A sustainable use of ochre from mine water treatment plants for phosphorus removal and recycling

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Abstract

Treatment of discharges from abandoned mines is producing large quantities of ochre (hydrous iron (III) hydroxides) that require disposal. At the same time, phosphorus pollution from agricultural runoff and sewage effluent is a serious threat to the water environment in industrialised countries. Ochre has the potential to be used in novel technologies for the removal of phosphorus from wastewater, due to its high sorption capacity for phosphorus (up to 30 g P kg^{-1}). Newcastle and Edinburgh Universities are currently conducting research to develop and test field-scale methods to use ochre for phosphorus removal from agricultural runoff and sewage effluent and to recycle the phosphorus-saturated ochre to agriculture.

Short-term studies in a Scottish river affected by agricultural runoff have demonstrated that in-stream filter units and barriers can reduce phosphorus concentrations. Longer-term field investigations comparing the effectiveness of different forms of ochre for phosphorus removal from agricultural runoff are under way at two farms. Ongoing trials at sewage treatment works, investigating the effectiveness of ochre-filled reaction vessels in removing phosphorus, show good reductions (from 3.04 to 0.33 mg P l^{-1}) if the hydraulics are satisfactory. To develop a total use cycle for ochre, pot experiments and field trials were conducted in which barley and grass were grown in soils amended with phosphorus-saturated ochre. The

results showed that phosphorus-saturated ochre can be used as a slow-release fertiliser with no adverse effects on the environment or crop yields.

Introduction

The flooding of abandoned mines frequently results in the formation of acidic, ferruginous water due to the oxidation of pyrite in the mine workings. To prevent the pollution of surface watercourses, mine water treatment plants (MWTPs) are employed to treat the most serious discharges. In MWTPs, the oxidation and precipitation of iron is enhanced either by the addition of chemicals (e.g., oxidising reagents, alkalis to raise pH and increase the rate of Fe (II) oxidation, and flocculants to assist floc formation and sedimentation) and/or by atmospheric oxidation in storage ponds or constructed wetlands with long retention times. MWTPs therefore accumulate large quantities of $Fe(OH)_3$ and $FeO^{\cdot}OH$ precipitate, collectively known as "ochre" (of the order of tens of tonnes per annum at a single site). Typically, this is stockpiled and, although a number of possible end-uses have been considered (e.g., colouring bricks/cement and in synthesizing coagulants for drinking water)**,** no single end-use has yet been identified which could consume the projected future production.

Our work demonstrates the potential of a novel environmental application of ochre, due to its high sorption capacity for phosphorus. Phosphorus pollution from point and diffuse sources is a serious threat to the water environment in the UK and other industrialized countries (D'Arcy et al. 2000). The transfer of phosphorus to rivers and lakes from sewage treatment works, septic tanks and agricultural runoff causes eutrophication, frequently resulting in algal blooms, fish kills and loss of water resources.

Phosphorus sorption onto iron and aluminium oxides and hydroxides and calcium carbonate (all components of ochre) in natural soils and sediments is well-understood (Barrow 1983; Parfitt 1989; Reddy et al. 1999). Phosphorus removal may also occur by precipitation, although this is believed to be less significant than removal by sorption. Heal et al. (2004) have discussed the removal mechanisms in more detail.

Previous work to examine the use of ferruginous materials for phosphorus removal from wastewater has been piecemeal. In the USA, Webster and Wieder (1997) found that the addition of ochre from acid mine drainage to fertilized soils reduced phosphorus concentrations in runoff. In Northern Ireland, Wood and McAtamney (1996) showed that the use of laterite as a substrate in experimental constructed wetlands removed

95% of phosphorus from landfill leachate. The treatment of dairy farm wastewater has also been investigated in bucket-scale subsurface flow constructed wetlands with an iron ore substrate (Grüneberg and Kern 2001). Other ferruginous media, such as peat doped with bauxite red (Roberge et al. 1999) and sand and olivine coated with iron aluminium hydroxyoxides (Ayoub et al. 2001), have been investigated for phosphorus removal from wastewater but few trials have been conducted at the field scale, and attempts to design novel treatment systems are limited. This paper demonstrates the potential of ochre for phosphorus removal and discusses current research on this topic in three main settings:

1. Removal of phosphorus from sewage effluent by ochre, either in constructed wetland systems or in dosing systems for tanks of sewage effluent;
2. Removal of phosphorus from agricultural runoff by ochre in-stream filter units or dosing systems in rivers and drainage ditches;
3. Recycling of ochre saturated with phosphorus from applications (2) and (3) as a slow-release fertilizer in agriculture.

