Electronic Supplementary Information

MOF@activated carbon: a new material for adsorption of aldicarb in biological systems

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Experimental Secction

General. High purity of europium and terbium chlorideswere purchased from Aldrich Chemical Co. Inc. and was used as received. Activated carbon was purchased of Dinamic Chemistry, Cod. 1073-1, batch n. 45985, received no previous treatment. All other chemicals were analytical grade.

Synthesis of Composites. As starting material for the synthesis of composites were chosen for succinic acid, $LnCl_3.6H_2O$ (Ln = Eu and Tb) and activated carbon for reaction *in situ*, using hydrothermal methodology previously published for the synthesis of MOFs. Then, the composite was obtained using succinic acid (0.5 mmol), added to 10 mL of water in teflon-lined stainless steel reactor and pH was adjusted to 5 with a solution of sodium hydroxide, subsequently, $LnCl_3.6H_2O$ (0.5 mmol) and 5 mg (1 wt %) of activated carbon were added. The reactor was sealed and mixture was heated at 393 K for four days. After this, the reaction system cooled slowly to room temperature. Colorless crystals were isolated along with the coal; the material was collected by filtration, washed with water and dried in air. This procedure was repeated using 50 mg (10 wt %) and 500 mg (1:1, wt/wt) of activated carbon. In cases 1 wt % and 10 wt % coal, an excess of MOF was obtained, but when the proportion was increased to 1:1, almost all polymer was formed within the pores.

Biological Tests. Biological tests were performed on rats with composite adsorption of aldicarb. For testing we used male rats of Wistar variety, weighing 350 g, from the vivarium of the Department of Animal Morphology and Physiology of the Federal Rural University of Pernambuco. The animals were housed for 40 days, subjected to a specific diet, but free of antibiotics supplementation; water *ad libitum* and light on the relationship of 12x12 hour light/dark. The animals were anesthetized with a

combination of xylazine hydrochloride 2% (10 mg / kg) and ketamine hydrochloride, 10% (60 mg / kg) with an intramuscular injection. After confirming the state of anesthesia, an incision was made in the ventral region at the time of the linea alba, where he was exposed to gastroenteric ileal portion of the animals. Then a portion was removed and made an ileal cannulation with a glass rod and bath with a continuous cold Ringer solution at 10^{o}C at pH 7.4. The handle withdrawal was subjected to cleaning with an isotonic solution and removing the serous membrane. There upon, the ileal tissue was removed, divided into several compartments each of 4 cm and filled with 3 mL 0.9% saline and submerged in individual containers containing 10 mL of Ringer's dextrose (5%), pH 7.4, and the temperature of 37 ^{o}C. At the end, eight groups of bags were formed, the first seven groups of ileal tissue bags was added 0.1 mL of adsorbent substrate diluted in 0.9% saline solution and pH 7.4 (activated carbon AC, MOF Tb and composites CP1, CP10, CP30, CP40 e CP50), at concentration 0.1 mg/mL. In the eighth group, used as control, the bags were given 0.1 mL of 0.9% saline. After this step, all the bags of all groups received 0.1 mL of Aldicarb even at a concentration of 0.2 mg mL^{-1} and 0.1 mL of atropine sulphate in a concentration of 1mg.mL^{-1}. All bags were subjected to conventional aeration procedure during the bioassays.

Similar tests were conducted by varying the hydrogen potential on the inside pockets of ileal tissue, through the use of solutions of 0.1 M of NaOH and 0.1 M of HCl. After increasing the animals were euthanized under anesthesia. At each time interval (1, 10, 30, 60 and 120 minutes) the external content of each preparation of ileal tissue bags were removed (500 μL) and the reading was performed spectrophotometrically. At the end of bioassays a third pocket of each group were separated for fixation in formaldehyde solution 10% buffered with 0.01 M PBS (Phosphate-buffered saline), pH 7.4. These biological structures were subjected to routine procedures for paraffin embedding and preparation of samples for reading histopathologica was donel. At the end of the experiments, the data were properly tabulated and the results of bioassays were expressed as mean and standard deviation.

