Low cost agroindustrial biomasses and ferromagnetic bionanocomposites to treat textile effluent

D.S. Cardona[1], A.R. Imamura[1], K.B. Debs[1], E.N.V.M. Carrilho[2], P.S. Haddad[1], G. Labuto[1*]

[1]Departamento de Química, Universidade Federal de São Paulo, Diadema, CEP 09913-030, São Paulo, Brazil
[2]Departamento de Ciências da Natureza, Matemática e Educação, Universidade Federal de São Carlos, CEP 13600-970 Araras – São Paulo, Brazil.
Keywords: biosorption, yeast biomass, cork biomass, reactive dyes
Presenting author email: geolabuto@gmail.com

The textile industry is one of the largest pollutants of water. In 2002, around 10.000 different dyes and pigments were used by textile industry with a world consumption of 7 x 10^5 tons (Kunz *et al*., 2002), being project a growth of 3.6% per year. The treatment of dyes effluent frequently employs sludge tanks enabled for remediation, which requires the control of microorganisms, dispenses considerable time in treatment, can generate bioproducts even more toxic than the treated effluent and need landfills for sludge disposal. The use of biomasses, ferromagnetic nanoparticles, and composites formed by their combination have been reported as an alternative to treat textile effluents with high contaminant removal capacity (Makarchuk, *et al*. 2016). In this way, agroindustrial biomasses, respectively, yeast residue from alcohol industry (YB) and powered cork (PC), ferromagnetic bionanocomposites produced by recovering of the mentioned biomasses with nanoparticles of magnetite and the magnetite nanoparticles (MNP) were employed to treat the remaining textile dyes from water after dyeing. The main advantages of hybrid materials is associate the magnetic characteristic, that allows an easy removal of adsorbent from water using a magnet, with the organic functional groups of biomasses which improves the sorption capacity of contaminants Saber *et al* (2015). Besides, this hybrids materials can add value to biomasses that are often agroindustrial wastes, or that have low market value.

The synthesis of MNP was carried out using a co-precipitation method (Molina *et al*., 2013), which consisted of the mixture of $FeCl_3 \cdot 6H_2O$ (4.0 mL) and $FeCl_2 \cdot 4H_2O$ (1.0 mL) both prepared in 1.0 mol/L HCl. This mixture was stirred for 30 min. at room temperature, while 200 mL of NH_4OH (0.7 mol/L) were slowly dropped through a burette. The resulting suspension containing magnetite nanoparticles (MNP) was centrifuged, and the magnetic precipitate was decanted and washed with purified water, followed by a rinsing with absolute ethanol and dried in a desiccator. A procedure adapted from Panneerselvam *et al.* (2011) was employed to produce the ferromagnetic nanocomposites of yeast biomass from ethanol industry (YB-MNP) and powered cork (PC-MNP). Thus, the procedure described to produce MNP was carried out excepted that the suspension was heated up to 80°C before adding 2 g of the biomasses for each 250 mg of MNP. This suspension was vigorously stirred by 30 min at 80°C, and the nanocomposites were washed with absolute ethanol and reserved in desiccator for posterior use. All materials were characterized by elemental analysis (CHN amounts), X-Ray diffractograms (XRD) and scanning electron micrograph (SEM).

The real textile effluent (RTE) was produced by dyeing a 100% cotton fabric previously (180 g/m^2) bleached, which was performed with a three primary colors composed by bifunctional dyes (Drimaren CL-2R, Drimaren CL-5B and Drimaren HF-RL, all Clariant S/A). The dyeing procedure and neutralization of waste were executed according to the dye manufacturer's recommendation. The dye bath ratio was 1:10 with a 5 g fabric mass and a total bath volume of 50 mL. The mixture of dyes remaining in the RTE was determined by fluorimetry spectrometry (excitation at 251 nm and emission at 450 nm) employing an analytical curve constructed with a simulated effluent produced without the dyeing step. Firstly, 10 mg of YB or PC were suspended in 10 mL of RTE to determine if it was possible to remove the remaining dyes from RTE. The suspensions were shacked (15 min, 240 rpm), centrifuged (5 min., 3000 rpm) and a fluorimeter was used to determine the reaming concentrations of mixture of dye in the supernatants. After that, masses around 10 mg of MNP, YB-MNP or PC-MNP were suspended in 10 mL of diluted solutions of the RTE (1.3, 1.50, 1.70, 2.00, 2.40, 3.00, 4.00 and 6.00 mg/L) and shacked according the YB and PC sorption procedure. After that, the magnetic adsorbents were decanted employing a neodymium magnet, the supernatants were removed and the reaming concentration of dyes mixture were determined by fluorimetry. The RTE dilutions were performed to evaluate the influence of initial concentration of remaining dyes on adsorption process. All experiments were carried out in triplicate.

Figure 1 shows the XRD for all studied adsorbents. It is possible to observe that YB-MNP and PC-MNP have the six characteristic peaks assigned to Fe_3O_4 nanoparticles, at the same form of MNP, confirming the absence of hematite or other iron hydroxides (Klug and Alexander, 1974). These diffractograms demonstrate that capping nanoparticles with YB and CP did not lead to any phase change of the MNP. In the Figure 2 it is possible to see the nanoparticles agglomerated on the surfaces of YB and PC. The minor contribution of %C presented for elemental analyses for YB-MNP and PC-MNP denote the presence of MNP as a contributor on the weighted employed for this analyses. The MNP present a small contribution of %C provides from residues of ethanol used to wash the material.

