



## OPPORTUNITIES FOR USING TWO LOW-COST METHODS FOR TREATMENT OF METAL BEARING AQUEOUS STREAMS

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### ABSTRACT

*The feasibility of two non-traditional approaches—use of reedbeds as a natural wetland, and adsorption on lignite and its maceral fractions—for their potential application in effluent treatment is discussed. The main mechanisms encountered in wetlands performance are briefly described, together with their advantages and disadvantages in practical operation as well as the various methods for metals extraction from the wetland sediment. The preliminary results from a pilot scale wetland operation for metallurgical effluents purification are analysed. The results obtained from the second approach, i.e. using the coal refined fractions, have shown the superior performance of the denser fraction which resembles to a certain extent the activated carbons. Isotherms determination and electrophoretic measurements have confirmed the above findings.*  
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### Keywords

Environmental; pollution; biotechnology

### INTRODUCTION

The heavy metals associated with acid mine drainage (AMD) or with effluents derived from metallurgical industries are a major problem as toxic contaminants of natural and industrial aqueous systems, and this has stimulated the development of new systems for their removal. Several methods are available as treatment techniques for heavy metals contaminated liquid systems, but the most common one involves precipitation of metals with hydroxides, by the addition of sodium or calcium hydroxide in the form of lime, and separation of the metal hydroxides, generally by settling in ponds. Other known methods use conventional ion exchange, solvent extraction, activated carbon adsorption, cementation, reverse osmosis and evaporation. Most of them however, in the case of diffused-source pollution, where contamination is more frequently found over large areas or large volumes at relatively low concentration, are economically non-viable, as they require a pre concentration step. Such a situation has recently been observed both in the developed Western countries and in the countries of Central and Eastern Europe. In the later case, where the main limiting factor of wastewater treatment is the lack of available funds, the search for less costly and easy to maintain techniques is very crucial.

The growing interest in wetlands is in part due to recognition that natural treatment systems offer advantages over conventional ones. The introduction of constructed wetlands (CW) for the removal of toxic metals from voluminous wastewaters and its combination with consequent biological extraction of contaminants from the sediments, is considered as a suitable integrated treatment approach which could be an advantageous option. On the other hand, it is known that the use of coals, and related materials such as peat or wood sawdust, has proved feasible in some instances where low residual metal concentration was obtained. Moreover some of the coal microlitotypes are known to resemble activated carbons, and their individual adsorptive characteristics have not been investigated thoroughly. A further benefit of using such adsorptive media is that it offers the prospect of developing a process for collection and recycling of heavy metals, which might be preferred to their disposal to the environment as occurs with other similar procedures.

In this context, the objective of the present study was to test the feasibility of both methods for metallurgical effluents purification.

## BACKGROUND

### Use of Wetlands

The cycling of metals in the environment is connected with changes in aerobic/anaerobic conditions. To enhance these processes of metal retention constructed wetlands (CW) have been demonstrated as an efficient treatment system, especially suitable for the decontamination of voluminous wastewater streams, such as acid mine drainages. Low-cost immobilisation of pollutants for long periods of time is the main purpose of wetlands for AMD treatment, especially in cases with moderate flow rate of the drainage and reasonable areas available for construction.

### Treatment of metal polluted wastewaters

Heavy metal removal by wetlands has received little attention to date because most existing systems treat domestic waste waters with low metal concentrations, but metal removal by sediment and plant uptake, accumulation and adsorption has been documented [1–6].

It should be stressed that since constructed wetlands are a relatively new technology, knowledge of how they function to reduce pollutants is limited. Most of the available information consists of comparisons of inflow/outflow metal concentrations [7]. Only a few attempts have been made to evaluate the metal retention processes within wetlands. Moreover, the problem for treatment of the metal enriched wetland sediments has not been considered thoroughly, since the systems currently in operation have not yet reached their retention capacity.

Different authors suggest various levels of metal removal by wetlands. According to Lan *et al.* wetlands removed about 95% of Pb, 80% of Zn, and 80–95% of Cd content in waste waters, and Mn, Cu, and As were also reduced [8]. Satisfactory figures for Fe removal—95% Fe, and 66% for Mn are also reported [9]. According to the same author the similar chemistries of Ni, Cu, Pb, Zn, Ag, Au, and U suggest the possible removal of these elements from mining and industrial drainage by CW too. Recent studies at the Colorado School of Mines reveal 99% reduction in Al, Cd, Cr, Cu, Zn and Fe concentrations, 94% reduction of lead, 84% or more reduction of Ni and relatively little removal of Mn (between 9 and 44%).

The main features of the treatment processes within wetlands are:

- i. wastewater is treated by bacterial activity (aerobic treatment takes place in the rhizosphere and anoxic/anaerobic treatment in the surrounding soil);
- ii. reeds rhizomes grow vertically and horizontally, penetrating the soil and providing a “hydraulic pathway”;

- iii. atmospheric oxygen passes to the rhizosphere via leaves and stems, then to the hollow rhizomes, and out through the reed roots creating a mosaic of anaerobic and aerobic activity;
- iv. filtration of suspended and colloidal material by the substrate or by surface plant debris;
- v. physico-chemical interactions with the growing medium, adsorption, absorption or ion exchange of metals onto soil matter, live plant material, plant detritus or algae. It is unlikely that the adsorption capacity of the substrates will be efficient for an extended time [10];
- vi. precipitation of metals in the oxidising and reducing zones catalysed by bacterial activity;
- vii. precipitation and neutralisation through the generation of  $\text{NH}_3$  and  $\text{HCO}_3^-$  by bacterial decay of biologic material;
- viii. co-precipitation and adsorption of metal ions on iron and manganese hydroxides;
- ix. complexation of metals by different complexing agents in the system;
- x. uptake of nutrients and metals by plants.

