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Evaluation of Aerobic Biodegradability of Some Chemical Compounds Commonly Applied in Paper Industry

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During recent years, problems of contamination of the environment with different pollutants have become very serious. There has been a constant increase in the number of chemicals synthesized and encountered in the environment. However, in spite of new chemicals occurring at the rate of 6000 per week, the number of chemicals in common use is estimated to about 65,000, of greater than 4,000,000 known (Ames & McCann,1981). These contaminants enter man and his environment through complex and interrelated pathways. They often become concentrated through the food chain, with minute quantities magnified thousands of time as they are consumed by high forms of life (Abdel Wahaab, 1995).

The need for standard test procedures for determining the biodegradability of this new product (and of estimating their potential impact upon the environment as well) is becoming self-evident. Many investigators have been proposed scenarios for testing and evaluating new products - see the early extensive review of (Ludzack & Ettinger, 1963a).

The Water Pollution Control Federation Subcommittee on Biodegradability has enunciated general principals that should apply in the testing of any substances (WPCF,1967). Between the two extremes of primary biodegradation and ultimate biodegradation the Subcommittee offer the concept of “Environmental Acceptable Biodegradation”(ECB). ECB concept defined as “susceptibility to biodegradation yielding end-products which are totally acceptable in the receiving environment”. These principles are of considerable value in the treatability studies of wastewater.

Wastewater produced from the paper industry is very complex in nature. The pollution in the wastewater of a paper mill depends on the raw material, the type and amount of filters and additives applied, and on the degree of circuit closure (Casey, 1980).

The hazardous impact of pulp and paper industry effluents can be attributed to a complex mixture of extractive compounds, including resin and fatty acids (Junna et al, 1982); tannins(Temmink, et al 1989); some lignin degradation products & chlorinated phenols, if chlorine bleaching is practiced (Galvao et al 1987), low molecular weight chlorinated lignin derivatives (Kringstad & Lindstrom, 1984), and a variety of other chemical compounds.

In Egypt the pulp and paper industry relies on agricultural residues as the source of raw material; rice straw and bagasse represent 90% of the fibers used in pulping. Using rice straw relies on a primitive technology for pulping the residues compared to the new and sophisticated developments pulping wood. The black liquor, containing about one half by weight of the straw quantity and all of the cooking chemicals, causes serious environmental problems.

The problem of appearance of non-biodegradable compounds in the ecosystem is that these pollutants do not decompose or get eliminated from the environment. Therefore, these raw materials and any of other additives used during the industrial processes has to be certified before use in order to avoid any future environmental contamination problems.

The aim of the present study is to investigate the biological degradability of some chemical compounds communally used in paper industry.

MATERIAL AND METHODS

The Zahn-Wellens Test (1991) determines the biodegradation and elimination of water-soluble organic compounds from the aqueous phase by aerobic microorganisms. The organic compounds are the sole source of carbon and energy in the medium other than the sludge. The concentration of the compounds used is such that the initial concentration of chemical oxygen demand (COD) is between 100 mg/l and 1000 mg/l. Measurement of the COD at the beginning and end of the test (7 days) and at seven regular intermediate time intervals. Evaluation of the biodegradability of the compounds was on the basis of these data.

Incubation took place in the dark at a temperature of 20°C. The solutions used in the experiment were: i) nutrient solution: anhydrous potassium dihydrogen phosphate (KH_2PO_4), anhydrous dipotassium hydrogen phosphate (K_2HPO_4, disodium hydrogen phosphate dihydrate ($Na_2HPO_4 . 2H_2O$) and ammonium chloride (NH_4CL), ii)magnesium sulfate heptahydrate ($MgSO_4.7H_2O$), iii) anhydrous calcium chloride ($CaCL_2$) and iii) ferric chloride hexahydrate ($FeCL_3.6H_2O$).

For each solution of the nine test compounds a suitable concentration of 3000 mg/l was chosen. The reference compound used in this experiment was sodium benzoate at a concentration of 3000 mg/l .

Preparation of the inoculum was carried out by collecting a sample of activated sludge from the aeration tank of a biological treatment facility.

The sample was mixed well and washed by adding tap water, allowed to settle, then decanting of the supernatant was carried out. Before use, determination of the concentration of the suspended solids was calculated. The inoculum was aerated at room temperature (20 “c) until it was used.