The YB and CP were capable to uptake, respectively, 46.5 ± 0.6 g/kg (95.8 ± 0.7%) and 42.2 ± 0.7 g/kg (88 ± 2 %) of the mixture of dyes present in RTE. In Figure 3 it is possible to observe that, in general, the sorption capacities rise with the increases of the initial concentration of textile dyes on diluted RTE, especially to YB-MNP. For the evaluated concentrations, the percentages of dye removed by the biocomposites and MNP for the diluted effluent were considerably lower than those obtained for the biomass applied to the integral effluent. However, it is important to note that adsorbent saturation studies have not been carried out in order to determine the maximum sorption capacity of the adsorbents.

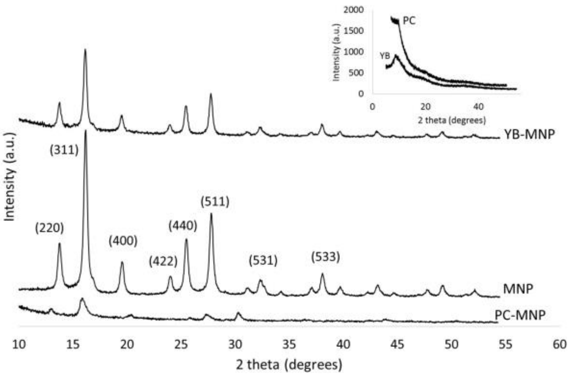
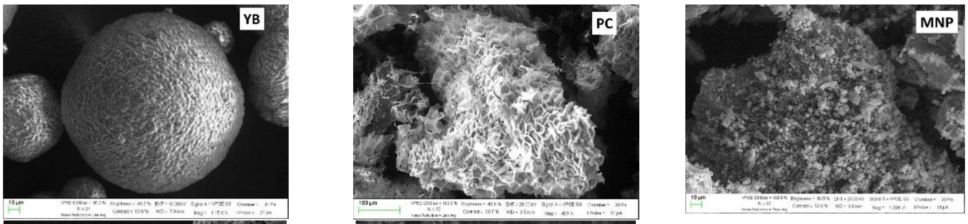
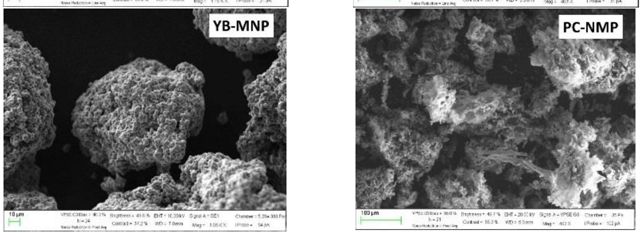


Figure 2. Powder X-ray diffractograms from YB (Yeast Biomass), YB-MNP (ferromagnetic nanocomposites of yeast biomass), PC (Powered Cork), PC-MNP (ferromagnetic nanocomposites of powered cork), MNP (magnetite nanoparticles), displaying the Bragg peak reflections of magnetite for the magnetic adsorbents.





Adsorbent Elemental Analyses

Adsorbent	%C	%H	%N
YB	41.0	6.21	6.14
YB-MNP	29.7	4.3	3.8
PC	63.53	8.21	1.00
PC-MNP	41.81	5.55	1.03
MNP	3.50	0.40	1.00

Figure 1. SEM images of YB (Yeast Biomass), YB-MNP (ferromagnetic nanocomposites of yeast biomass), PC (Powered Cork), PC-MNP (ferromagnetic nanocomposites of powered cork), MNP (magnetite nanoparticles), and elemental analyses of all adsorbents.

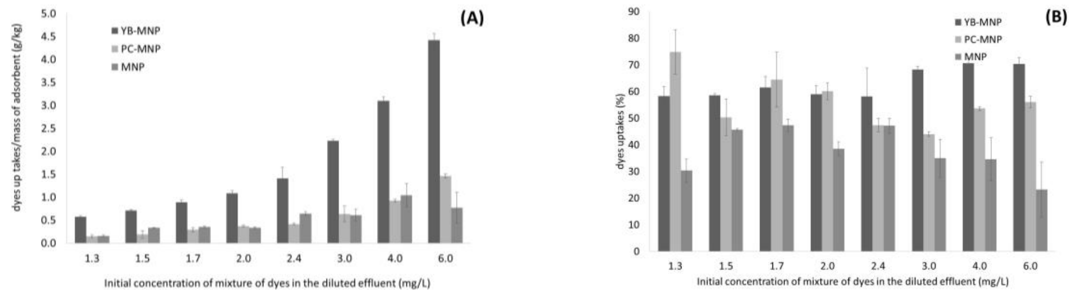


Figure 3. Influences of initial concentration on A) removed masses of dyes and B) Efficiency of sorption (%).

According to the obtained results, all materials are capable to remove textile dyes from RTE with a higher capacity of YB-MNP. The magnetic behavior tuned possible to remove the magnetic adsorbents from effluent employing a simple magnetic field. The studies performed with YB and CP and the original RTE denotes the potential of textile dyes removal of the evaluated materials.

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Acknowledgements: The authors acknowledge the financial support from Fapesp Processo 2016/0627-4