Scanning Electron Microscopy. The samples were fixed on a support of aluminium using a carbon tape. The images of scanning electron microscopy were obtained using a Shimadzu SS-550 with tungsten filament working at 15 kV, work distance 17, probe 4, with an EDS attachment.

Luminescence Spectroscopy. The excitation and emission spectra were obtained in the laboratory spectroscopy of rare earths from the Chemistry Department of the Federal University of Pernambuco. The photoluminescence spectra were obtained in a modular spectrofluorometer Horiba Jobin-Yvon Fluorolog-3 with double excitation, using a 450 W xenon lamp. The emission was collected in a monochromator with a 0.1 nm resolution equipped with a photomultiplier.

Powder X-ray Diffraction Patterns (XRD). Powder X-ray diffraction patterns were collected in a Bruker D8 Advance diffractometer with Cu Kα radiation (1.5418 Å) operating at 40 kV and 40 mA over the 2θ range 5-70°.

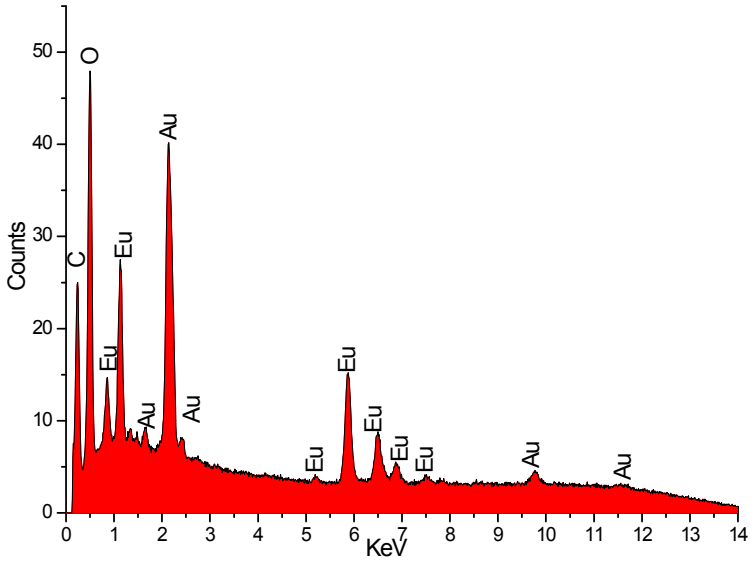


Figure S1. EDS of MOF with europium.

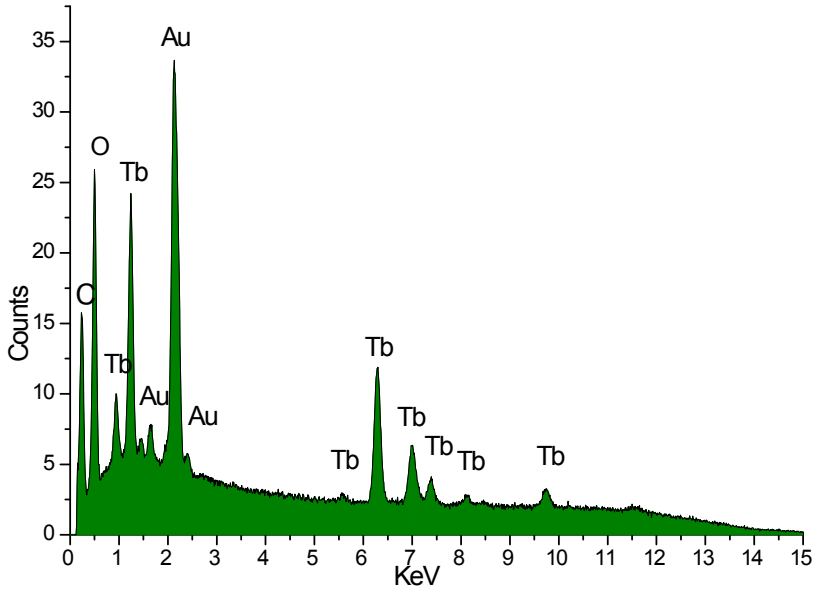


Figure S2. EDS of MOF with terbium.

