

# Hidden inefficiencies: The importance of identifying different contributions to overall catalytic activity

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There are increasing concerns about the adverse health effects, including endocrine disruption, of persistent organic micropollutants. At present, industrial water treatment plants lack the technologies to remove these particular contaminants. The most common experimental approaches use oxidation by ozone or activated hydrogen peroxide, but these suffer from significant drawbacks, including high costs and the introduction of secondary pollution. A promising alternative is to use catalytic systems that require no activation, and thus maximise efficiency.

In these systems, adsorption and truly catalytic degradation are competing processes, but the former is much less desirable as it is limited by adsorption capacity. By separating these contributions and studying the structure-performance relationship that governs their ratio, it is possible to maximise true catalytic activity, which ensures high long-term activity.

## Pollutants of emerging concern

Globally, 1 in 3 people do not have access to safe drinking water.<sup>1</sup> Households and the intensive industry and agriculture of developed countries often introduce persistent organic pollutants into their waste streams. The most common sources of these pollutants are pharmaceuticals, personal care products, pesticides, and antibiotics.<sup>2</sup> Most of these compounds are only partially removed by the seasonal biofilm build-up in water treatment plants.<sup>3</sup>

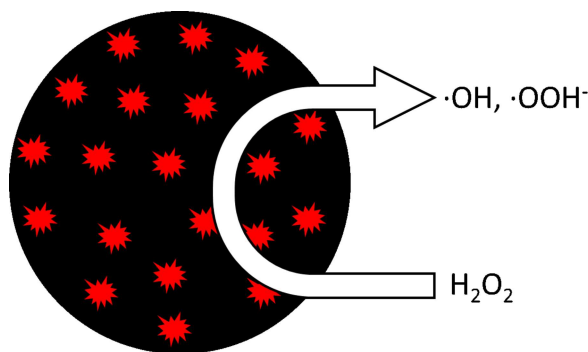
There is an increasing number of persistent organic micropollutants that have been shown to have potentially serious negative health effects, including endocrine disruption. Some of these include bisphenol-A, plasticisers, like nonylphenol, and poly- and perfluoroalkyl substances (PFAS). Many of these pollutants have been found in surface waters, groundwater, and drinking water.<sup>4</sup> The ideal solution to this problem would be to prevent these compounds from reaching surface waters but failing that, there is a pressing need for sustainable, highly active tertiary water treatment solutions.

## Challenges of current experimental water treatment methods

The most common experimental tertiary water treatment methods use coagulation-flocculation, adsorption on activated carbon materials, ozonation, advanced oxidation processes (AOPs), and various bioremediation processes.<sup>2</sup> Some of these methods do not destroy pollutants, just transfer or concentrate them into another phase, while others suffer from high costs and/or slow detoxification. Most AOPs use Fenton chemistry, a metal-catalysed oxidation process that generates powerful, non-selective oxidant radicals from hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) (see **Figure 1**). Catalysts are usually dispersed on a support as this stabilises the active component, makes separation easy and enhances activity. An attractive alternative to widely used mineral supports like zeolites are carbon materials as these can offer unique synergistic effects stemming from the excellent electronic and thermal conductivity of graphitic carbons and are generally quite cheap and abundant.

## Acid oxidation

AOP research is generally done by using a dye as a model pollutant, and assessing how quickly the dye is removed by a catalytic system. Despite extensive research in this field, it is often overlooked that overall dye removal is made up of adsorption and truly catalytic degradation contributions, which are not equally desirable.



**Figure 1.** Mechanism of Fenton chemistry; hydrogen peroxide is broken down by the catalyst into reactive oxygen species (ROS), mainly hydroxyl radicals and superoxide radical anions.