Although there is some uncertainty, current studies of wetland geochemistry suggest that the dominant removal process is by item vi [5].

An important mechanism of metal removal within wetlands is bacterial sulphate reduction inducing metal precipitation by formation of metal sulphides in anoxic environments with abundance of sulphate, pH above 5 and readily degradable organic matter [10]. The hydrogen sulphide and bicarbonate by-products of bacterial sulphate reduction immobilise a number of potentially toxic metals such as Cd, Hg, Cu, Pb, Ni, Zn, and Ag and raise the pH of the water, which also causes metal precipitation. Microbial reduction of sulphate to sulphide, followed by precipitation of heavy metal sulphides, is the predominant process accounting for the removal of over 90% of the Fe, Cu and Zn and for the pH rise from 3 to 6 in the CW [11]. The concept behind wetlands construction is the planting of emergent plants that will eventually yield enough organic matter to support continued sulphate-reducing bacterial activity after organic amendment addition is terminated. In addition, oxygen leaking out of the plant roots oxidises the surrounding substrate, supports aerobic micro-organisms and therefore may oxidise and immobilise toxic metals. If insufficient organic matter is available, sulphate reduction is of minor importance in precipitation of metals in anaerobic zones. Sulphide formation in freshwater systems is generally limited by the low  $\text{SO}_4^{2-}$  concentrations, but this should not be the limiting factor in AMD since several studies have found high rates of sulphate reduction [10,12]. Although the process is inhibited by low pH ( $\text{pH} < 5$ ), it is reported that even in cases of AMD with  $\text{pH} < 3$ , the pH of the pore water in the substrate is consistently 6–7 [12].

There are several different ways to enhance the natural production of biogenic hydrogen sulphide. The addition of calcium sulphate (gypsum) and modification of the wetland designs to increase the movement of the drainage through anoxic sediments may significantly stimulate the bacterial sulphide production. Different organic compounds may be used as a source of electrons, ranging from rather expensive substrates, to cheap additives, such as hay-extract, municipal wastewater, etc.

The main advantages of the wetland systems, which suggest their suitability for waste water treatment are:

- provide effective and reliable waste water treatment for domestic and some industrial waste waters to secondary and tertiary standards;
- low construction and maintenance costs;
- simple construction;
- can be located at the place of waste water production;

- low training requirements for the personnel;
- they are robust and able to withstand fluctuating hydrologic and contaminant loading rates, suitable for high water flows;
- low energy requirements;
- they are environmentally and aesthetically acceptable and may provide indirect benefits such as green space, wildlife habitats and recreational and educational area;
- suitable climatic conditions and abundance of naturally growing wetland plant species.

Disadvantages of constructed wetlands for waste water treatment relative to conventional systems are:

- relatively large land area requirements for advanced treatment;
- lack of any consistent guiding principles, imprecise design and operating criteria [13];
- biological and hydrological complexity and difficulty in understanding the process dynamics and mechanisms taking place within wetlands. There is a considerable site-to-site variability in apparent water quality improvement;
- possible problems with pests;
- require one or two growing seasons to achieve optimal efficiency;
- lack of long term information and experience with these systems. Only crude estimates of the finite capacity of CW to retain metals exist;
- wetlands at their retention capacity require sludge removal and disposal.

Usually it is advisable to precede the CW with some form of preliminary/primary treatment. In the case of acid mine drainage the incorporation of pH neutralisation ponds is recommended. The use of stabilisation ponds or macrophytes alone can hardly remove a substantial amount of heavy metals from the waste waters, and the use of at least two parallel cells is suggested to increase the operational and maintenance flexibility of the system.

#### **Treatment of wetland sediments**

The retention of heavy metals by the sediment of wetland, reed bed, or root-zone systems may be substantially enhanced using microbial sulphate reduction. This process occurs in anaerobic water-saturated sediments, and other anoxic ecosystems. Sulphate reduction is mediated by a special group of micro-organisms, which can mineralise (oxidise) organic matter in the anoxic conditions [11]. The acceptor of electrons generated by this process is sulphate, which is reduced to sulphide. There are two requirements for the enhancement of such a process:

- i. appropriate amounts of sulphate should be present in the system (in the incoming water, or added to the system directly);
- ii. micro-organisms should be supplied with adequate amounts of electron donor.

The levels of sulphate are usually not the limiting factor, especially in the waste waters originating from mining/metallurgy, although the addition of sulphate in the form of gypsum has been reported to stimulate the process [12]. However, the appropriate source of electrons may be a limiting factor. Several studies using generator gas, ethanol, or waste organic-rich liquor have been published [14, 15]. The use of bio mass

grown on the surface of a wetland has been able to produce a 'hay extract', i.e. the liquor obtained by fermentation of the harvested shoots [10]. Organic-waste like sludge may be a feasible alternative, since there are hardly any limitations on the content of heavy metals in such organic waste being used for the metals-retaining wetland. The source of organic substrate may also be a compost, such as the mushroom compost or other wastes [16,17].

**Production of sulphide in the system immobilises metals in several ways:**

- i. sulphide reacts immediately with divalent cations of metals, forming insoluble metal sulphides;
- ii. precipitated material is retained in the sediment by the mechanisms of filtration, decantation, or particle adhesion;
- iii. sulphate reduction is accompanied by a substantial increase of pH. The most important source of alkalinity is the dissociation of sulphide in water:



and formation of bicarbonate (product of degradation of organic acids) which removes acidity as CO<sub>2</sub> gas:



Increased pH mediates other processes of cationic metal immobilisation, such as the adsorption on minerals or organic matter, precipitation, etc.[18].

