

WATER PURIFICATION WITH MAGNETIC PARTICLES

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Abstract. CSIRO (Commonwealth Scientific and Industrial Research Organization) has for some years carried out research into more efficient ways of purifying water and wastewater. More intensive processing has been achieved by the use of finely divided solid reagents which can be regenerated and reused. The age-old problem of quickly separating the very small particles of loaded reagent from the accompanying liquid has been solved by utilizing a magnetic reagent in the form of magnetite, Fe_3O_4 . A water clarification process is fully developed for the production of potable supplies from low quality ground and surface waters, with five plants in operation or under construction in Australia, the United Kingdom and Taiwan. The method has been extended to the removal of heavy metals from tailings dams, which has also reached full-scale with a plant near Canberra, to other industrial effluents, and more recently to sewage treatment. Successful pilot plant studies of the latter in Melbourne and Sydney have led to the decision to carry out a large-scale trial at Malabar, near Sydney.

Introduction

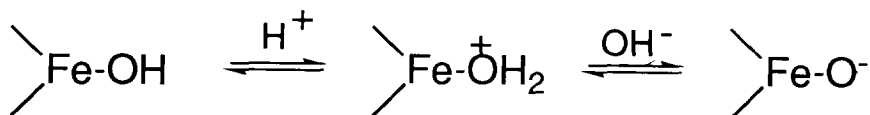
Australia has a particular interest in developing more efficient ways of purifying water and wastewater. CSIRO, which is the country's largest publicly funded research organisation, has been carrying out research in this area for many years. A number of processes have been developed, including one based on thermally regenerated ion exchange resins, called SIROTHERM. The most successful process to date has been one which is based on the coagulating ability of fine particles of magnetite pretreated with caustic soda. This process is known as SIROFLOC. Five water purification plants are now in operation or under construction in Australia, the United Kingdom and Taiwan. The method has also been extended to the removal of heavy metals from tailings dams, to other industrial effluents and more recently to sewage treatment.

The Water Purification Process

The origins of the SIROFLOC process were 'jar test' experiments carried out in early 1977. Fine particles of magnetite (1–10 μm), which had been pretreated with a caustic soda solution, were mixed with a raw water containing both turbidity and colour. The colour comes from the decay of 'humus' materials while the turbidity consists of colloidal siliceous clays. Under slightly acidic conditions the magnetite has a positive surface charge; the impurities (colloids, microbes and colour) all possess a negative surface charge and hence adhere to the surfaces of the magnetite. Rapid and efficient removal of both turbidity and colour is achieved. The soluble coloured anions of fulvic and humic acid are

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first rapidly adsorbed by the magnetite to reverse its charge. When turbidity is present, a coagulant in the form of a cationic polymer is added to bind the negatively charged turbidity particles to the now negative surface of the magnetite. On alkali treatment, the magnetite itself attains a negative charge and the like-charged impurities are sloughed off. The reversible charge feature of magnetite as a function of pH is driven by the equilibria



The contacting of 5 to 20 g/L of magnetite with the raw water is carried out in a series of three stirred tanks, at pH 5 to 6. The cationic polyelectrolyte is added in the third tank, at levels up to 1 mg/L depending on the turbidity load. This removes any residual colour and turbidity, reduces the amount of magnetite which is necessary, and allows the use of higher pH levels. Total contact time is of the order of 6 to 7 minutes. After magnetisation the loaded magnetite is quickly and easily separated from the product water in a clarifier, the size of which is about half that of equipment used in the conventional technology.

The flocculated, settled magnetite containing the impurities is pumped from the bottom of the clarifier as a concentrated slurry and alkali is added to regenerate the surface of the magnetite (pH 11.4). The negatively charged colloidal impurities are repelled from the like-charged magnetite and can be washed off to allow the cleaned magnetite to be reused in the process. The separation of the magnetite from the wash liquor can be achieved with magnetic drum separators. These are simple stainless steel hollow drums with rotate through a bath of the diluted magnetite and impurities (see Figure 1). Permanent magnets are mounted inside the drum in the lower arc, and the magnetite is attracted to its surface as the drum surface passes these magnets. Raw water is used for washing and, depending on the flow scheme, the amount can be from 2 to 5% of the raw water flow. The magnetite is returned to the contact tanks. It is demagnetised merely by the turbulence encountered in its washing and transport. The wash water contains the original colloids concentrated 20 or more times; there is no gelatinous sludge. Disposal can often be back to the source stream or the sea. Alternatively, the wash water can be further treated and recycled, but the need depends on the location and relative cost of the raw water. The process is, overall, about five times faster than normal methods.

