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REMEDIATION OF SPECIFICALLY POLLUTED WASTE EFFLUENTS USING NATURAL ZEOLITES

Far-reaching changes of natural environment have occurred in most of the larger estuaries, recipients and aquatic bodies all over the world for the last century and a few of them can be considered to have retained many traces of their original character. Nowadays about 30% of our planet suffers from desertification. This paper tries to outline some overview of current remediation techniques dealing with the removal of nutrients and toxic metals after a challenging introduction describing worldwide pollution problems.

1. INTRODUCTION

Industrial development is inevitably accompanied by environmental pollution; however, over the last several decades most of the highly developed countries have introduced control of sewage and industrial discharges into environment, in contrast to the developing countries which are not able to control strictly their pollution or often ignore it because of a backward economy [1], [2].

As a result, the rates of production of many chemicals of concern, i.e., organohalogens, toxic metals, oil, radionuclides, nutrients, have altered in recent decades, rising in the tropics and subtropics or in the far north. The rate of global utilisation of these compounds has not dropped, while their demand, especially in developing countries, has increased with expanding populations and industrialisation. Everlasting and complex pollution problems, especially those of pollutants' sufficient volatility, have thus emerged as a major concern over aerial transport on both regional and global scale. Thus, global pollution loads have increased and shifted somewhat, with emphasis on geographic region, over the last century. Many trace elements are now being mined at a pace which exceeds their natural mobilisation rates by more than an order of magnitude. The contribution of anthropogenically derived metals to the total metals has been quantified for certain local environments [3], [4].

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For example, the catchment of San Francisco Bay has been radically altered through extensive urbanisation, the introduction of massive water management schemes, the agricultural development of the naturally arid Central Valley of California and the loss of some 96% of the historical area of wetlands [5].

Each of these changes exerts significant impact on both the hydrodynamics of the estuary and its ability to assimilate contaminants, thus providing the potential for synergism of the increases in pollutant loading and other changes in the estuary.

This pattern is repeated in many regions of the world and the resultant changes are not restricted to industrial catchments, but are also evident on much greater scale. Management of the sites polluted with nutrients, heavy metals, organohalogens and oil is inseparably connected with the assessment of the various remediation alternatives which may be applied.

This paper is intended to discuss various remediation methods, mostly for liquid wastes applied on a practical scale. Finally, some bioindication and biomonitoring pattern of refinery site are sketched.

2. AQUATIC POLLUTION WITH NUTRIENTS AND PUBLIC HEALTH

Nutrients loads in the Northern Adriatic Sea and the Po river estuary deteriorated over several decades causing extensive algal blooms, which was accompanied by mucilage production by diatoms. The eutrophication of inland and coastal waters due to nutrient discharges may be associated with several problems [6].

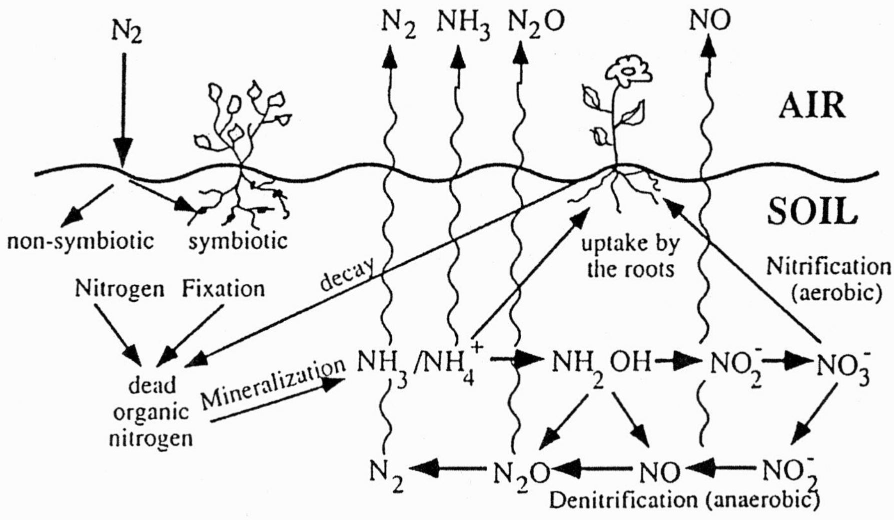

Fig. 1. Ammonia cycle in nature

The Peel Harvey Estuary in Western Australia provides an excellent example because in this area superphosphate fertilisers are used in farmland. Apart from the physical protection of the estuary against vessel traffic, oxygen sags are experienced at night and fisheries productivity suffers as a result.

Certain species of dinoflagellates may give rise to very significant impact on public health while producing toxins which pass via the food chain even to human, resulting in paralytic shellfish poisoning (PSP). There is evidence that this dinoflagellate species is spreading geographically through the Indo-Pacific and cause numerous PSP incidents by consumption of shellfish [7].