Sulphate reduction has been shown to be a feasible and cost-effective alternative to immobilise heavy metals in anaerobic sediments. Several reedbed installations for the treatment of acid mine drainage have been demonstrated at full scale [10,19], and the successful sanitative immobilisation of metals in lake sediment using the addition of gypsum has also been reported [12]. However, the decontamination of such reed bed sediment is still a problem. In the life cycle of constructed wetlands, metals may reach rather extreme concentrations, up to several grams per kilogram in the sediment, thus posing a serious threat to the environment. In conditions of inadequate operation of the wetland, especially when some of the sediment emerges above the water surface and becomes aerobic, a reverse leaching of metals may occur [20]. Therefore, a periodical clean-up of such sediment has to be considered [21].

In general, the removal of heavy metals from contaminated soils or sediments is technologically complex. Remediation of the sediments is currently limited to the following techniques:

- i. phase separation (classification);
- ii. molecular separation (extraction or evaporation);
- iii. solidification [21,22].

Furthermore, most of these techniques have been demonstrated successfully only in ex-situ configuration, the sediment being excavated and transported to the treatment system, where it undergoes rather drastic treatment. Phase separation is used on the non-homogenous distribution of metals in different particle size fractions of the sediment. For example, a substantial amount of total metal contamination is adsorbed on fine clay minerals. However, the weight percentage of these clay minerals may not be high—less than 20%. Therefore, the sediment must be treated in order to separate different particle size phases. Relatively clean sand and other large particles may be re-used, for example, for filling the new reedbed, so that the contamination is further concentrated into a smaller mass and can be easily treated. Examples of such techniques are hydrocyclones or fluidized beds [23]. This technique is used world wide and extensive technological experience is available [19,24,25].

Molecular separation techniques are directed towards extraction of the contaminating molecules from the bulk sediment. Liquid extraction with mineral acids is mostly used [26]. However, rather drastic treatment

conditions (pH 1–2) limit the applicability of such techniques to very special cases. After such treatment, performed mostly with hydrochloric acid, the sediment is heavily damaged. Complicated post-treatment can limit the hazards associated with further release of cations from this material after clean-up, but its reuse is practically impossible. Furthermore, the regeneration of the spent extractant may be the most complicated step in the whole operation, since at such low pH, ions other than the selected contaminating metals are also solubilised. Evaporation of heavy metals is applicable only for the species which are volatilized at higher temperatures. Currently, only mercury and arsenic have been treated successfully on a large industrial scale [27,28]. Some other extractants are also proposed, however with as yet limited practical application [29]. Solidification is the third commonly used technique, although it is not aimed at the physical removal of metals from the sediment. The treated material is mixed with a solidifying agent, which, after its solidification, physically protects the material from percolation. Therefore, such material may be disposed of at lower cost and risks. The applied solidifying agents can be concrete/cement, organic polymers, or melting of the minerals by electric arc, which after cooling forms a glass-like inert mass [19,24,30].

Very few applications of in-situ removal of metals from soils have been recorded. In-situ soil washing with a diluted aqueous solution of hydrochloric acid (pH 3.5) has been used to remove cadmium from soil [31]. Pump-and-treat principle is applied in The Netherlands to wash soil heavily contaminated by a zinc smelter [32]. A promising in-situ technique appears to be electroreclamation, which uses electroosmotic and electrokinetic phenomena between a set of electrodes inserted into the soil [33,34]. However, its feasibility for reedbed sediments has still to be tested. To screen and evaluate potential techniques for the treatment of reed bed sediments, the extent and character of the contamination has to be determined. The following points are of importance:

- Metal concentrations, and the presence of different metallic elements, particularly anion-forming metals (As), or other hazardous contaminants (PAH's, PCB's, etc.).
- The chemical form of metals in the sediment. Suppose that much of the metal is bound as sulphide precipitates, then immediately after initiation of the treatment, strong acidification and leaching of metals should be considered. This may negatively affect any cementation or polymerisation techniques, as well as treatment of the material in general.
- The physical characteristics of the contaminants in the soil, i.e. determination of the size fractions containing the contamination, detection of specific precipitate particles which may be removed by classification, etc. should be investigated.
- The reedbed sediment will possibly contain high levels of raw organic matter, which may negatively affect numerous physical-chemical processes of treatment.

Combined with the presence of sulphides, as mentioned above, a preliminary stabilisation of such material will be needed before the technique is applied.

Little is known of most of the above aspects, since the problem of remediation of reedbeds loaded with heavy metals has not as yet been extensively investigated. However, assuming a reedbed lifetime of 5–20 years, such questions will undoubtedly arise in the near future.

A feasible alternative seems to be the use of microbial leaching (bioleaching). This is a process of bacterial oxidation of reduced sulphur or iron-containing compounds, such as  $\text{Fe}^{2+}$  ions, elemental sulphur, metal sulphides, etc. This process solubilises metals either directly, as in the bacterial oxidation of ZnS, where highly soluble zinc sulphate is formed, or indirectly, as when extraction takes place due to highly acid conditions, or solubilisation is by the action of aggressive ferric ions [35]. This process is applied at industrial scale in the minerals industry, and recent literature reports on its possible application for the extraction of metals from contaminated sewage sludge and other solid waste, and eventually from soils or sediments [22,36,37,38]. Reedbed sediments loaded with sulphides may be ideal materials for such a process. Bioleaching of contaminated sediments dredged from the River Rhine estuary appears to be

feasible. Such bioleaching processes may not need to be performed in fully-agitated systems. Heap-leaching, or percolation of a thin (0.5 m) layer of the sediment on a hydrogeologically isolated bed may provide alternatives worthy of further study [21]. By such methods sulphate reduction carried out in a wetland may be followed and combined with bioleaching. Spent extractant from bioleaching may be further processed using conventional physical-chemical or biological processes, depending on the amount of water, concentrations of metals, etc. An alternative is to continue with the use of sulphur conversion, i.e. to first remove metals from the extractant in an anaerobic reactor, performing sulphate reduction. Secondly, the metals-containing sulphide sludge may be recycled and the excess sulphide (if any) reused. A recycling of sulphur is eventually possible, closing the so-called microbial sulphur cycle [39,40]. However, further research is required in this area.

