MACEIÓ - ALAGOAS
EBA 15
15° ENCONTRO BRASILEIRO SOBRE ADSORÇÃO
15th Brazilian Meeting about Adsorption

Green magnetic composite based on glucosamine mesoporous carbon for multi-component adsorption

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Abstract

This work aimed to produce a green magnetic composite based on mesoporous carbon from glucosamine, green iron nanoparticles produced with water hyacinth as a natural reducing agent, and proanthocyanidin, which is a natural crosslinking agent. The composite was characterized and applied in the adsorption of malachite green (MG), crystal violet (CV), atenolol (ATN), and sodium diclofenac (SD), in single and multi-component experiments. The composite showed an adsorption capacity of 713,26 and 606,79 mg/g for MG and CV, respectively. In multi-component experiments, with the pharmaceuticals and the dye MG, the composite showed an excellent synergic effect, increasing the adsorption capacity in 57% and 404% for ATN and SD, respectively. The composite was also evaluated in the removal of MG and CV from a river water sample, with adsorptions of 91% and 98% for MG and CV, respectively. The composite showed an excellent reuse capacity, that remained in 70% event after 7 cycles reuse. The adsorption mechanism was studied by FTIR and XPS analyses, and it was observed the important role of electrostatic and π-π interactions in the process.

Keywords: green chemistry; water purification; malachite green; sodium diclofenac.

1. Introduction

Organic contaminants, as dyes and pharmaceuticals, are widely consumed and discharged poorly treated in the aquatic environment [1]. These contaminants are toxic, recalcitrant, can be bioaccumulated, and are difficultly treated because of their stability [2].

The conventional treatment it is not efficient to remove these chemicals. Thus, adsorption emerge as a low-cost and versatile technology for water decontamination [2]. Among the adsorbents, mesoporous carbons have been highlighted due to the high surface area, control of pore structure, and the use of non-toxic and cheap carbon sources [3].

The carbon-based materials can be combined with metal nanoparticles to form magnetic materials to facilitate the removal of the material from the liquid phase [4]. Iron nanoparticles can be produced by a green route with plant extracts, as water hyacinth, which are an alternative to hazardous reagents, high temperatures and pressure, with higher stability [5].

Thus, this project aimed to produce green iron nanoparticles from water hyacinth obtained from phytoremediation processes in a wastewater treatment plant. The green iron nanoparticles were used in the production of a new composite with mesoporous carbon from glucosamine, and proanthocyanidin, as a natural crosslinking agent. The magnetic composite was applied to the adsorption of dyes and pharmaceuticals in single and multi-component experiments. The removal of malachite green (MG) and crystal violet (CV) dyes was fully studied through kinetics, isotherms and thermodynamics. The composite was also evaluated by its selectivity into a river water sample, recycling experiments, and the adsorption mechanism.

2. Methods

2.1. Magnetic composite production

The mesoporous carbon was produced by a mixture of glucosamine and colloidal silica. The paste was pyrolyzed in a furnace tube under Ar flow, at 800 °C for 1 h, and heating rate of 3.2 °C/min.

In parallel, the water hyacinth from a wastewater treatment plant (Rio Claro) was collected, washed, dried and grounded. A solution of Fe(II), Fe(III), plant extract, and oleic acid was produced to obtain the green iron nanoparticles [6]. Then, the iron nanoparticles (FeNPs), the mesoporous carbon (G-MPC) and proanthocyanidin were mixed [7], to produce the composite G-MPC@FeNPs. The materials were characterized by their morphology and physicochemical characteristics.

2.2. Adsorption experiments

The performance of the materials towards the adsorption of contaminants was evaluated under several conditions, including contact time, materials concentration, ultrasound assistance, temperature, and pH. The adsorption process was evaluated by kinetics, isotherms, and thermodynamics. Also, the composite selectivity for the dye MG was evaluated in the presence of other dyes (methyl orange – MO and safranin – SF), and pharmaceuticals (sodium diclofenac – SD and atenolol – ATN).

2.3. Recycling experiments

After each cycle of adsorption, the composite, G-MPC@FeNPs (30 mg), was washed with acetone to desorb the dyes (60 min in orbital shaker). To the following cycles, the composite was redispersed and evaluated once again by its adsorption capacity.