Demonstration of the potential of ochre for phosphorus removal: laboratory results

Ochre extracted from MWTPs has a very high water content (80-95%) unless it has been stored in drying beds in good weather conditions. If it has not been air-dried, it is difficult to handle and transport, and consequently most investigations of its phosphorus-removal properties have used the air-dried form. Dried ochres from different MWTPs have similar chemical properties but may have different physical properties. Those from two MWTPs in Scotland, Polkemmet and Minto, have a similar chemical composition and mineralogy (identified by x-ray diffraction as a mixture of ferrihydrite and goethite, α-$FeO{\cdot}OH$) but very different particle-size distributions (Fig. 1). Polkemmet ochre dries into clods that are readily crushed to a coarse, granular texture which has a high saturated hydraulic conductivity (26-32 m day^{-1}, equivalent to coarse sand). In contrast, Minto ochre dries to a fine powder with a considerably lower saturated hydraulic conductivity (0.7-1.7 m day^{-1}). The cause of the different physical properties of the two materials is unclear but is thought to be related to differences in the operation of the MWTPs. At Polkemmet, hydrogen peroxide and a polymer are added to the mine water to encourage oxidation and flocculation of iron, whilst at Minto, the mine water is unamended.

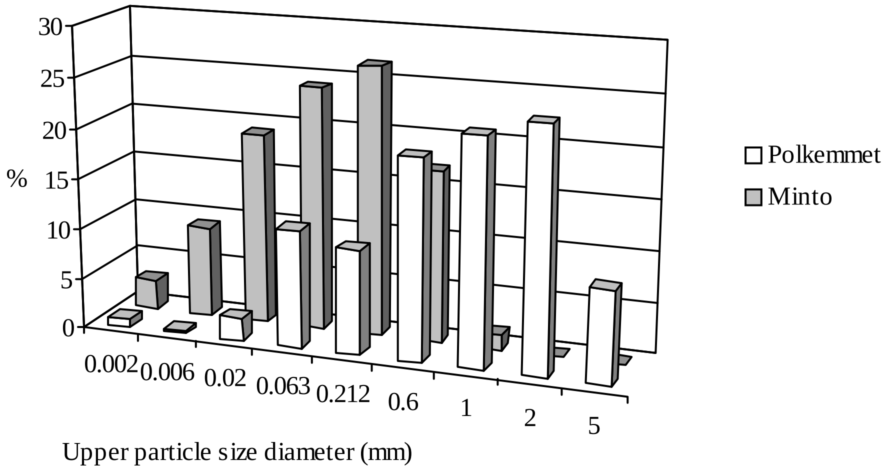

Fig. 1. Particle-size distribution of air-dried ochres from two MWTPs, Scotland

The maximum phosphorus adsorption capacities for Polkemmet and Minto ochres are orders of magnitude higher than those measured in other sorbents (Table 1). Solution pH was found not to affect the removal rate of phosphorus due to the buffering capacity of the ochre (8-11% CaO and 8% MgO content). Laboratory batch experiments with sewage effluent (containing 5.28, 3.50, and 1.77 mg l^{-1} total, inorganic, and organic phosphorus, respectively) showed that all phosphorus forms are removed rapidly (<1 to 15 minutes) by both ochre types.

Table 1. Maximum phosphorus adsorption capacities (mg P (g substrate)$^{-1}$) of different materials (after Drizo (1998) and Mann (1997))

Material	Adsorption capacity
Gravel	0.03-0.05
Bottom ash	0.06
Steel slag	0.38
Blast furnace slag	0.40-0.45
Fly ash	0.62
Shale	0.75
Laterite	0.75
Zeolite	1
Polkemmet ochre	26
Minto ochre	30.5

The physical properties of ochres influence their suitability for different phosphorus removal applications (Table 2). Coarse-grained forms are more suitable for phosphorus removal in filter units or in the substrate of constructed wetlands. Fine-grained forms are difficult to contain and easily clog filter units, but rapidly remove phosphorus from wastewater because of the larger surface area of the particles. Such materials are more suitable for dosing applications, as long as adequate sedimentation is provided. Laboratory dosing experiments with 10-litre columns of sewage effluent and agricultural runoff showed that a single addition of ochre settled completely within eight hours and removed up to 80% of phosphorus from the water column. A method for producing robust, spherical granules (2-12 mm diameter) of fine-grained ochre by the addition of Portland cement, a surfactant and water has been developed by Newcastle University to facilitate the handling and use of this form of the material.