Two test vessels containing at least 500 ml of the test compound were prepared. A sufficient amount of solution of the test compound was added to obtain a COD concentration ranged from 300 to 1000 mg /l in the final mixture. The pH value was adjusted to pH 7±0.5. Activated sludge was added in an amount corresponding to 0.2 g /l suspended solids in the final mixture. The test medium was made to a total volume of two liters. One blank containing only activated sludge was prepared to operate in parallel with each test series. In order to check the activity of the inoculum, at least one control vessel with a solution of reference compound was prepared to operate in parallel with each series. Another vessel for abiotic control using only the test compound (no inoculum) was prepared. To start the test, all vessels were agitated using stirrers. Samples were taken after 3 hours followed by daily samples over a period of 7 days. The samples were centrifuged and filtered through glass wool. COD concentrations in the filtrate were measured for each vessel in duplicate according to APHA (1995). Biodegradation was measured as a percentage of COD removal of the test compound, and calculated according to the following Equation:

$$\text{Degradation (\%)} = \frac{(COD_{cor(0)} - COD_{Bio(0)}) - (COD_{cor(t)} - COD_{Bio(t)})}{(COD_{cor(0)} - COD_{Bio(0)})} * 100$$

$COD_{cor(0)}$	=	is the corrected COD of the sample at zero time
$COD_{cor(t)}$	=	is the corrected COD of the sample at time (t) plus the blank difference. The blank difference = the difference in COD value between time (t) and the preceding value
$COD_{Bio(0)}$	=	is the COD of the Biomass at zero time
$COD_{Bio(t)}$	=	is the COD of the Biomass at time (t)

RESULTS AND DISCUSSION

The essential steps in the historical, manual papermaking process were sheet forming, pressing, drying, sizing, and calendering. This fundamental process has not changed since long time ago. The use of starch, paper auxiliaries or other organic additives results in a marked increase of the oxidizable effluent components, measured as BOD or COD. Dyes and fillers can lead to discoloration and /or turbidity of the effluents.

Results of the biodegradation of nine compounds commonly used in paper industry were evaluated. The reference compound used is Sodium Benzoate. The biodegradation line of the reference compound reached 99.0%. This is confirming excellent activity of the inoculum used in these series of experiments.

The Anti-Coating Ester product is used in the manufacturing processes of tissue and hygienic paper only. It's applied directly to the dryer as release agent to prevent the fiber sheet from sticking to the cylinder surface. The chemical structure of this product is mainly Ester of long chain fatty acids. This product demonstrates good biological degradation. COD removal reached to 38.2% after 24 hours incubation and increased gradually to 95% on the 7^{th} day of the experiment (Figure la). It is worth mentioning that this product is highly biodegradable and could be applied safely in paper manufacturing processes without any environmental impact.

Formamidin-Sulfinic Acid (FAS) is used paper manufacturing as bleaching agent. The result illustrated in Figure (la) demonstrates poorly biological degradation of this product. Only 62.1% removal in COD was achieved after 7 days incubation. The residual COD value is still high (185 mg/l). These results show clearly that FAS compound has to be restricted in use and/or substituted by another biodegradable product.

Hedifx-M/35 is applied in paper manufacturing process to avoid any contamination of the wire by sticky precipitation of the fiber suspension (i.e. conditioning the wire). The general structure of the product is an ammonium salt bonded with methyl groups. The results indicated that this product is hardly or even non-biodegradable. Only 12.7% removal in COD was achieved after 7 days (Figure 1a). Therefore, this product should be restricted in use or substituted by another biodegradable product to avoid any of environmental contamination.

The chemical nature of Basoplast 200D is fatty alkyl diketene emulsion with a low cationic charge density. This product is a very effective size for paper made in neutral and slightly alkaline media, especially in paper made from furnish that contains chalk. Results of biodegradation experiment indicated that this product is easy biodegradable. It seems that the product has affinity to be adsorbed on the surface of the activated sludge flocs. COD removal reached 72.6 % following only 3 hours exposure. The percentage removal in the COD value after 7 days was 85.3% (Figure lb).

The chemical nature of Basoplast PR 8053 is fatty alkyl diketene dispersion with a medium concentration, for sizing paper in neutral pH range. The product is very effective for sizing papers made from furnish that contains groundwood or recycled paper. No significant difference between Basoplast 200D and Basoplast PR 8053 in biological degradation line over the period of the experiment. COD

