoparticles is approximately 100 times higher than for the same weight of millimetre-sized pieces of iron. This provides more opportunity for more dissolved oxygen to come into contact with the iron and speed up its corrosion. Corrosion takes place within a few minutes. For large pieces of iron, complete corrosion may take years or even decades.

Formation of Oxidants

The release of Fe^{2+} and generation of hydrogen peroxide are the necessary ingredients for a process first identified in 1894 by Henry J.H. Fenton in Cambridge. Fenton's reagent generates powerful oxidants called hydroxyl radicals ($^{\bullet}OH$) through the reaction of ferrous iron and hydrogen peroxide:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$$

It is one of the few methods available to generate these powerful oxidants without requiring light, additional energy or sophisticated equipment (e.g. ultrasonic probes, ozone generators or e-beams). Ferric iron (Fe^{3+}) reacts with hydroxyl ions to form a ferric hydroxide precipitate, an early stage of rust. The hydroxyl radicals would normally react with and oxidise Fe^{2+} to Fe^{3+}, but the presence of organic chemicals means that the hydroxyl radicals can be used to target the breakdown toxic organic chemicals instead. For example, the herbicide molinate, an organic chemical used widely in the rice industry, is

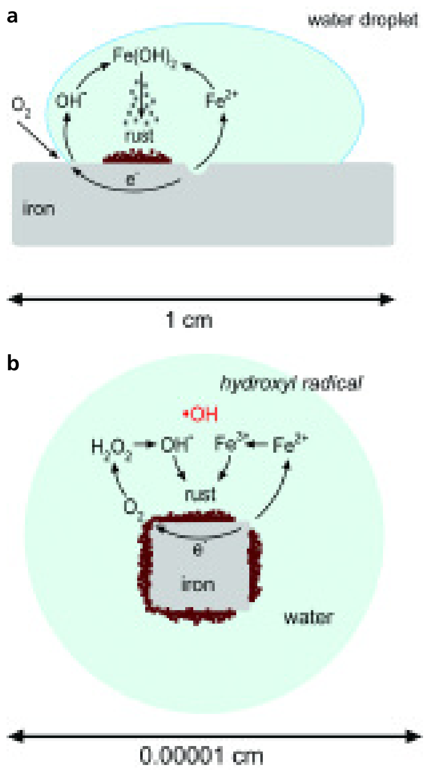

Figure. 1 (a) Conventional rusting process. (b) Nanoparticle rusting process.

broken down with iron nanoparticles in the presence of air. It there is no air (or oxygen), then the iron nanoparticles do not corrode and molinate does not break down.

Powerful Oxidants

Hydroxyl radicals are highly unstable because they contain an unpaired electron in their molecular structure and will "steal" an electron or hydrogen atom from the nearest compound to convert into the more stable hydroxyl ion or water. They are therefore highly reactive and rapidly oxidise virtually all compounds. Other commonly encountered oxidants such as bleach or hydrogen peroxide are less reactive because they contain paired electrons in their molecular structures.

Repeated exposure of a toxic organic compound to hydroxyl radicals can lead to its complete oxidation, converting the organic into harmless products such as water, carbon dioxide and mineral acids. In most situations, however, complete oxidation is not necessary and partial

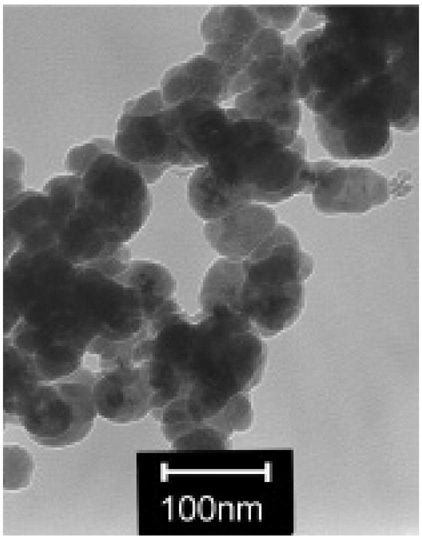

Figure 2. Electron microscope image of iron nanoparticles.

breakdown into smaller and less harmful compounds is sufficient.