### **Adsorption on Low Rank Coals**

Low rank coals such as brown coal or lignite exist as large easily worked deposits in many countries. They are classified by the American Society for Testing and Materials (ASTM) as having a calorific value of less than 83000 BTU lb<sup>-1</sup> (19.3 MJkg<sup>-1</sup>) on a moist but mineral-free basis. The chemical structure of these coals includes carboxylic and phenol hydroxyl groups and it has been shown that these groups are capable of ion exchange with calcium and barium [41]. Further contact with dissolved or suspended materials could lead to hydrophobic interactions with the carbon skeleton. Their vast porosity facilitates access to the functional groups and increases the total surface area available for adsorption to take place. Various investigations have been performed to assess the feasibility of using lignite as an ion exchange media for extraction of metals. Preliminary work showed that it is possible to almost totally extract copper, nickel, chromium, cadmium, lead, zinc, mercury, cobalt, silver, iron, manganese, vanadium, germanium, antimony, aluminium and uranium from solutions with an initial concentration of 1 g/L [42]. Other work has been directed towards metal winning from solutions ranging from weakly acid to slightly alkaline. Saha *et al.* have reported a multistage adsorption of nickel, with a view to adapting this method to continuous or semi continuous flow-sheets [43]. A successful demonstration of the feasibility of removal of organic reagents from solvent extraction effluents by adsorption onto lignite has been reported [44]. Low grade coal was also used for treatment of pregnant solutions, from thiourea leaching of gold bearing ores and tailings, as an alternative to activated carbons [45]. It was found that by incorporation of a two stage adsorption process, securing metals selection on the adsorption stage, it is possible to reduce the costs associated with the subsequent metallurgical treatment. Here it should be pointed out that this approach is feasible because the loaded sorbents need no regeneration and can be incinerated in the final precious metals winning step. In every work cited the following parameters are reported to be of paramount importance for proper process performance: sorbent-sorbate ratio, contact time, pH and flow rate of solution. As regards metals winning from sorbents the following options are suggested: ignition/melting, desorption/elution.

The suitability of this method for industrial application will generally depend on many factors, including the residual metal concentration required, the extraction performance compared with other methods, availability and costs of the coal at the plant site, the operational system selected and overall costs. As regards the principle of operation in practice, it is suggested that contacting of the media with solutions and subsequent filtration may be preferable for large volumes of solutions with diffused pollution. This could be performed either in an agitated reactor or by passing the solution through a packed bed, which could be deep and stationary or shallow and moving. In all cases, however, further intensive research is needed in order to assess overall costs and application feasibility.

## **EXPERIMENTAL**

### **Constructed Wetland for Treatment of Copper Refinery Effluents in Bulgaria**

#### **Objective**

An experimental pilot-scale wetland system was established to evaluate the possibility of application of constructed wetlands for the treatment of copper refinery effluents. The site selected is located in the area

surrounding Pirdop Copper Refinery, Bulgaria (one of the biggest in Europe), which utilises the Outokumpu Flash system. A persistence feature of the plant operation is the fluctuation in the input feed (sulphide concentrates), which causes variations in the pollutant concentration of the waste waters disposed. The main metal-polluted stream leaving the copper smelter is that from the electrolysis department. Its acidic wastewaters are neutralised with calcium hydroxide prior to discharge to the tailings lagoon. The pH in the lagoon is maintained in the range 10–12 and most of the metals are precipitated as hydroxides. Of greatest concern are the elevated concentrations of As and Se, which are not sufficiently precipitated in the tailings lagoon and thus pollute the river Topolnica, which subsequently feeds an irrigation dam. Hence, the major environmental problem in this region is the contamination of land and fresh waters with metals, particularly arsenic.

The local climate is suitable for growing reeds. There is an abundance of naturally occurring wetland plants (*Typha latifolia* and *Phragmites spp.*) around the experimental site, some *Phragmites spp.* even growing in the tailings lagoon. The soil in the region is rich in clay, which enables the sealing of the beds. Since this is an on-going experiment, the results refer only to the vegetation period of 1995.

### Construction of the experimental reedbeds

The wetland receives a representative amount of outflow wastewaters from the sedimentation lagoon of the plant via specially devised pipe lines. The average elemental base-line concentrations in the water discharged from the lagoon are given in Table 1. Sediment and plant metal concentrations were also analysed.

TABLE 1 Characteristics of the Effluent Entering the Wetland

Element	Cu	Zn	Fe	Mn	Cd	Ni	As	Se
Concentration, mg/L	0.5–5	0.1–0.5	1–2	<0.1	<0.1	<0.1	0.2–0.5	0.1–0.5

The wetland system consists of three reedbeds in sequence and was set up to provide consequent water treatment in aerobic and anaerobic conditions. The first and last reedbeds were overland flow beds (0.15 m in depth) and the second bed was anaerobic (0.5 m in depth). The total area of established reedbeds was approximately 220 m<sup>2</sup>. An additional fourth overland flow bed was established in order to supply comparative background data. The daily hydraulic load rate to the system was 46 l/m<sup>2</sup>.

### Preliminary Results and Discussion

After commissioning, water samples were collected from the inlets/outlets of the reedbeds at regular intervals in order to assess the metal removal performance of the wetland.

During the start up period, which coincided with unusually high metal concentrations in the inflow wastewaters (mg/L; Cu—10–24, Fe—5–14, Zn—1, etc.), high removal of metals was observed. All the metals of concern were removed up to 99%. Arsenic removal ranged from 67 to 81%. The only exception was selenium, for which no substantial removal was observed.

