Removal of malachite green by adsorbents from paper industry waste materials

Thermal analysis

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Abstract The objective of this work is to study the removal of malachite green (MG) from water by adsorbents obtained from pyrolysis of two paper industry waste materials: one de-inking paper sludge (HP) and one organic sludge from virgin pulp mill (RT). Both adsorbents showed elevated MG removal. Maximum adsorption Q_0 obtained by Langmuir equation was higher for the adsorbent from HP (HP-3, 982 mg/g) than RT (RT-3, 435 mg/g). However, K_L (Langmuir) and $1/n$ (Freundlich) indicated that affinity and intensity of adsorption is higher for the adsorbents from RT. Thermal analysis (TG, DTG and DTA) of adsorbents before and after MG removal was performed in N_2 atmosphere.

Keywords De-inking · Sludge · Malachite green · Thermal analysis

Introduction

Paper and pulp manufacturing separates cellulose fibres using both mechanical and chemical processes and generates important amount of waste materials. An increasing proportion of recycled fibres are used in paper industries due to their important environmental and economical benefits in the last years [1]. However, paper recycling results in the production of large amounts of wastes such as de-inking paper sludge composed by removed inks, clay fillers, coating of used paper, chemical additives and short cellulose fibres. In Spain, more than 200.000 tons of de-inking sludges were produced during 2006 [2]. Due to their high organic matter content, they could be used to improve soil fertility [3] increasing agricultural yield [4]. Other possible way of valorisation is composting but high ratio C/N of paper sludges can limit their utilisation [5]. In the last years, other uses include the use of some paper mill waste materials in the cement and brick industry [6]. Several works have showed the interesting sorption properties of materials obtained from different thermal treatments of paper sludges in the removal of phosphate [7], aqueous metals [8] or malachite green [9].

Malachite green (MG) is a basic dye widely used to colour wool, silk, cotton, jute, leather and paper. Also, malachite green has been extensively used all over the world in the aquaculture industry to treat parasites, fungal and bacterial infections in fish and fish eggs [10]. However, many adverse effects could be produced from the consumption of malachite green due to its genotoxic and carcinogenic effects [11–13]. Adsorption on activated carbon is one of the most effective methods for the removal of different dyes and organic compounds from aqueous solutions [14–17]. Due to the high cost of commercial activated carbons, many efforts have been focused on low cost carbon-based adsorbents production from pyrolysis of waste materials such as sewage sludges [18, 19], agricultural by-products [20] or other organic residues [21–23].

The main objective of this work is to study the removal of malachite green (MG) from water by adsorbents obtained form pyrolysis of two kinds of paper industry waste materials: one de-inking paper sludge from paper

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press manufacturing (HP) and other organic sludge from virgin pulp mill (RT). Thermal analysis (TG, DTG and DTA) of adsorbents after MG removal was performed in N_2 atmosphere.

Experimental

Raw material

Two paper mill waste materials were selected and used as adsorbent precursors: one de-inking paper sludge from paper press manufacturing (HP) and other organic sludge from virgin pulp mill (RT). Both samples were air-dried, crushed and sieved through 2-mm mesh.

Raw material characterisation

Paper mill waste materials selected for this work were widely characterised elsewhere [8]. pH and electrical conductivity (EC) were measured after stirring a mixture of each sample and distilled water (4 g L^{-1}) for 2 h in a Crison micro-pH 2000 and a Crison 222 conductivimeter, respectively. Total organic matter (TOM) of both samples was determined by burning samples at 540 °C during 4 h [24] in a Heron 12-PR/300 furnace. Organic carbon (OC) was determined by $K_2Cr_2O_7$ by Walkley–Black method [25]. Cation exchange capacity (CEC) was determined with $NH_4OAc/HOAc$ at pH 7.0 by the Sumner and Miller method [26]. Ca, Mg, N, K, Fe, Cr, Ni, Cu, Zn, Cd, Pb of samples were extracted with HCl and HNO_3 and determined following 3051a USEPA [27] method using a Perkin-Elmer 403 atomic absorption spectrophotometer. $CaCO_3$ was measured by treating the sample with HCl measuring the evolved CO_2 manometrically.

Adsorbents preparation

Adsorbent materials were prepared as follows: 20 g of paper mill waste material was placed in a covered ceramic cup placed in a nickel recipient. The cavity between the two recipients was filled up with fuel coke particles (<1 mm). Samples were pyrolysed in an electrical furnace by increasing the temperature to 650 °C at a rate of 3 °C min^{-1} leading to HP-3 and RT-3, respectively. In both cases, the final temperature was maintained for 2 h.

Adsorbents characterisation

Adsorbent materials were widely characterised elsewhere [8]. Textural characterisation was made from the data of sorption–desorption of N_2 at 77 K in a Micromeritics ASAP 2010 volumetric system. The surface area was evaluated from the BET equation. Mineral content was determined by heating 10 g of sample in an electrical furnace at 540 °C during 4 h in air atmosphere. pH, CEC, and EC of adsorbents were determined by the same procedure described in section "Raw material characterisation".