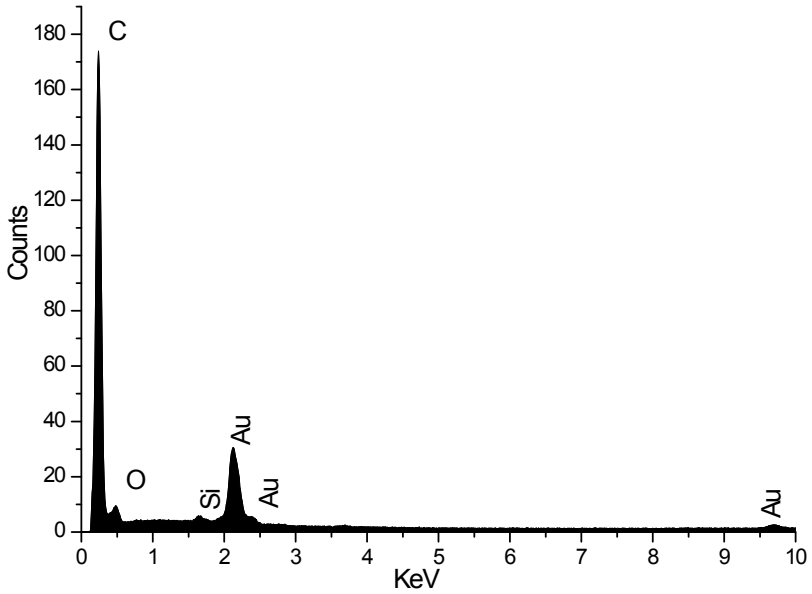


Figure S3. EDS of composite (outside of porous) with 50% activated carbon.

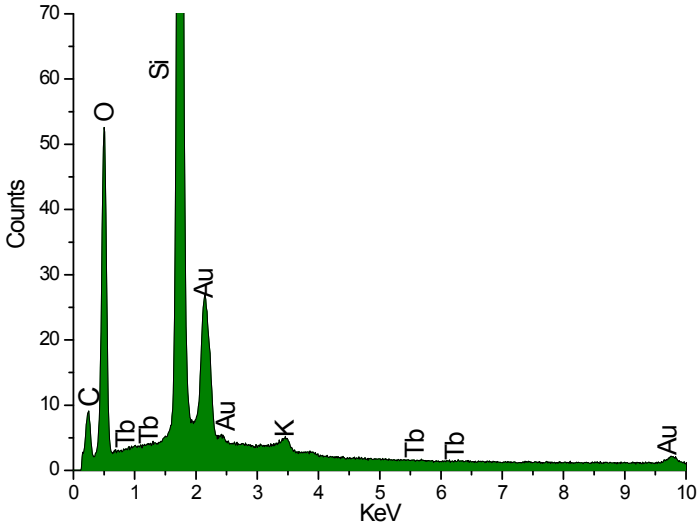


Figure S4. EDS of composite (inside of porous) with 50% activated carbon.