However, a decline in the wetland performance was detected later in the summer. One possible explanation of this finding is the saturation of the clay-rich soil lining of the beds and the further covering of the sediment with precipitates of metal salts and hydroxides [46]. Moreover during this period the concentrations of iron and non-ferrous metals in the inflow wastewaters decreased to the levels of discharge permissible in the country, the total inflow concentrations for iron being below 0.03 mg/L. The concentration of the major pollutants (As and Se) in the inflow remained at the same level (0.5–2 mg/L), with no consistent removal observed for them. The latter observation agreed with previous findings, where the presence of iron hydroxides was associated with arsenic removal [47].



## Effluent Treatment by Low Rank Coal and its Maceral Fractions

### Objective

The objective of the second approach studied was to subject the effluents of concern to adsorption by coal and its microlytotype fractions, i.e. macerals. A comparison between the individual performance of these fractions towards differential removal of certain elements from the studied effluents was also carried out.

### Materials and Methods

#### Adsorbents

A Bulgarian lignite, with principal characteristics shown in Table 2, was used. It was ground successively by jaw crusher and tema-mill, and the size class 10–75  $\mu\text{m}$  was employed.

TABLE 2 Characteristics of the lignite studied

Ash content, %	30
Moisture, %	26
Volume weight, $\text{g}/\text{cm}^3$	1.33
Assay, %	
S	0.57
Volatile	36.9
Carbon	41.4
Calority, cal.	3200

Sink/float fractionation of the coal was carried out by vigorous agitation, followed by gravity separation of 10 grams coal in  $\text{ZnCl}_2$  media (heavy liquid) at various densities. Solvent extraction funnels with 500 ml volume were used. Owing to previous petrography studies the following densities were allocated to the given maceral groups—Table 3 [48].

TABLE 3 Microlitotype fractions with respective densities

Petrographic microlitotype	Density, $\text{g}/\text{cm}^3$
Liptinite	< 1.25
Vitrinite	1.25–1.35
Inertinite	> 1.35

Microscopic studies of polished and thin sections of coal fractions were performed under both reflected and transmitted light using a Leitz microscope.

#### Sorbates

The following solutions were prepared or used as obtained. In every case an attempt was made to simulate the outflow effluents from "Pirdop" smelter, i.e. those studied in the wetland case:

- i. synthetic multi elemental solution having the following concentration:  $\text{mg}/\text{L}$ , Cu—300, Pb—20, Fe—430. This was obtained by dissolving pure metallic powders in 0.1 N  $\text{H}_2\text{SO}_4$ ; pH of solution was 1.8.
- ii. outflow effluent taken from a metallurgical copper refinery, slightly fortified with the targeted elements in order to resemble the maximum values found in the real effluents. The principal concentration was ( $\text{mg}/\text{L}$ ): Cu—25, Pb—10, Ni—2.5, Zn—1.2, Fe—15, and pH was 5.6.

## Procedure

Solid-liquid agitation was carried out in a wrist-action shaker. Plastic bottles were used as agitation vessels. Filtration was performed by gravity. The adsorption of elements was determined by measuring their concentration before and after contact with the adsorbent. Liquid assays were performed on an atomic adsorption spectrophotometer "Varian 10".

Adsorption isotherms were constructed by the addition of successive amounts of 0.5, 0.75, 1 and 1.5 grams of coal in 50 ml stock solutions. Agitation time was kept constant—15 minutes. Initial copper concentration in solution was 120 mg/L, pH was 4.8.

Electrophoretic measurements were performed on a Rank Brothers II electrophoresis instrument with flat cell arrangement. Measured electrophoretic mobilities were expressed as zeta potential by means of the Smoluchowski equation. The standard procedure described in the manufacturer's manual was followed. Coal samples were milled successively in a tema-mill and in an agate mortar, in order to obtain a size range under 10  $\mu\text{m}$ . Agitation with the pH adjusted solution was carried out for 15 minutes before filling the measuring cell of the instrument.

## Results and Analysis

The microscopic observations indicated that, despite the coals being relatively young in terms of coalification age, a separation had obviously taken place, and fractions resembling the inertinite with an altered plant cell structure were identified in the 1.35 sink [46].

### Adsorption tests

As an initial starting point, it was decided to commence with an investigation of the effect of coal to effluent ratio on the degree of elements adsorption from the artificial solutions. These results are summarised in Figures 1 to 3.

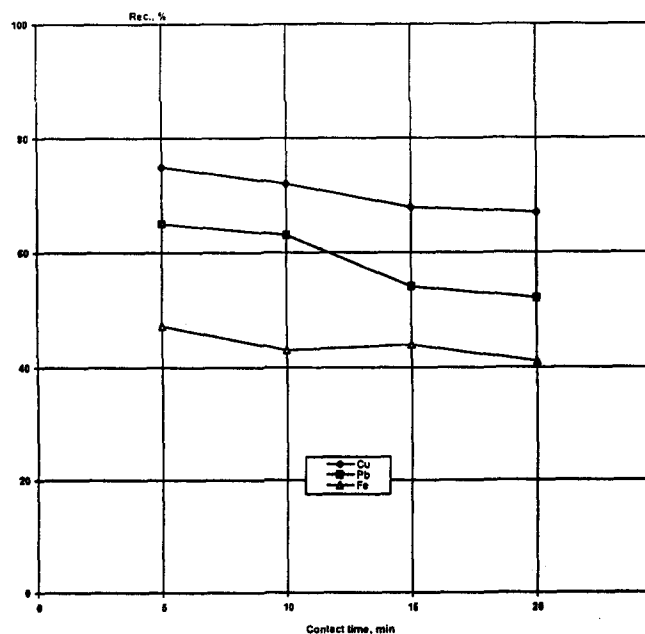


Fig.1 Adsorption of Cu, Pb and Fe from Synthetic Solutions with Non-treated Raw Lignite with Concentration 5 g/L

