Magnetite Nano Particles Modified Biodegradation of Lignin and Lignocellulose Constituents in the Pulp and Paper Industry Black Liquor

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The study aimed to investigate the ability of biological treatment to decontaminate pulp and paper contaminated industrial wastewater using exogenous and/or indigenous bacteria either with or without magnetite nanoparticles. Also, the study aimed to investigate the synergistic and/or antagonistic effects of the tested bacterial species under the tested operation conditions. Water samples were collected from **RAKTA**, **EL-AHLYA** and **ELMAMOORA** companies for paper and carton manufacturing in **Alexandria** governorate, **Egypt** during the course of the study. **Ten** indigenous and exogenous bacteria strains were investigated for the remediation of the contaminated influent as free living (batch mode) either individual or as mixed culture. The most promising strain was selected and decorated with magnetic Fe_3O_4 Nanoparticles. Wastewater quality parameters included **Temperature**, **pH**, **DO**, **TSS**, **TDS**, **BOD**, **COD**, bacterial **TVC** and **total tannin** and **lignin** were determined before and after treatment and the removal efficiencies were calculated.

Six indigenous isolates (**A1**, **A2**, **A3**, **A4**, **A5** and **A6**) obtained from paper contaminated industrial wastewater and four exogenous bacterial species (***Pseudomonas stutzeri***, ***Bacillus licheniformis***, ***Pseudomonas otitidis*** **MCC10330**, and ***Bacillus sphaericus***), kindly provided from **IGSR** (Institute of Graduate Studies & Research, Alexandria University) collection were investigated. They exhibited superior ability for total tannin and lignin remediation. The **10** selected bacterial species were investigated as individual or mixture for their ability to remediate pulp and paper contaminated wastewater.

The selected bacteria were screened for the remediation of pulp and paper effluent achieved the following result:

A. Raw pulp and paper wastewater contained very high levels of **COD** and **BOD** (**4963** & **2655** mg/l respectively), high **TDS**, **TSS** and **DO** levels (**538**, **239** and **4.19** mg/l respectively) as well as **20** mg/l of total tannin and lignin seeded into the wastewater.

B. ***P. otitidis*** **MCC10330** and ***P. stutzeri*** exhibited high activity (**83.7** and **84.5** % **RE**) towards the biodegradable organic compounds (**COD** and **BOD**) respectively, which is confirmed by being the most efficient consumer of the **DO** in the raw effluent leaving only **0.04** mg/l. The lowest achieved **RCs** of **COD** and **BOD** (**809** and **411** mg/l respectively) are still higher than their **MPL**s (**80** and **60** mg/l) respectively

C. ***P. otitidis*** **MCC10330** removed **79.50** % of the **TSS** leaving **49** mg/l which is lower than its **MPL** (**60** mg/l).

D. Isolate **A1** increased the effluent **TDS** level by **89.8**% (**2710** mg/l) due to degradation of the included pollutants that is slightly higher than its **MPL** (**2000** mg/l).

E. ***P. otitidis*** **MCC10330**, ***P. stutzeri*** and isolate **A2** showed the highest biodegradation activity (**50** %) towards total tannin and lignin, which are equivalent to residual concentration **10** mg/l.

F. Except for **TSS**, none of the tested contaminants reached safe limits for discharge according to the law (**48/82**) which may be due to break down complex contaminants into simple dissolved salts, inoculum size or operation conditions.

G. Therefore, and being the most active, **2** species ***(P. otitidis* MCC10330** and ***P. stutzeri*)** were selected to be investigated for treatment pulp and paper contaminated effluent in a batch mode as individual and mixed cultures.

Using the selected bacteria in a batch mode for the bioremediation of the pulp and paper contaminated industrial effluent achieved the following results:

A. Raw pulp and paper wastewater contained (mg/l) **COD, 815**; **BOD, 420; TDS, 625; TSS, 168** and of total tannin and lignin, **30.**

B. The highest **RE** of the **TSS**, **COD**, **BOD** and total tannin and lignin were achieved by ***Pseudomonas otitidis*** (**71.4, 87.8, 83.3** and **53**% respectively), reaching **RC**s of **48**, **99**, **70** and **14** mg/l respectively. Compared with their **MPL**s of the tested parameters, only **TDS** and **TSS** residue was compiling with their **MPLs** (**2000**, **60** mg/l). **COD** and **BOD** level were close to their **MPLs** (**80** and **60** mg/l). ***P. stutzeri*** increased **TDS** by **60**% (**RC=1574 mg/l),** which still compiling with its **MPL** (**2000** mg/l)

C. It is concluded from the batch bioassay that ***P. otitidis*** is the most active and the most promising candidate for further treatment. Although, high **REs** was achieved by ***P. otitidis*** during the batch assay, some parameters still higher than their **MPL**s for the safe discharge. Therefore, another technology was adopted where cells of ***P. otitidis*** was immobilized with magnetite nanoparticles to enhance biodegradation and/or bioaccumulation of the included contaminants.

Using the selected culture ***Pseudomonas otitidis* MCC10330** modified with magnetite nanoparticles for the remediation of industrial contaminated pulp and paper wastewater effluent achieved the following results:

A. Raw wastewater contained **7.0**, **7.61**, **686**, **898**, **450**, **245** and **21** mg/l of **pH**, **DO**, **TDS**, **TSS**, **COD**, **BOD** and total tannin and lignin respectively.

B. Magnetite-bacterial cells assembly recorded the highest removals (**64.1**, **52.0**, **54.3** and **66.6** %) of **TSS**, **COD, BOD** and total tannin and lignin after **1, 4** and **4** h reaching **RCs** of **322**, **216**, **112** and **7** mg/l respectively.

C. The control (**Fe_3O_4 NPs**) recorded the highest removals of **TSS**, **COD, BOD** and total tannin and lignin (**82.8**, **52.7**, **50.0** and **57.1** %) after **2, 4** and **4** h respectively which is attributed mainly to physical adsorption process.

D. The **RC**s of **pH**, **DO** and **TDS** in the effluent treated with the proposed system are accepted for safe discharging, while **TSS, COD** and **BOD** levels are higher (**5.35**, **2.7** and **1.86** folds) than their **MPL**s respectively.

E. Although the very short time (**4** h) applied for this bioassay, considerably very high reductions were achieved. Some of the tested pollutants still higher than the **MPL**s for the safe discharge which may be attributed to the short treatment time, small inoculum size or dose of the nanoparticles.

The optimized conditions for the maximum lignin adsorption and removal using **Fe_3O_4 NPs** were found to be achieved at **pH 6**, **Fe_3O_4** NPs dosage of **100** mg and **10** min contact time.

In conclusion, the proposed magnetite coated - bacterial treatment system is highly recommended for the treatment of industrial as well as other wastewater types. To overcome levels of pollutants that are not compiling with the environmental laws, it is highly recommended to scale up a suitable unit for the remediation. Finally, the proposed system represents a very promising, renewable and cheap biotechnology for the treatment of wide range of contaminated effluents not only in the industrial sector but also for domestic and agricultural wastewater.