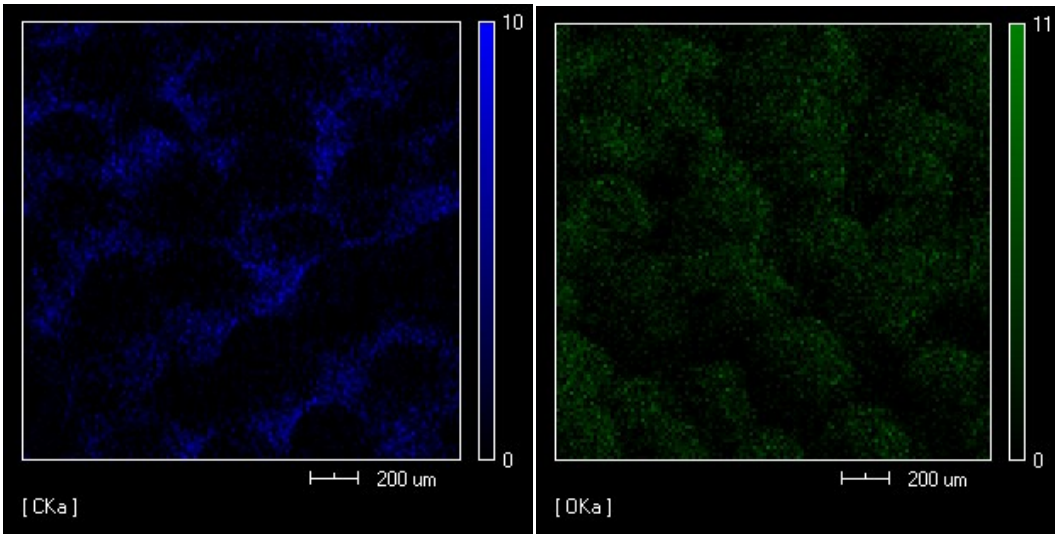


Figure S5. EDS maps of the composite; outside and inside the pore, respectively.

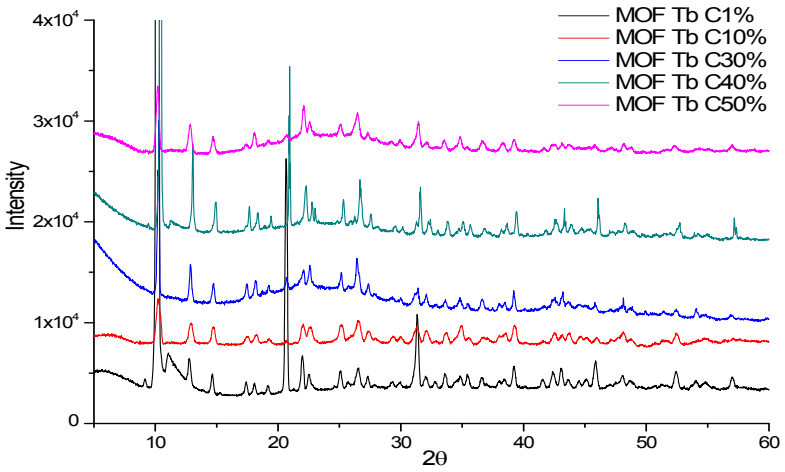


Figure S6. Diffractogram of AC, MOF Tb, CP1, CP10 and CP50

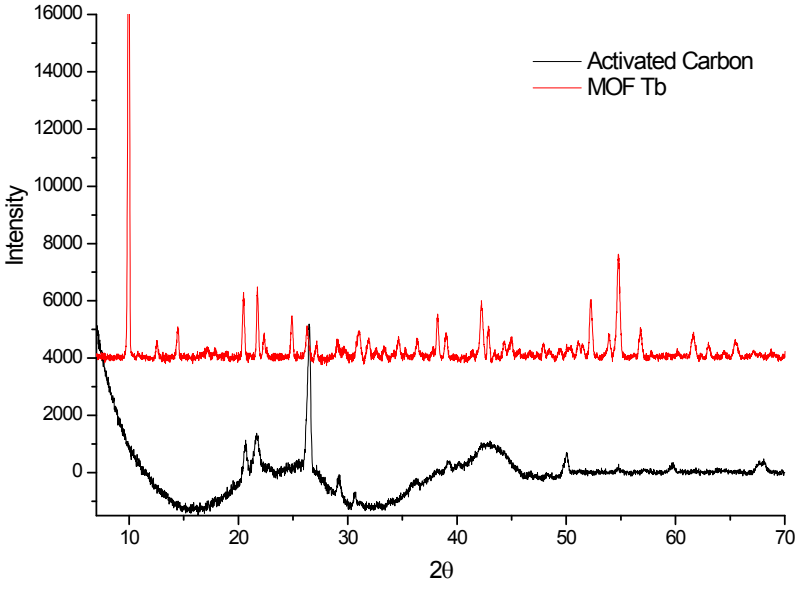


Figure S7. Diffractogram of AC and MOF Tb.