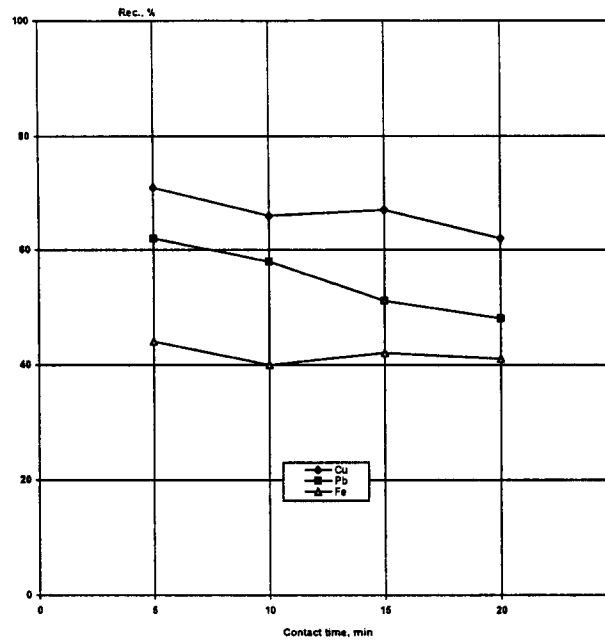


Fig.2 Adsorption of Cu, Pb and Fe from Synthetic Solutions with Non-treated Raw Lignite with Concentration 10 g/L

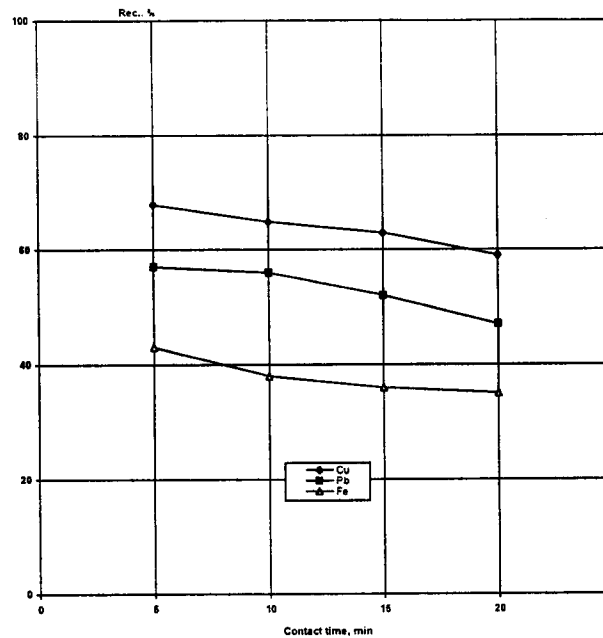


Fig.3 Adsorption of Cu, Pb and Fe from Synthetic Solutions with Non-treated Raw Lignite with Concentration 15 g/L.

It is evident from these results that the non-treated lignite does adsorb the targeted metals to a certain, but not to a desired extent, and the increase in contact time above 5 minutes does not lead to a better uptake of elements. The optimal concentration of lignite was 5 g/L and further increase does not lead to enhanced removal, possibly due to coal swelling. Similar tests were performed with the various “maceral” groups of the lignite, but the results have shown no significant difference in their performance compared to that for the “raw” lignite. This could probably be attributed to the high metal concentration in the synthetic effluent.

On the basis of these findings, it was decided to proceed with treatment of the real metallurgical plant effluent (additionally fortified) (solution ii) and to focus particularly on copper and zinc removal. The effects of lignite fractionation and adsorbent concentration were investigated in this set of experiments, with a contact time of 5 minutes considered sufficient in view of the results obtained with the artificial solutions. These observations are summarised in Figures 4 and 5.

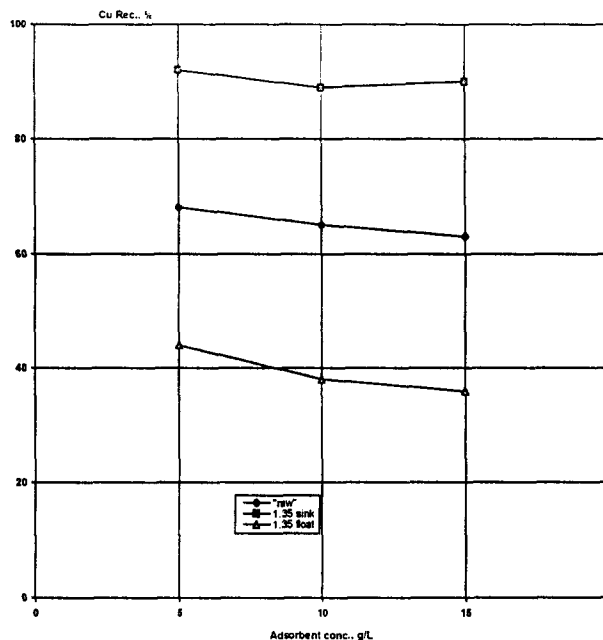


Fig.4 Effect of the Adsorbent Type on the Degree of Copper Adsorption from Metallurgical Effluent (Contact Time—5 min.)