Basically ammonia is not a poison. It is produced by almost all living organisms (e.g., fish and also humans), thus it has no cumulative, toxic effects as lead or mercury (figure 1). Excessive concentrations of nutrients such as nitrates and phosphates in waters stimulate algal growth and lead to plankton blooms, producing obnoxious tastes and odours of water, excessive plant growth causing stagnation and disruption of aquatic ecosystem [8].

2.1. PHYSICOCHEMICAL TREATMENT METHODS, INCLUDING NATURAL AND COMPOSITE MATERIALS IN CONJUCTION WITH BIOPROCESSES

The use of conventional ion-exchange resin for the removal of nitrogen compounds from waters has not been found extraordinarily attractive because of its high cost, difficulties with handling of regenerant effluents, thermal and radiolytic instability, etc.

Clinoptilolite, naturally abundant mineral, can selectively exchange ammonium for all other cations commonly present in municipal wastewaters such as Ca, Mg and Na, except for K. On the basis of better economy and superior selectivity preference to ammonia, clinoptilolite application may replace the conventional water treatment technologies in some partial stages [9], [10].

Operating expenses of biological nitrification–denitrification (BND) variant are slightly lower than those of ion exchange using clinoptilolite; however, the investment expenditures for BND are higher. The lower investment expenditure and other benefits of final, almost in every case tertiary, physicochemical treatment favour the clinoptilolite technology. Nevertheless, biological technologies, being more conventional, allow a complex degradation of water pollutants [11], [12].

REM NUT is the process that allows conservation of natural resources. It was developed in the 1980s in Italy in order to remove both ammonium and phosphate ions from wastewater and to recover them in the form of a slow-releasing fertiliser, struvite (figure 2). The process is based on the use of ammonium-selective natural zeolite and phosphorus-selective commercial anion exchanger able to remove nutrient ions from sewage. Due to such treatment sewage meets the required standards and may be discharged. Both ion exchangers are regenerated in closed-loop recirculation of neutral

0.6 M NaCl from which struvite is precipitated by magnesium and phosphate salts. REM NUT process has not reached a full-scale application so far [13].

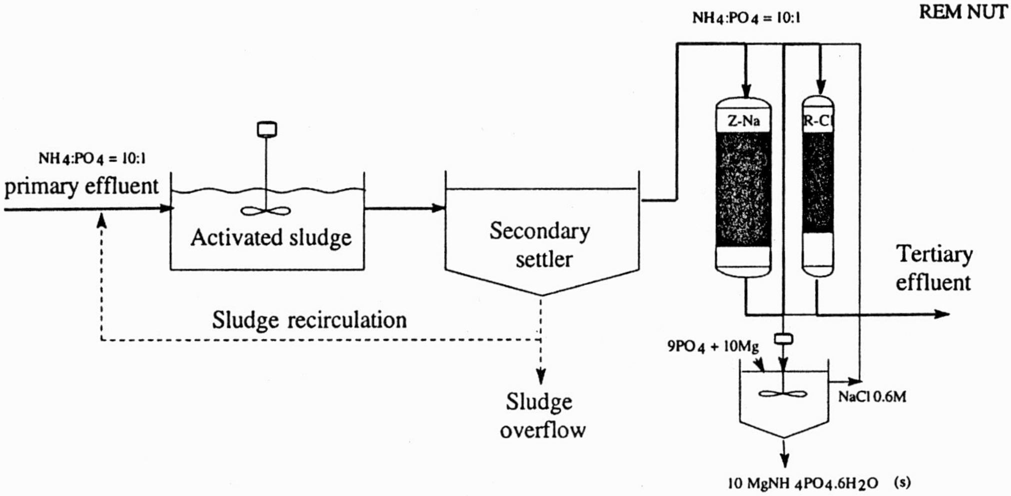

Fig. 2. REM NUT process layout applied to municipal wastewater treatment (Z–Na = NH_4-selective zeolite in the Na-form, R–Cl = P-selective anion resin in the Cl-form)

In 1986, at Water Research Institute in Bratislava a laboratory model was designed before pilot scale operation for ammonium removal from both drinking and tannery wastewaters started its operation. While this laboratory model during one cycle treated to an acceptable level of 0.5 mg/dm^3 a volume of 675 dm^3, the pilot clinoptilolite column allowed treatment of 85 m^3 of water, i.e. 4-day operation of such a bed removed 81 g ammonia from the treated water [10], [12].