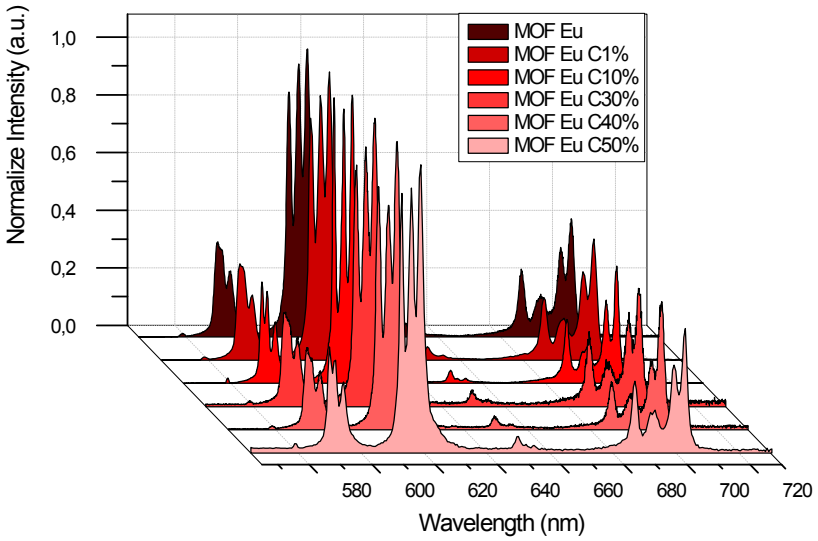


Figure S8. Emission spectrum of the MOF with Eu^{3+} with succinate linker (λ_{exc} = 395 nm) and activated carbon composites with solid state at room temperature.

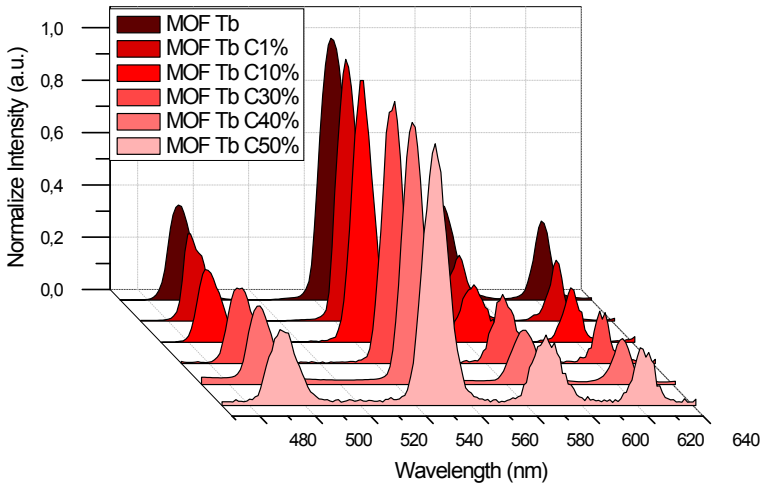
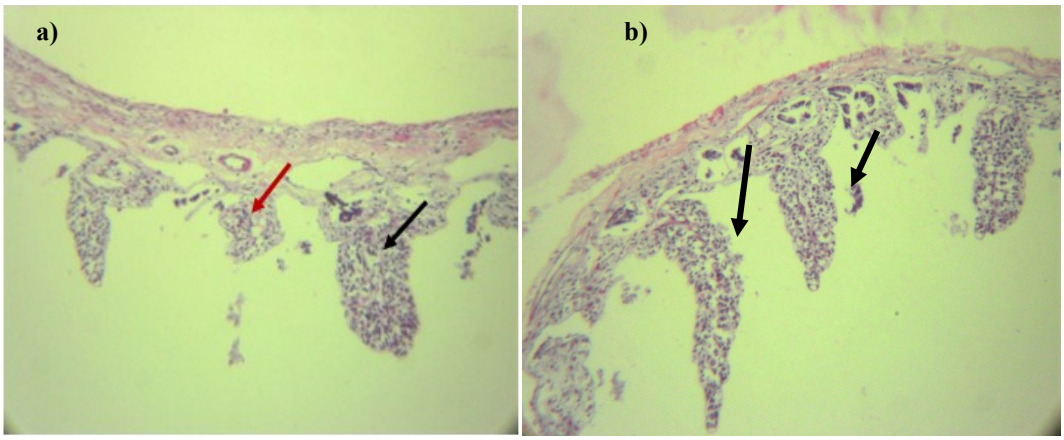


Figure S9. Emission spectrum of the MOF with Tb^{3+} with succinate linker (λ_{exc} = 374 nm) and activated carbon composites with solid state at room temperature.