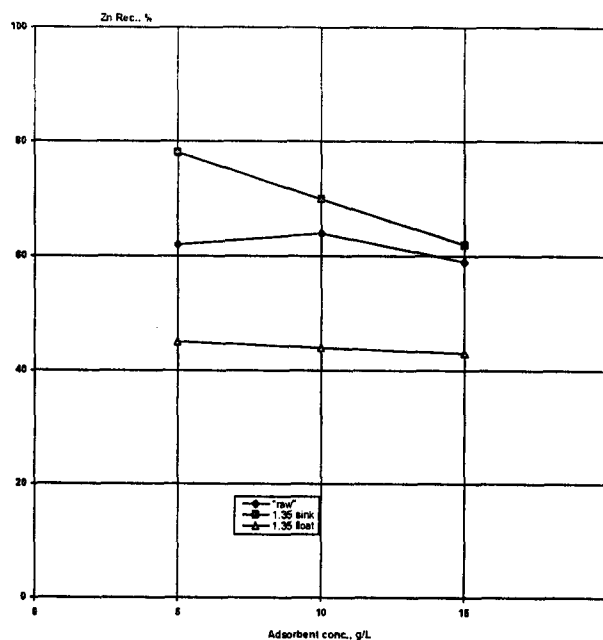


Fig.5 Effect of the Adsorbent Type on the Degree of Zinc Adsorption from Metallurgical Effluent (Contact Time—5 min.)

Figure 4 and 5 suggest that for both copper and zinc, the "raw" lignite recovery curve always lies between those for the sink and float fractions. This relationship is particularly clear in the case of copper uptake (Figure 4), where the 1.35 float fraction fails to adsorb copper above 40% in the whole range of adsorbent

concentration investigated, while the sink fraction marginally outperforms the two others. Thus it can be concluded that coal processing has yielded a fraction richer in carbon, possessing superior adsorptive characteristics, this obviously being the inertinite, reporting preferentially to the 1.35 sink. Zinc concentration, however, was found to increase in the solution, i.e. adsorption recovery has decreased (Figure 5). This can be attributed to the action of the acidic effluent treated, which is back-leaching the Zn accumulated within the coals' micropores during their soaking in  $ZnCl_2$ . It should be noted that Ni and Pb removal presented no problems for any of the adsorbents.

#### Isotherms construction for copper adsorption

Adsorption isotherms for copper uptake were determined for the raw, 1.35 float and 1.35 sink fractions and are shown in Figures 6 to 8 respectively.

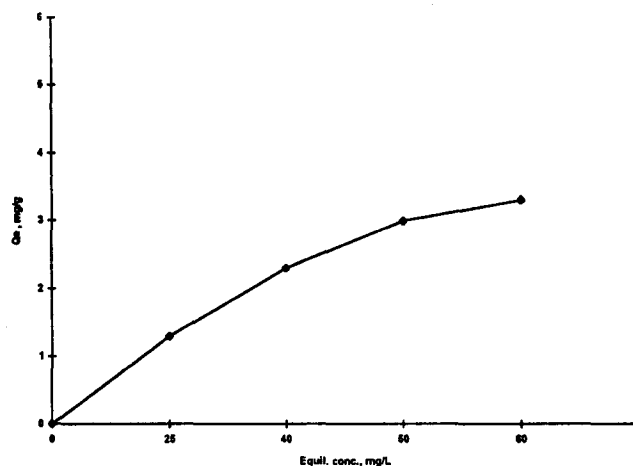


Fig.6 Copper Adsorption Isotherm for "Raw"-Non-treated Lignite

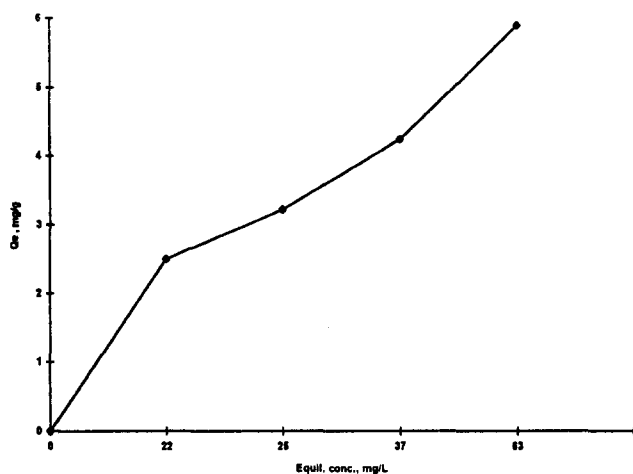


Fig.7 Copper Adsorption Isotherm for 1.35 Float Fraction

The upward shape of the curve for the 1.35 sink is generally a good characteristic for this fraction. Obviously its adsorptive capacity is higher than that of the rest of the adsorbents studied (about twice that of the raw lignite). This phenomenon can be explained by the fact that part of the ash in the lignite is eventually substantially removed during the heavy liquid separation, reporting to the lighter fraction and thus leaving much more active sites for adsorption of the other fractions. However, the best  $Q_e$  value reached—less than 10 mg/g—suggests weaker adsorptive behaviour of these fractions than of the activated carbons.

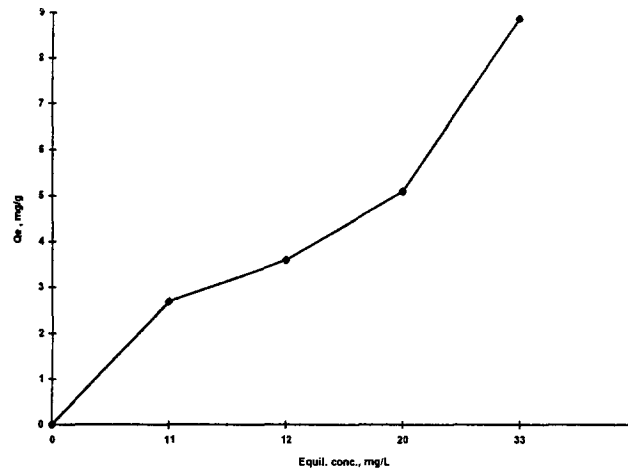


Fig.8 Copper Adsorption Isotherm for 1.35 Sink Fraction

#### Electrophoretic mobility study for 1.35 sink fraction

Zeta potential studies aimed at determination of the surface state of the adsorbents with a view to revealing the possible mechanisms involved, and the effect of pH. During this study a surface treatment, i.e. washing of the 1.35 sink fractions with NaOH or distilled water, was applied. The results are shown in Figures 9 to 11.