Table 2. Uses of different types of ochre to reduce phosphorus concentrations in agricultural runoff and sewage effluent

Ochre type	Agricultural runoff	Sewage effluent
Coarse-grained	In-stream barrier Filters on field drains	Reaction vessel Wetland substrate
Fine-grained	Dosing agent in powder form, then settlement Granules in in-stream barrier/filter	Dosing agent in powder form, then settlement Granules in reaction vessel Granules in wetland substrate

Field demonstrations of phosphorus removal by ochre

Treatment of agricultural runoff with ochre

Approximately 40% of agricultural land in the UK (excluding rough grazing) is underlain by subsurface field drains, which have been shown to be a major conduit of soluble and particulate phosphorus export to watercourses in storm events, even when best management practices are implemented (Dils and Heathwaite 1996). Although it is not feasible to install treatment works or constructed wetlands for every field drain, treatment with ochre may form a cheap, low-maintenance means of reducing phosphorus exports from field drains. Treatment at the field scale could take the form of in-stream filters containing coarse-grained dried material or fabricated granules. Alternatively, dosing with fine-grained ochre, followed by settlement, has already been demonstrated in laboratory experiments to reduce phosphorus concentrations in simulated agricultural runoff.

Short-term studies in a Scottish river affected by agricultural runoff have demonstrated that in-stream barriers, containing coarse-grained ochre, can reduce phosphorus concentrations. In-stream filter units, containing 6 kg of ochre, reduced phosphorus concentrations (from 0.18 to 0.06 mg P l^{-1}) and altered the algal community, from one dominated by algae typical of eutrophic conditions to one dominated by algae typical of mesotrophic conditions. In a separate study of an in-stream barrier containing five different ochre-grit mixtures, those containing 100% and 50% ochre reduced phosphorus concentrations to less than half the inflow value over a one-month period. Longer-term field investigations comparing the effectiveness of coarse-grained and granular ochre for phosphorus removal from agricultural runoff are being conducted at two UK farms.

Treatment of sewage effluent with ochre

With stricter controls on sewage discharge into receiving waters (e.g., the EU Urban Wastewater Treatment Directive (Farmer 2001)), the development of new methods for phosphorus removal are required. Currently, phosphorus removal at wastewater treatment works (WWTWs) is often achieved by the addition of costly dosing agents such as iron (III) chloride and iron (III) sulphate. Fine-grained ochre is an alternative dosing agent as it has a high capacity for phosphorus adsorption. Laboratory-scale experiments show that it compares favourably with other dosing agents, apart from the generation of larger volumes of sludge for disposal (Table 3).

Table 3. Comparison of fine-grained ochre with other dosing agents used for phosphorus removal in wastewater treatment works

Reagent	Dosage [mg l^{-1}]	P removal [%]	Comments
$FeCl_3$	10	90	Most often employed
$Al_2(SO_4).16H_2O$	200-250	95	High cost
$Ca(OH)_2$	500-700	80	Precipitation occurs at high pH
Fine-grained ochre	2700	94-95	Not pH dependent. Use of waste material, but larger sludge quantities.

Field trials at WWTWs are investigating the effectiveness of reaction vessels containing coarse-grained ochre or ochre granules in removing phosphorus. Preliminary results from Leitholm WWTW, Berwickshire, Scotland, in which a tank containing ~1200 kg of the coarse-grained material was installed at the inflow to a tertiary treatment wetland in November 2003, show that although phosphorus removal did not increase, there was no release of potentially toxic metals that could have adsorbed onto the ochre in the MWTP (no significant differences between before and after concentrations at $P<0.05$ (2-sample t-test)). More detailed spatial sampling and analysis of surface waters in the tank and the tank overflow showed that the reason for the limited phosphorus removal in the tank is short-circuiting of flow so that the full phosphorus removal capacity of the ochre is not utilised (Fig. 2). The theoretical contact time of the mean inflow with ochre in the tank is 15 minutes, sufficient for removal of 90% of the phosphorus, if the flow is distributed throughout the tank.

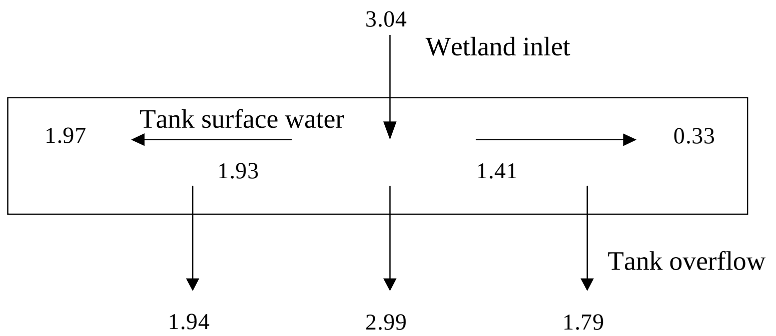

Fig. 2. Soluble reactive phosphorus concentrations (mg l^{-1}) in water samples from different locations in the ochre-filled tank, Leitholm WWTW, 25 November 2003

Constructed wetlands are effective in removing nitrogen from sewage effluent but are less efficient in removing phosphorus (Cooper et al. 1996). From the phosphorus removal capacity measured in pilot filter experiments (Heal et al. 2003), the operational lifetimes of ochre-based wetlands for wastewater treatment were estimated to be decades longer than for other wetland substrates that have been tested for phosphorus removal (Table 4).