3. Results and discussion

3.1. Materials characterization

Mesoporous carbon (G-MPC)

The material showed irregular particle size, and uniform in spheroid-shape porous structure with 25 nm (Fig 1a). The chemical analysis showed the presence of aromatic rings, C–H, and C–O, groups, which confirms the fabrication of the MPC. Also, the composite showed the presence of carbon (86.0%), oxygen (8.4%), and nitrogen (5.3%) by the XPS analysis. The zeta potential analysis showed that the material was negativelly charged in all pH evaluated (0 to –15 mV), which is common for carbon-based materials, rich in oxygen groups [8].

Green iron nanoparticles and composite (N-MPC-G@FePAS)

The green iron nanoparticles had size of 14 nm. The chemical analysis showed the presence of O–H, CH_2, COO^-, and Fe–O groups, due to the presence of oleic acid and plant biomass [7].

The composite, G-MPC@FeNPs, showed a porous tridimensional structure and dark spots (iron nanoparticles), as shown in Fig 1b.

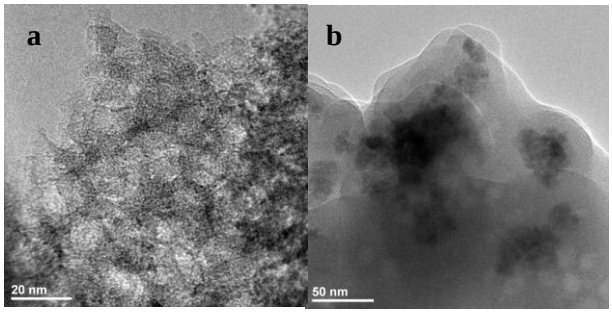

Fig. 1. TEM image of the materials: (a) G-MPC; (b) G-MPC@FeNPs.

Also, the chemical analysis of the composite indicated the presence $\pi - \pi$ interactions and hydrogen bonds between the MPC and the other components of the composite. It was observed the presence of sp^2-hybridized carbons from proanthocyanidin. XPS analysis of the composite showed the presence of carbon (73.7%), oxygen (24.3%), nitrogen (1.7%), and iron (0.3%).

3.2. Adsorption experiments

Influence of several parameters on the adsorption of dyes

The composite was evaluated towards the adsorption of MG and CV. The best performance of the composite was at pH 6 (248 mg/g) and pH 10 (294 mg/g) for MG and CV, respectively. At acid pH (2 and 4), the lower adsorption occurred due to the competition of the dye and H^+ ions by the active sites in the composite [2].

The ultrasound assistance and the temperature little affected the MG and CV dyes adsorption. To the following experiments, the ultrasound assistance was not applied to the composite, and the temperature of 25 °C was chosen.

For the contact time, the times of 60 min and 30 min was chosen for MG (251.3 mg/g) and CV (301.0 mg/g) dyes, respectively. After these times, the adsorption capacity of the materials decreased. It was also evaluated the influence of the adsorbent dosage. For MG, the increment in material dosage caused a decrease in adsorption capacity due to the overlapping and aggregation of the materials particles [9]. For CV dye, the increase in materials dosage caused an increase in adsorption capacity, with the best performance at 0.4 g/L.

Kinetic, isothermal and thermodynamic studies

The results obtained best fitted the pseudo-second order kinetic model for both dyes, MG and CV, indicating the presence of abundant active sites in the material and/or that the contaminants molecules could bind to various active sites in the composite [2].

The isotherm plot (Ce x qe) showed a curve type S2 for MG and type L4 for CV, as described by Giles model [10]. The experimental data best fitted Dubinin Radushkevich model for MG, indicating that the adsorption could happen in both homogenous and heterogenous surfaces. For CV, the adsorption data best fitted the Redlich-Peterson model, indicating the combination of Freundlich and Langmuir isotherms.

The thermodynamics study indicated that the adsorption process is spontaneous ($\Delta G° < 0$), and physisorption ($\Delta H° < 4.18$ kJ/mol) for both dyes.

3.3. Multi-component experiments

The adsorption capacity of the composite towards MG and CV dyes was evaluated in the presence of other dyes (MO and SF), and pharmaceutical drugs (SD and ATN), as observed in Fig 2. In binary system the adsorbent was selective for MG dye. When in multi-component experiment with SF, both dyes (MG and SF) were little less removed, since they are cationic and compete for active sites in the composite. Regarding the pharmaceuticals, ATN and SD had their adsorption increased in 57% and 404%, respectively. Probably it happens due to the electrostatic and $\pi - \pi$ interactions [1].