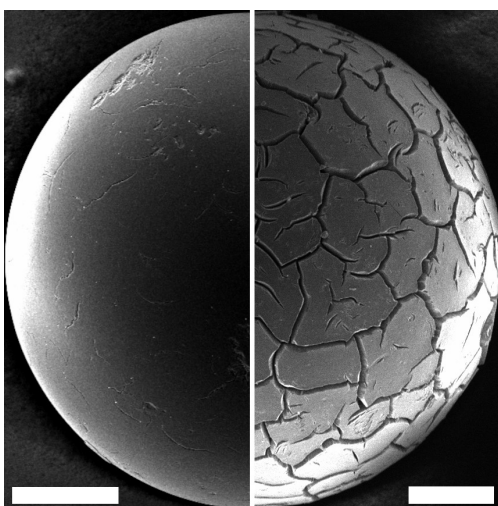
A catalytic water treatment system that removes organics predominantly through adsorption will eventually get saturated, at which point a significant drop will be seen in dye removal, and the catalyst will require regeneration. It is therefore important to study the factors affecting the balance between adsorption and true catalytic degradation and to maximise the latter's contribution.

As a demonstration of the importance of this distinction, acid oxidation of the support was used to alter the ratio of adsorption to degradation in carbon bead-supported mixed metal oxide composite catalysts (see **Figure 2**).

The adsorption characteristics of the carbon beads were tested in an experiment where a commonly used azo dye was used as a model pollutant, and both adsorption capacity and kinetics were studied with untreated carbon beads (CB) and oxidised carbon beads (oCB). Morphological characterisation of CB and oCB samples reveals that acid oxidation reduced the surface area by 17.2% while the number of surface oxygen functional groups roughly doubled. As a result of acid oxidation, the overall adsorption capacity was reduced by 36.3%, while the adsorption rate was slowed down approximately 15-fold.

The combination of reduced surface area and a higher concentration of polar functional groups explains why adsorption driven mainly by apolar interactions between graphitic surfaces and the aromatic groups in the dye molecules was significantly hindered.

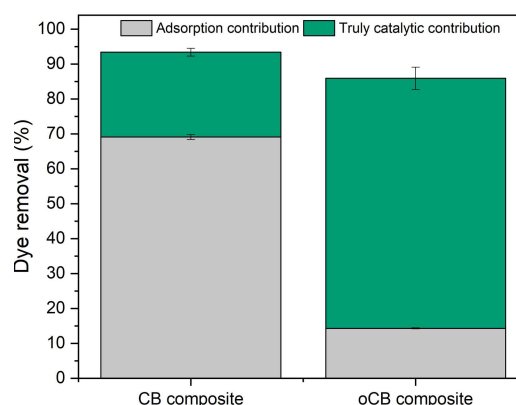
The saturated adsorbents were then regenerated by consecutive hot water washes, which is a commonly used method for this purpose<sup>4</sup>. Saturated CB released about 3 % of the adsorbed dye, while the same value for oCB is 9.5 %, both of which are very low, and indicate that adsorption would be virtually irreversible in practical applications.



**Figure 2.** Scanning electron micrograph of untreated (left half) and acid oxidised (right half) carbon beads. Scale bars represent 100  $\mu\text{m}$ .

## Catalytic activity

A catalytic organics removal experiment was used to measure the activity of CB and oCB supported catalysts, where ROS generated from  $\text{H}_2\text{O}_2$  are used to degrade a dye in a neutral aqueous medium. The above differences in surface morphology and surface chemistry translate into surprisingly large differences in catalytic activity. Most research only considers overall dye removal which, in the case of the CB supported catalyst, is 93.4 % of the dye in 60 minutes, compared to 85.9 % in the case of the oCB supported one. However, if overall dye removal is separated into its different contributions, the oCB supported catalyst is observed to be roughly 3-times more active. In the case of the CB composite, only 24.3 % of dye removal comes from true catalytic activity, which raises to 71.6 % for the oCB composite (see **Figure 3**).



**Figure 3.** Comparison of different contributions to overall organics removal after 60 minutes between CB and oCB supported catalysts.

Further experiments are necessary to examine how this translates into long-term catalytic activity when the same batch of composite catalyst is reused multiple times. Nevertheless, these results are a strong indication that it is crucial to minimise adsorption of organics in macroscale carbon supported AOP catalysts in order to maintain long-term catalytic activity and reusability.

## References

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