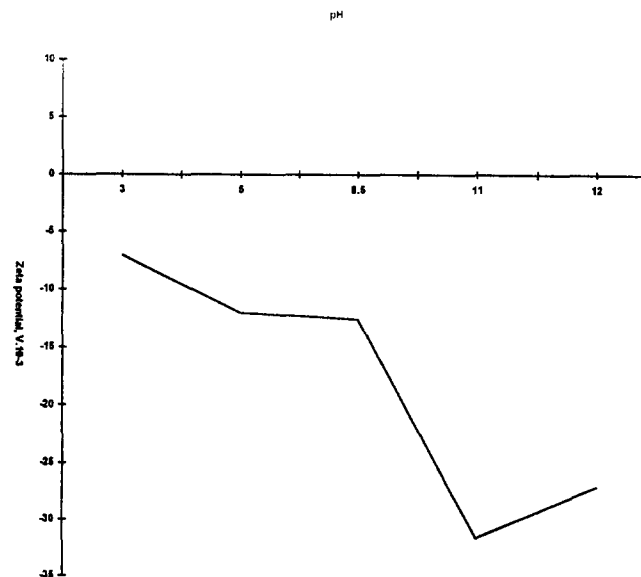


Fig.9 Effect of pH on  $\zeta$  Potential for 1.35 Sink Non-washed Fractions

The relationships between zeta potential and pH suggest that washing of the 1.35 sink fraction with water reverses the negative zeta potential to positive at lower pH values. This could probably be attributed to adsorption of hydrogen ions at surface sites. The negative zeta potential at higher pH could be due to the product of OH reaction with acidic surface groups (such as carboxylic, phenolic etc.)

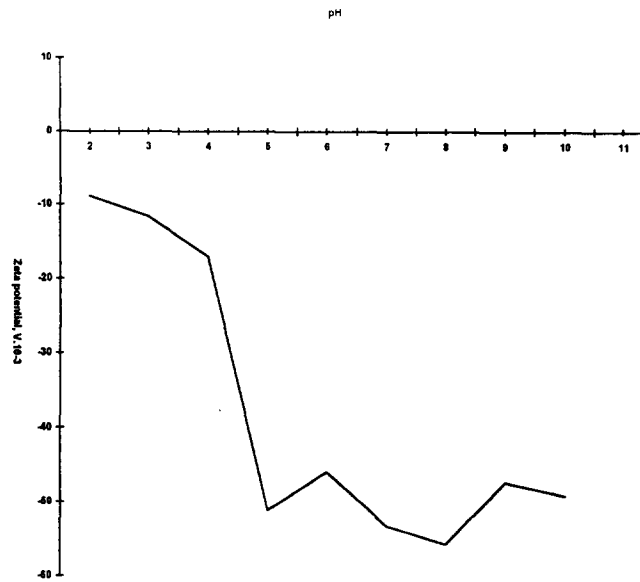


Fig.10 Effect of pH on  $\zeta$  potential for 1.35 Sink (washed with NaOH)

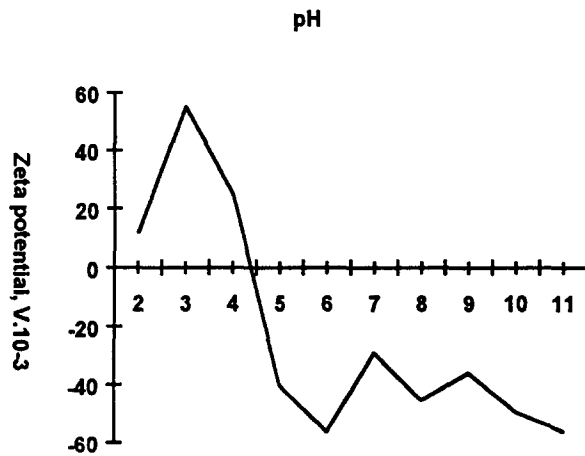


Fig.11 Effect of pH on  $\zeta$  Potential for 1.35 Sink (washed with Distilled Water)

### CONCLUSIONS

The initial performance of a pilot scale constructed wetland system was found to be satisfactory as a secondary treatment facility for metallurgical effluent purification. All the metals of concern were removed to a desired degree.

- Over a long term period however, a decline in operation was observed, possibly due to saturation of the bed linings, and changes in inflow concentration of elements.
- The separation by heavy liquids for the purpose of sink–float fractionation yielded relatively pure samples of the various maceral groups found in the lignite and was beneficial in rejecting the ash. Microscopic observations of thin and polished sections confirmed that separation took place and the most carbon enriched fraction, resembling charcoal, was the 1.35 sink, which, according to previous work, should be the inertinite group.
- The maceral fractions did not have better adsorptive characteristics than “raw” lignite, in the case of the treatment of artificial liquors. However the inertinite group proved superior when real effluents were treated.
- The adsorption isotherms constructed for copper have also confirmed the above findings, thus indicating the importance of the carbon fusicisation process for adsorption related phenomena.
- Provided an effective and easy to maintain coal refining technique is made available (such as flotation) the results achieved in the coal adsorption study could be exploited when materials with selective adsorptive properties are required, producing minimal environmental impact.

### RECOMMENDATIONS

It is hoped that this short review, and the experimental results, will aid decision making in the implementation of low-cost and environmentally tailored approaches, such as passive treatment systems involving wetlands, or adsorption on naturally occurring adsorbents. It is evident that both methods have merits and limitations and further intensive research is needed to determine which is most suitable for a particular case. This is already underway to a certain extent, the results hopefully being the subject of future publications.

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