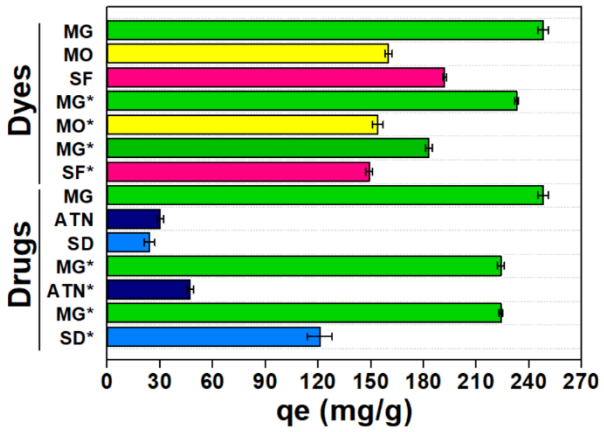

Fig. 2. Multi-component experiment of MG with dyes (MO and SF), and pharmaceuticals (ATL and SD). *indicates the experiment in binary system. Contaminants concentration of 100 mg/L, adsorbent concentration of 0,2 g/L, 25 °C, pH 6 and 60 min.

3.4. Composite reuse

The composite proved to be capable of maintaining the dyes adsorption efficiency for 7 cycles of reuse, with efficiency of 80% for MG and 69% for CV (Fig 3). This characteristic is desirable in the economic and environmental aspects, considering water treatment.

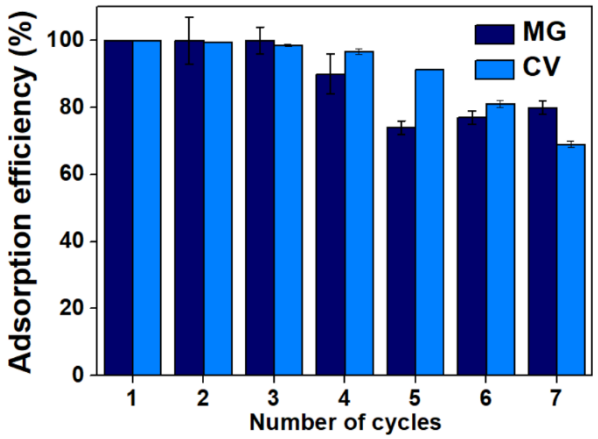

Fig. 3. Composite recycling. Contaminants concentration of 100 mg/L, adsorbent concentration of 0.2 g/L, 25 °C, pH 6 and 60 min for MG, and pH 10 and 30 min for CV.

3.5. Adsorption mechanism

The adsorption mechanism was studied by FTIR and XPS post adsorption and showed that hydrogen

bonds and π – π interactions [1] have important role in the adsorption process, as shown in Fig 4.

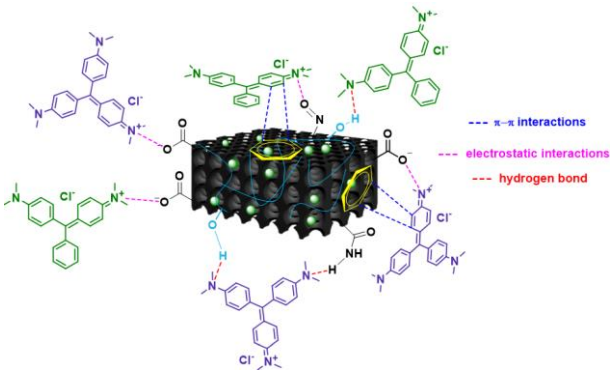

Fig. 4. Adsorption mechanism.

4. Conclusions

It was produced a green magnetic composite based on green iron nanoparticles and mesoporous carbon from glucosamine. This material was excellent for dyes and pharmaceutical adsorption, showing a synergic effect when in multi-component experiment. The material also showed an excellent efficiency in recycling process, which is a desirable property for large application goals.

Acknowledgements

This project was supported by São Paulo Research Foundation (FAPESP 2022/09912-1, 2022/14834-0, 2019/25228-0, 2023/02041-8, 2013/07296-2), Fundo de apoio ao ensino, pesquisa e extensão (FAEPEX 2207/23 and 2529/23), National Council for Scientific and Technological Development (CNPq grant 311419/2022-4), and Coordination for the Improvement of Higher Education Personnel (CAPES, Financial code – 001). We also thank the Brazilian National Biorenewables Laboraroty (LNBr, CNPEM) for zeta potential analysis and Dra. Josiane Aparecida de Souza Vendemiatti for SEM analysis.

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