The pilot-scale installation for ammonia removal from mixed tannery wastewater and municipal sludge at Moravian Wastewater Reclamation Facility in Otrokovice in former Czechoslovakia (WRFO) operated with the capacity up to 1 m^3 per hour and consisted of 3 pressure steel columns with clino-bed volume of 70 dm^3 each, 4 regenerant storage tanks of a volume of 0.75 m^3 and 1 counter-current air stripping tower, having a diameter of 0.6 m and the operating volume of 0.9 m^3 filled with 32×50 mm PVC tubes [9], [12].

One of the most preferencial benefits of this advanced treatment process, which is based on selective ion exchange using clinoptilolite and on the mass closed loop operation, is the recovery of the elutriants, shifting the stripped ammonia back to the tannery processing plant [14].

Wastewater treatment plant in Otrokovice delivers up to 55 000 m^3 of water per day, conventionally treating a volume of 18 000 m^3 per day (200 dm^3/s), consequently the process was designed for the entire capacity of the treatment plant according to the scheme in figure 3.

TYPIFIED AMMONIA REMOVAL ON CLINOPTILOLITE

WASTE WATER TREATMENT PLANT OTROKOVICE
18 000 m^3/d (200 l/s)

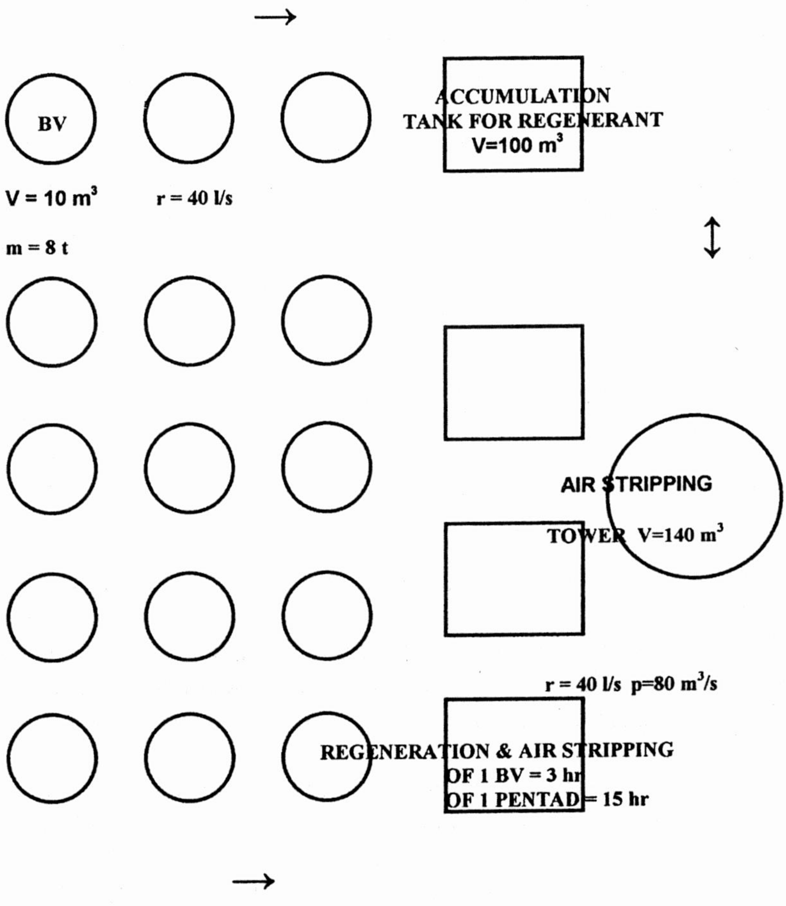

Fig. 3. Process layout for ammonia removal from municipal wastewater in Otrokovice using Slovakian clinoptilolite, including chemical regeneration of clinoptilolite beds and regenerant recovery by air stripping

A technical phosphoric acid and magnesia (MgO) added to the wastewater rich in ammonia precipitate a slightly soluble salt, i.e. $MgNH_4PO_4 \cdot 6H_2O$ (MAP). The MAP is a valuable fertiliser, whose precipitation does not require the basins of huge volumes. The above process brings also other benefits, i.e. short retention time and avoiding the nitrogen and nitrogen oxides escape into atmosphere as in the case of BND method [15].

Air stripping for nitrogen removal is based on very simple principles. This process offers a reliable means of ammonia removal when applied under appropriate conditions, i.e. pH, air-water contact, temperature and tower design. However, general environmental impacts of the stripping process must be evaluated. They may be itemized as follows: air pollution, washout of ammonia from the atmosphere and noise. If we are not able to cope with these three factors in any given situation, the potential process advantages (simplicity and low cost) may become only of academic interest [16].