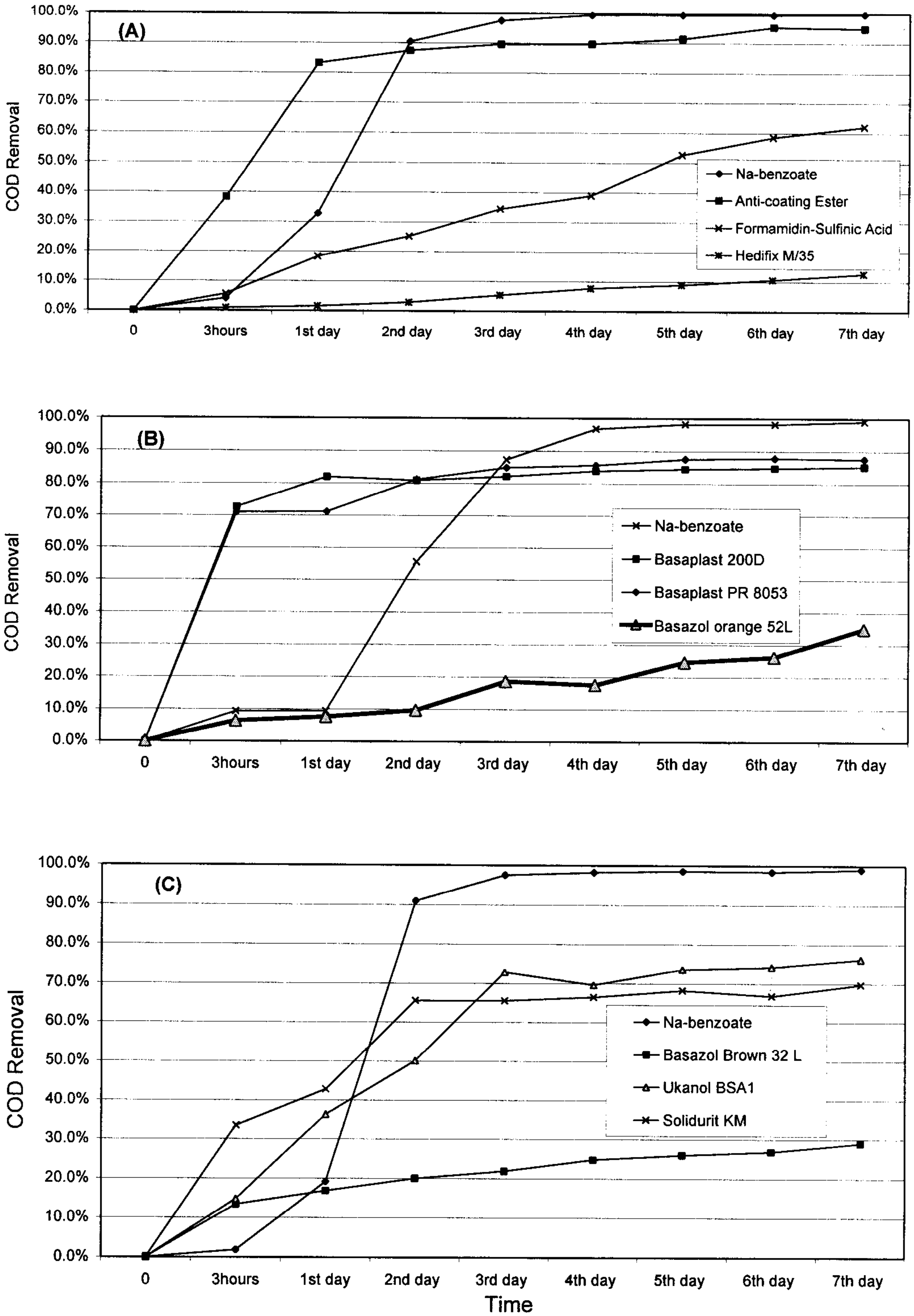

Figure 1. Bio-degradation of paper auxiliaries as a percentage of COD removal

removal reached 70.9 % following 3 hours exposure. The percentage removal in the COD value after 7 days was 87.6% (Figure lb).

Basazol Orange 52 L is an effective alternative to acid orange dyes because of its higher affinity for wood-containing furnish and its brilliance on papers made from furnish of this type. Figure (lb) demonstrate that this product is hardly biodegradable, even after 7 days exposure. Only 34.9 % removal in COD value was achieved. High residual concentrations of this type of dyes in the industrial effluent could cause serious impact on the performance of the biological treatment plant.

Basazol Brown 32 L (Methine Brown Dye) can be used to dye paper in the acid to slightly alkaline pH range. Paper made from raw materials that contain lignin, such as groundwood, unbleached chemical pulp and recycled paper can be dyed without any additional chemicals. The largest area of application of this dye is in the production of recycled packaging papers. Biological degradation of Basazol Brown 32 L in aqueous as percentage of COD removal indicated that the product is not easy biodegradable by the microorganisms. A maximum removal value of 29.0% in COD was achieved after 7 days retention time, with a residual concentration of 272 mg/l as non-biodegradable value. Therefore, good dying systems to minimize and/or prevent waste dyes in the industrial effluent must be taken into consideration (Figure lc).

The chemical nature of Ukanol BSA 1 is Acrylat-Copolymer . It is an adhesive material, used as special glue for barrier coated & hydrophobic paper surfaces. This product is moderately biodegraded, COD removal started by 36.4% after 24 hours followed by 50.1% in the 2nd day and increased gradually to 76.2% following 7 days digestion (Figure 1c). The residual value is still relatively high (75 mg/l)

Solidurit KM is Poly-Acrylamid material. These products are applied in paper manufacturing as wet strengthening agent. The products are intended to increase the tensile strength, tearing strength, bursting strength and the abrasion resistance of the wet paper. Results of the biological degradation processes using microorganisms indicated low removal value in COD (69.8%) after 7 days digestion (Figure lc). The residual COD value is relatively high (65 mg/l). It is worth mentioning that 33.5 % removal of COD was achieved after only 3 hours incubation. The removal in COD value is not actually biodegradation of the product but may be due to the physical adsorption of that product on the activated sludge floc surface.

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