Malachite green adsorption

Standard MG solutions from 10 to 4000 mg L^{-1} were prepared using malachite oxalate green salt $C_{52}H_{54}N_4O_{12}$, supplied by PANREAC. To evaluate MG adsorption, 20 mL of each solution was mixed with 0.05 g of absorbent and stirred during 2 h at 300 rpm. Previously, experiments at 30, 60, 90, 120 and 180 min were performed and it could be observed that after 2 h equilibrium was achieved. After this time, solutions were filtrated to separate the suspension of adsorbent particles and the MG final concentration was evaluated using a UV–VIS Spectrophotometer Shimadzu 1203 at a wavelength of 617 nm.

MG adsorption was modelled using the Langmuir and Freundlich isotherms. These models are widely used to present data for water and wastewater treatment applications [22, 28].

The Langmuir equation can be written as follows:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e}$$

where q_e (mg/g) is the MG adsorption onto the adsorbent at equilibrium; C_e (mg L^{-1}) the residual concentration in the liquid phase at equilibrium; Q_0 (mg g^{-1}) the maximum adsorption capacity per unit of mass necessary for the formation of a complete monolayer on the surface and K_L (L mg^{-1}) is a constant related with affinity of the points of union.

The Freundlich equation can be written as follows:

$$q_e = K_F C_e^{1/n}$$

where K_F ([mg $L^{1/n}$]/[g mg $^{1/n}$]) and n (adimensional) are the Freundlich constants characterising the system and indicating, respectively, the capacity and intensity of the adsorption. The adsorption is favourable if $1/n < 1$.

Thermogravimetric analysis (TG, DTG and DTA) of adsorbents before and after MG removal was carried out in a thermobalance Labsys Setaram. About 20 mg of sample was heated at 10 °C min^{-1} until 900 °C in N_2 atmosphere, with a flow rate of 40 mL min^{-1}.

Statistical analysis

Three replicates for each determination were performed. The statistical significance of the results obtained was assessed by multiple ANOVA (Duncan's multiple range tests) with a probability level of 95%.

Results and discussion

Raw materials and adsorbents properties

Tables 1 and 2 summarise main properties of HP and RT waste materials. A wide characterisation of samples was performed elsewhere [8]. Both materials show similar pH and EC values. In both cases, pH was lightly basic due to the presence of carbonates. CEC of HP was more elevated than in case of RT (25.37 and 19.10 $cmol_{(c)}$ kg^{-1}, respectively). Organic matter content of RT was higher than HP (88.7 and 35.0 wt%, respectively). During de-inking process of paper-press, removal of inorganic additives of paper, principally $CaCO_3$ and clays, was produced leading to waste materials with high inorganic content. Finally, the OC determined by oxidation with $K_2Cr_2O_7$ was very low (3.75 and 4.14 wt% for HP and RT, respectively) due to the elevated chemical stability of cellulose fibres present in both kind of paper mill waste materials [8].

Table 2 shows metal content of both samples. In general, HP has higher metal concentration than RT (except of Cd). This could be related to the presence of inks and clays in de-inking sludges. High Ca and Mg concentrations of HP were related with their elevated content of carbonates.

Tables 3 and 4 summarises main properties of HP-3 and RT-3 adsorbents. A wide characterisation of both samples was performed in previous works [8]. pH and EC was similar for both adsorbents. Mineral content of HP-3 was higher (81.8 wt%) than for RT-3 (43.7 wt%). BET surface area and CEC of RT-3 were higher than for HP-3. Finally, the superficial charge density calculated from BET surface area and CEC values were higher for HP-3.

Malachite green adsorption

Experimental data show that MG removal by HP-3 was over 98% until initial concentration of 1000 mg L^{-1} fixing on 51% for the highest initial concentration of 4000 mg L^{-1}. In the case of RT-3, experimental data removal presented a similar trend for lower concentration whereas only 20% of MG was removed for the highest initial concentration. Experimental results obtained at lower concentrations were similar to values obtained by groundnut shell waste based powdered activated carbon

[29] and higher than removal percentage achieved by pine bark (69.3 wt% for an initial concentration of 100 mg L^{-1}) [9].

The obtained Langmuir fittings were reasonably good for the materials tested (Table 5 and Fig. 1). Also, Freundlinch fittings (Table 6 and Fig. 1) showed R^2 values similar to those corresponding to the Langmuir model. Q_0 represents the Langmuir adsorption capacity when the surface is saturated with MG. In other words, Q_0 is the maximum value of q_e [30]. Q_0 values obtained were similar to that achieved by S. Rajgopal et al. for the MG removal using activated carbons from rubberwood sawdust [31]. Comparing the MG adsorption capacity of both adsorbents, the HP-3 Q_0 was higher than RT-3 Q_0 (982 and 435 mg g^{-1}, respectively). In previous works, it was established that HP-3 leads to higher Cu^{2+} removal from water probably due to their higher oxygenated surface groups, high average pore diameter and elevated superficial charge density [8] although RT-3 presented the highest BET surface area (Table 4).