Nevertheless, some other treatment alternatives to ammonia removal have been developed since several decades, i.e. breakpoint chlorination, membrane processes, electroreclamation, immobilisation, aquacultures with harvesting the plants hyperaccumulating ammonia, although recently the most favoured technology is BND process [17]. Here, the form of oxidized nitrates is reduced by microorganisms to gaseous nitrogen in the bio-reactors with methanol or a waste carbon, whereas denitrifiers are removed from the process streams, by settling down, and next are returned to the denitrifying reactor or wasted. The process is carried out in currently operating biological carbonisation units as the cost-effective, one-reactor system or proposed as separately operating carbonisation (C) and nitrification–denitrification (N–D) or as the expensive three-unit system (C–N–D) [18].

3. TRACE METAL POISSONING AND THREAT OF RADIONUCLIDES

The most widely documented examples of the impact of water contamination with such trace metals as mercury and cadmium on a public health were Minimata and Itai-Itai diseases. Both arsenic and chromium are also noxious for human organisms (Blackfoot desease) [4], [5].

In addition, the radionuclide emission from nuclear reactors and reprocessing facilities and significant amounts of radioisotopes from the fallout following nuclear bomb testing enter aquatic environments [5], [19].

Reactor incidents have occurred almost regularly in the nuclear industry since the 1960s, including major events at Three Mile Island in the U.S.A. and at Chernobyl in Ukraine. The latter involved a supercritical event, which led to an explosion of reactor core, followed by the burning of the graphite moderator on its exposure to the atmosphere [19].

3.1. POTENTIAL BIOINDICATION AND REMEDIATION ALTERNATIVES

Due to the orographic depression between the Eastern Alps and the Western Carpathians and the characteristic atmospheric circulation with predominance of NW wind direction, the deposition of trace metal aerosols from closed industrial activities was expected to contribute to bioaccumulation capacities of some environmental species in the vicinity of the refinery studied.

The current waste management of the petrochemical company of Slovnaft in Bratislava is based on independent, self-solid waste incineration. Since the 1980s, approximately 40% of the hazardous waste produced by the company has been incinerated in the existing, not far from state-of-the art technology, rotary kiln (Babkock, Germany) and storey-type combustion chamber (Polyma, Japan).

Long-lived earthworms Lumbricids sampled in an imission zone of south-eastern site of Slovnaft refinery were used as bioindicators of environmental pollution with vanadium, nickel, cadmium, chromium and lead. Trace metal aerosols may have been originated due to various processes of waste incineration in this area as well as crude oil refining [20], [21].

In the feather of *Phasianus colchicus*, the concentrations of such selected metals as lead, cadmium, chromium, nickel and vanadium were determined. The birds were hunted in the zone characterised by the most intense immission fall. The results were compared to metal contents in the members of a lower trophic chain in the immission zone: soil (fulvo-carbonate), lucerne (*Medicago sativa* L.), earthworms (*Lumbricidae*), green algae (*Cladophora glomerata*) from the sewage lagoon as well as to the highest admissible contents of toxic metals in agricultural products according to state regulations.

Nevertheless, only cadmium, nickel and chromium in earthworms occurred in high concentrations.

As mentioned above, spreading of both trace metals and radionuclides in the environment along with intoxication of humans via trophic chain may be reduced or controlled using various soil recultivation, remediation, immobilisation or fertilising techniques, including application of natural zeolites.

In April 1986, such attempts were made to extinguish the fire and to reduce the levels of radioactive particulates released at Chernobyl, involving the dropping of about 5 000 tonnes of clays, including zeolites, sand, lead and other materials onto reactor from the air [5], [22], [23].

Natural zeolites modified by organics as new-tailored natural materials for removal of cations, anions and even organic pollutants may present fairly large potential for water utility companies. Batch and column sorption experiments have been performed to study a significantly enhanced removal of toxic oxyanions, i.e. chromate and arsenate, from aqueous effluents using inland clinoptilolite modified by the octadecylammonium acetate (ODA). The arrangements of the surface-attached ODA chains have been an important factor of the difference in the adsorption states of the guest species (oxyanions). In contrast to the properties of clay, whose surface has been usually altered by surfactant modifiers, similarly modified natural zeolite represent fairly large potential for environmental applications, especially on the basis of superior hydraulic characteristics [24].

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OCZYSZCZANIE SPECYFICZNIE ZANIECZYSZCZONYCH ŚCIEKÓW ZA POMOCĄ NATURALNYCH ZEOLITÓW

Przez całe ubiegłe stulecie obserwowano na całym świecie znaczące zmiany środowiska naturalnego w dużych estuariach i zbiornikach wodnych, z których tylko nieliczne zachowały pierwotny charakter. Obecnie około 30% naszej planety zamienia się w pustynię. Ten artykuł próbuje przedstawić nowe techniki oczyszczania odnoszące się do usuwania składników pokarmowych i toksycznych metali, a także opisuje problemy skażenia dotyczące całego już świata.