Commercial Plants

Three full-scale 'Sirofloc' plants of capacity 20 to 35 ML/day have been constructed to treat waters ranging from complex anaerobic, highly coloured ground water to surface waters having high levels of colour and moderate to low levels of turbidity. Some of the operating data are shown in Table I.

Two further plants are under construction, at Littlehempston, Cornwall and Kao-shiung, Taiwan. Variants of the process are showing great promise for a variety of water purification needs. These include cleaning up the effluent from paper making, and the purification of sewage. A full-scale installation has been tested at Woodlawn, ACT, for

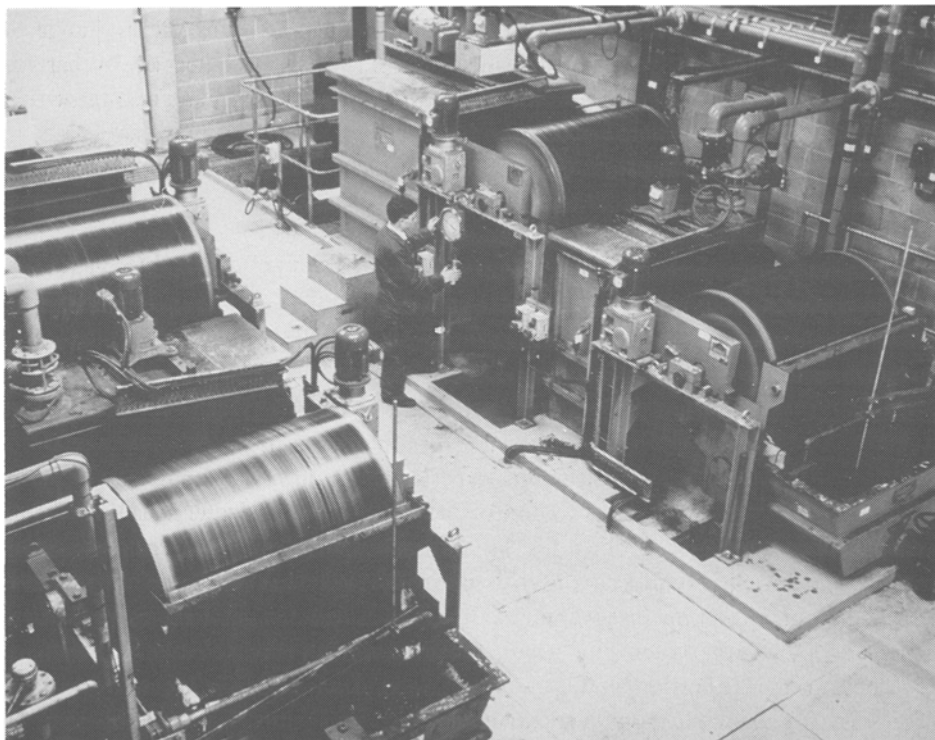


Fig. 1. Magnetic drum separators used at Redmires, Yorkshire, to wash alkali-regenerated magnetite used in a 20 ML/day plant.

TABLE I

Water	Raw water	Product
<i>Mirrabooka, Western Australia</i>		
Turbidity, NTU	20-40	<1
Colour, Pt-Co units	60-120	5
Iron mg/L	1.5-4	<0.8
<i>Bell Bay, Tasmania</i>		
Turbidity, NTU	3-10	0.6
Colour, Pt-Co units	60-100	<5
<i>Redmires, Yorkshire</i>		
Turbidity, NTU	3-5	0.5
Colour, Pt-Co units	30-50	<5
Aluminium, mg/L	0.4	0.02

NTU: Nephelometric turbidity units.

the precipitation and removal of heavy metals from a tailings dam. In one mode of operation the entire heavy metal content of the wastewater is removed by hetero-coagulation with magnetite at high pH; in another, by operation at a lower pH, a zinc-rich liquor suitable for recycling may be obtained by precipitation of the impurity metals.