Figures S10. a) Intestinal mucosa under the action of aldicarb and the composite 1 and b) 10% (400x).

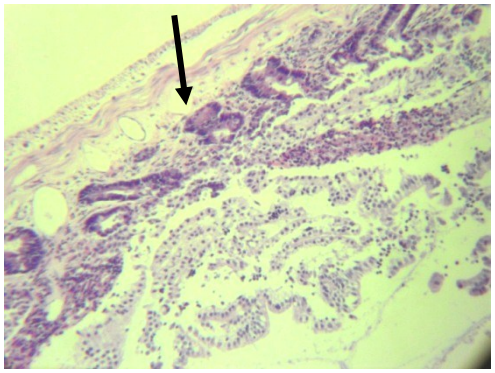


Figure S11. Ileal mucosa under the action of aldicarb and composites at 40% of activated charcoal (800x).

Table S1. Mean aldicarb concentrations (µg/mL) observed *in vitro* in 120 min, the outer parts of the preparations containing, respectively, AC, MOF Tb and composites CP1, CP10, CP30, CP40 and CP50, all with pH 7.4.

Treatments	Time (min.)				
	0	10	30	60	120
Control	0	29.79±4.02	30.79±2.89	31.93±2.65	32.16±2.75
AC	0	25.07±2.77	26.51±2.50	27.46±2.00	29.16±1.42
MOF Tb	0	25.45±2.20	26.05±2.89	27.27±2.79	28.54±2.73
CP1	0	27.98±3.71	29.45±3.26	30.22±3.20	32.03±3.84
CP10	0	26.29±0.85	27.50±0.67	27.71±0.53	29.59±0.57
CP30	0	19.35±3.13*	20.97±2.20	19.85±2.46	16.75±2.73
CP40	0	18.50±1.38*	18.52±2.43	18.21±2.51	16.89±1.69
CP50	0	17.24±0.53*	15.92±0.57	17.35±0.90	17.53±1.72

NOTE: AC-Activated Carbon; MOF Tb; CP1 and CP10, CP30, CP40 and CP50 – Composites. Each measured value represents the average of three preparations. * Significant values for $p < 0.01$.

Table S2. Mean percentages of aldicarb adsorption observed *in vitro* after 10 minutes. The preparations contain, respectively, activated carbon (AC), MOF Tb, and the composites contain 1, 10, 30, 40 and 50% of activated charcoal at different pH.

Treatments	Preparations at pH 1.5	Preparations at pH 12
AC	46.12±4.98	69.09±9.53
MOF Tb	40.71±4.88	51.86±7.26
CP1	54.73±7.39	29.05±3.78
CP10	44.09±6.08	26.52±2.27
CP30	66.05±6.86*	10.13±1.16
CP40	78.38±9.71*	21.95±2.18
CP50	77.03±8.24*	20.10±1.73

Note: Each value represents the measured mean of three preparations. * Statistical difference for $p < 0.01$.

Table S3. Mean aldicarb diffusion rate after 10 min as a function of the type of treatment, and approximate percent of aldicarb adsorption relative to the control preparations.

Treatments	Average diffusion rate (ng / cm ². min)	% Adsorption
Control	103,482±13,966	0
AC	87,067±9,614	15.86
MOF Tb	88,390±7,642	14.58
CP1	97,167±12,883	6.10
CP10	91,305±2,947	11.77
CP30	67,218±10,873*	35.04*
CP40	64,253±4,778*	37.91*
CP50	59,882±1,836*	42.13*

NOTE: Percentage of adsorption compared to control preparations. AC - Activated Carbon; MOF Tb; CP1, CP10, CP30, CP40 and CP50 – Composites containing terbium. * Significant difference for a value of $p < 0.01$; $n = 3$ for each kind of preparation.