Iron Nanoparticle Spray

Harnessing the power of the Fenton reaction and hydroxyl radicals, researchers are developing an iron nanoparticle spray to neutralise toxic spills and make clean-up safer. Toxic chemical spills can be caused from leaky containers, dropping and breaking bottles or during freight accidents.

The present method of dealing with toxic organic spills involves either hosing it away or using a zeolite absorbent used in cat litter to mop it up. Neither of these methods actually destroys the chemicals or reduces their toxicity.

But because iron nanoparticles produce hydroxyl radicals that oxidise almost all organic compounds, they can be added to a chemical spill to quickly break down toxic organics into smaller, less toxic compounds. The neutralised chemical spill can then be safely cleaned up with a lower risk of contamination of the environment.

Safety

Nanoparticles are in use today. Some sunscreens contain nanoparticles of zinc oxide that give a transparent appearance. Other nanoparticles are being used in cosmetics, computer chips, self-cleaning windows and stain-resistant clothing.

There are legitimate concerns about the safety of nanoparticles. The greatest concern is that we simply do not know enough about them and there are few studies assessing their safety. Of the studies done, it has been found in some experiments with rats that ultrafine particles produce a greater inflammatory response compared with larger particles with the identical composition. However, the response depends on the material, whether there are single ultrafine particles or in larger aggregates, and many other factors.

There is a clear need to carefully assess the toxicity of nanoparticles and not assume that they will behave like their larger cousins. Iron is officially regarded as non-hazardous based on its health effects, although it is highly flammable.

Clearly, iron nanoparticles are highly reactive – much more than larger pieces of iron – and inhalation of the particles could pose a health risk. Despite potential dangers, there are enormous benefits too.

The challenge is to understand the potential health and environmental risks, minimise those risks, and use the unique properties of nanoparticles in a safe way for the benefit of the environment and society.

Andrew Feitz is Senior Research Fellow at the School of Civil and Environmental Engineering, The University of NSW.

THE FENTON REACTION INSIDE YOU

There is increasing speculation that the Fenton reaction is one of the drivers for ageing. Reactive oxygen species such as superoxide (O_2^-)and hydrogen peroxide (H_2O_2) are produced in the human body when food is broken down in the presence of oxygen to form carbon dioxide and water. Superoxide is being made in our bodies all the time and is formed when oxygen gains an electron during respiration. It is often converted into hydrogen peroxide. Hydrogen peroxide is also formed by white blood cells as a first line of defence against microorganisms invading the body.

Superoxide itself is not a very powerful oxidant, but it is the reaction between hydrogen peroxide and trace amounts of iron – the Fenton reaction – that can lead to the production of hydroxyl radicals ($^\bullet OH$) and promote premature ageing. Iron is an essential dietary requirement used to produce red blood cells, but excessive iron can be problematic.

Because hydroxyl radicals can oxidise virtually all organic compounds, they can directly attack DNA and cause mutations, leading to cancer. They can attack collagen and exacerbate skin ageing, interfere with processes in the mitochondria and promote muscle wasting, and break down cell membranes. These oxidative stresses on the body, among others, can lead to disease and premature ageing.

Fortunately, the body has evolved a range of mechanisms to combat hydroxyl radicals. One way to limit the rate of hydroxyl radical production is to bind the free iron in proteins so there is no free iron to catalyse the breakdown of hydrogen peroxide. Ferritin and transferrin are examples of such proteins.

The body also possesses enzymes that speed up the conversion of hydrogen peroxide to water, eliminating it from the body.

Antioxidants are also a vital defence: phenolic-type molecules (such as those found in red wine, vegetables and fruit) are able to mop up hydroxyl radicals and stop radical propagation; vitamins (especially vitamins E and C) are able to repair cellular molecules oxidised by hydroxyl radicals; and hormones (such as melatonin and cofactors like coenzyme Q) are also powerful antioxidants.