The Sewage Treatment Process

The traditional approach to the treatment of domestic and/or industrial sewage has been to apply biological techniques which convert organic matter in the sewage into a solid biological sludge and CO₂. A number of processes have been developed to apply these techniques, e.g., trickle filtration and biological activated sludge. While these processes have been successfully applied worldwide they do have limitations imposed by their inherent biological nature. Compared to chemical processes they are slow, sensitive to upset and have long start up and shut down periods. Also, because they largely convert organic matter to biomass, a large volume of difficult to dewater sludge is also produced, which can present disposal problems.

Physicochemical techniques have been used to clarify raw sewage but they, in turn, have also been found to have disadvantages. In particular, high chemical cost and the production of a large volume of gelatinous sludge have, in many instances, made physicochemical clarification an unattractive option for sewage treatment.

In this particular application magnetite particles of size 5–20 μm are used. After being washed in a dilute caustic soda solution the particles are mixed with partially settled raw sewage and the mixture stirred for only 1 to 2 minutes.

During this period, extra chemical coagulants such as ferric sulphate and/or polyelectrolyte are added; they act synergistically with the magnetite in clarifying the raw sewage to a level of 30–40 mg/L BOD. Lower levels can be achieved simply by increasing the dose of coagulant chemical.

The magnetite particles are recovered from the clarified sewage by magnetic flocculation and settling, and are then passed to a washing stage. Here the magnetite particles are treated with a dilute caustic soda solution which strips the sewage organics from the particle surfaces to form a liquid 'sewage concentrate', concentrated by a factor of about 30 over the original raw sewage. The washed magnetite particles are recycled to the clarification step, while the sewage concentrate is passed to a further treatment stage, such as anaerobic digestion or chemical precipitation.

At present the process is being trialed on a 100 kL/day pilot plant to confirm its perceived advantages. One obvious benefit is speed, with a combined total residence time of sewage in the mixing and clarification stage of between 10 and 15 minutes. This time compares favourably with a biological activated sludge plant where the normal residence time of sewage is around 8 hours. Other perceived advantages include flexibility, ease of start up, and insensitivity to shock loading, especially of toxic materials. The process also removes phosphate and, as outlined above, can be designed to produce a small volume of highly concentrated sludge.

The main disadvantage of the process is chemical cost, which can be reduced by

recovery and reuse of the inorganic coagulant. However, in situations where a large area of suitable land is not cheaply available, the magnetite process offers a large saving in capital cost, which should more than offset any extra chemical cost. The magnetite process will not remove any purely soluble ammonia or nitrate. Ammonia is toxic to fish unless highly diluted and if its removal is necessary then good nitrification can be achieved on an aerated polishing sand filter.

As with the other magnetite processes, the sewage process is licenced to an Australian firm, Austep Pty Ltd, (PO Box 6206, Melbourne, Victoria, 3004). who are party to a development agreement with CSIRO and the Sydney Water Board. A 200 KL/day pilot plant for the Sydney region has been constructed and is now in successful operation. This plant will be used to assess the suitability of the process for various location in the Sydney region. A decision to proceed with a large scale test treating 5 ML/day of sewage at Malabar has now been made.

Conclusion

The magnetite-based technology is protected by a number of world-wide patents. The 'SIROFLOC' team is composed of N. J. Anderson (process chemistry, magnetite regeneration), B. A. Bolto (polyelectrolyte chemistry, microbiological applications; Program Leader, 1974-90), D. R. Dixon (surface and colloid chemistry, uptake of inorganic ions, metal recovery), L. O. Kolarik (first laboratory process demonstration, surface chemistry, magnetite pretreatment), A. J. Priestley (process and pilot plant design and operation, potable water and sewage treatment; Project Leader, 1983-90), W. G. C. Raper (process chemistry; Project Leader, 1977-82), D. E. Weiss (concept of regenerable magnetite; Chief of Division (to 1979)).

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