Table 4. Estimated operational lifetimes for constructed wetlands using 3 or 5 m^2 wetland area per person with shale or Polkemmet ochre as a substrate with three concentrations of sewage effluent. Substrate assumed to be 0.6 m deep

Substrate	Operational lifetime [years]					
	3 m^2 per person[a]			5 m^2 per person[a]		
	20 mg l^{-1}	5 mg l^{-1}	3 mg l^{-1}	20 mg l^{-1}	5 mg l^{-1}	3 mg l^{-1}
Shale[b]	1.6	6.5	10.7	2.7	10.7	17.8
Ochre	18.8	75	125	33.5	134	224

[a] Each person assumed to produce 0.2 m^3 sewage day^{-1}. [b] Data from Drizo (1998).

Recycling of phosphorus-saturated ochre as a fertiliser

When the phosphorus removal capacity of ochre is finally exhausted, the 'spent' material will require removal and disposal. A more sustainable alternative to landfill disposal is to recycle the phosphorus as a fertilizer. Pot experiments and field trials comparing barley and grass grown in soils amended with phosphorus-saturated ochre with plants grown with conventional phosphorus fertiliser showed that ochre additions improved soil fertility and increased soil pH, while maintaining the same crop yields as conventional fertiliser. At the end of the growing season, there was more available phosphorus in the ochre-amended soil than in soil treated with conventional fertiliser, indicating that phosphorus-saturated ochre has the further desirable property of acting as a slow-release fertilizer, reducing the need for future phosphorus fertilizer applications.

A possible concern about applying ochre to land is the accumulation of potentially toxic metals. UK regulations permit the application of wastes to agricultural land providing they do not contaminate the soil or plants growing on that soil (Waste Management Licensing Regulations 1994). The most relevant guidelines for assessing soil contamination arising from ochre applications relate to the application of sewage sludge to agricultural land (MAFF 1998). Mean metal concentrations in ochre-amended soils at the end of the field trial were well below guideline values, and annual additions of metals associated with the application would not exceed those allowable for sewage sludge (Table 5).

Table 5. Maximum permissible soil metal concentrations (mg kg^{-1} dry soil) and annual metal addition rates (kg ha^{-1} y^{-1}) over 10 years for sewage sludge application (MAFF 1998) compared with values arising from ochre addition

Metal	Max. permissible soil conc.[a]	Concentration[b] in ochre-treated soil	Max. permiss-ible addition	Addition in ochre[c]
Zn	200	85 ± 21	15	3.5
Cu	100	16 ± 2	7.5	0.6
Ni	60	70 ± 11	3	2.8
Cd	3	< 1.6	0.15	< 0.06
Pb	300	52 ± 10	15	0.3
Cr	400	156 ± 70	15	6.7
As	50	0.13 in P-sat ochre	0.7	0.004

[a] Soil pH 5.5-6.0. [b] Mean ± 1 st. dev. [c] Addition of 40 t dry ochre ha^{-1} y^{-1}, equivalent to recommended fertiliser application for barley of 85 kg P_2O_5 ha^{-1} y^{-1}

Conclusions

Laboratory experiments have demonstrated that ochre, formed as a by-product from mine water treatment, has a high capacity for phosphorus removal from agricultural runoff and sewage effluent, as a result of sorption to the high concentration of iron oxides and hydroxides contained within the material. Potential applications of phosphorus removal by ochre are widespread, including sewage effluent treatment in constructed wetlands and by dosing systems, and treatment of agricultural runoff by in-stream filter units and/or dosing and settlement systems. A total use cycle of ochre has also been demonstrated; after phosphorus saturation, it can be used as a slow-release fertilizer with no adverse effect on soil quality and crop yield. Field-scale testing of ochre within sewage treatment works showed that although there is no mobilization of potentially toxic metals, further work is required on the hydraulic design of the filter systems to maximise phosphorus removal capacity. The use of ochre for removal of excess phosphorus in the aquatic environment is particularly attractive, not only because treatment costs are potentially lower than more traditional methods, but also due to the sustainability advantage of using a by-product of treating mine water discharges to address another water problem (eutrophication).

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