However, the strength of the affinity of the union points seems to be higher for RT-3 adsorbent according to their higher K_L (0.231, Table 5) [30]. Also, Freundlich parameters ($1/n < 1$) indicated that adsorption is favourable for both materials. Adsorption is less favourable in the isotherms with higher $1/n$ values [30]. So, according to Freundlich parameters, MG adsorption is less favourable for HP-3 than RT-3.

Figure 2 shows TG (wt%) and dTG (%/min) of MG in N_2 atmosphere. Three areas could be observed: A small peak appears at 158 °C; then, a maximum of weight loss appears at 196 °C and finally, a third broad band with maximum weight loss at 413 °C that finishes at 480 °C. Figure 3 shows dTG of MG and MG adsorbed on HP-3 and RT-3 (400 mg MG/g of adsorbent). Figure 1 shows as the ratio of 400 mg MG/g of adsorbent was achieved for initial MG concentration of 1000 mg L^{-1} for HP and 2000 mg L^{-1} for RT. The release of adsorbed moisture promotes the first mass loss observed at temperature lower than 125 °C. MG decomposition is produced from 150 to 500 °C in threes areas, and finally, at temperatures higher than 700 °C $CaCO_3$ decomposition of adsorbents takes place. It could be observed as MG decomposition is greatly influenced by the presence of adsorbent. Thermal

Table 1 Main properties of paper mill waste materials

Paper mill waste	CEC/$cmol_{(c)}$ kg^{-1}	pH	EC/μS cm^{-1} 25°C	TOM/%	OC/%	N/%	$CaCO_{3eq}$/%
HP	25.37a	7.8a	88a	35.0a	3.75a	0.43a	24.4a
RT	19.10b	7.7a	75a	88.7b	4.14b	0.14b	6.1b

Values in a given column followed by the same letter are not significantly different ($P = 0.05$) using Duncan test

Table 2 Metal content of paper mill waste materials

Paper mill waste	Metal content/mg kg^{-1}									
	Ca	Mg	Na	K	Cu	Ni	Cd	Zn	Pb	Cr
HP	65969a	288a	1252a	323a	367a	170a	9.8a	1918a	57a	11.1a
RT	12813b	266a	1404a	203b	up*b	2.1b	24.8b	up*b	up*b	up*b

* *up* unappreciated

Values in a given column followed by the same letter are not significantly different ($P = 0.05$) using Duncan test

Table 3 Adsorbent materials properties

Adsorbent material	CEC/cmol$_{(c)}$ kg^{-1}	pH	EC/µS cm^{-1} 25 °C	Mineral content/wt%
HP-3	11.3a	10.3a	126.1a	81.8a
RT-3	20.4b	9.2b	110.6a	43.7b

Values in a given column followed by the same letter are not significantly different ($P = 0.05$) using Duncan test

**Table 4** BET surface area, micropore and mesopore volume of adsorbents

Adsorbent material	BET/ m^{2}g^{-1}	Micropore area/ m^{2}g^{-1}	Mesopore area/ m^{2}g^{-1}	V micropore/ cm^{3}g^{-1}	V_{mic}/ V_T	Average pore diameter/ nm	ρ^*/ cmol$_{(c)}$ m^{-2}
HP-3	88.40	42.51	45.89	0.014205	0.14	4.5303	$1.28 \cdot 10^{-4}$
RT-3	274.74	166.61	108.13	0.061020	0.41	2.1597	$7.42 \cdot 10^{-5}$

* ρ superficial charge density calculated from BET surface area and CEC values as follows: $\rho = 10^{-3}$ CEC/BET

Table 5 Langmuir isotherm parameters

Adsorbent material	K_L/L/mg	Q/mg/g	R^2
HP-3	0.101a	982a	0.85
RT-3	0.231b	435b	0.96

Values in a given column followed by the same letter are not significantly different ($P = 0.05$) using Duncan test

Table 6 Freundlich isotherm parameters

Adsorbent material	K_F/(mg L$^{1/n}$)/(g mg$^{1/n}$)	$1/n$	R^2
HP-3	58.34a	0.427a	0.88
RT-3	36.86b	0.343b	0.94

Values in a given column followed by the same letter are not significantly different ($P = 0.05$) using Duncan test
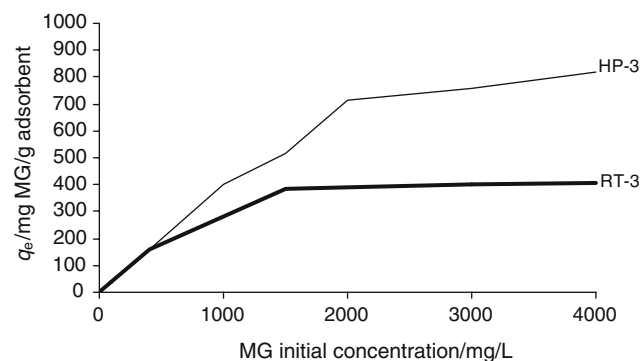
Fig. 1 Experimental data of MG removal data (q_e)

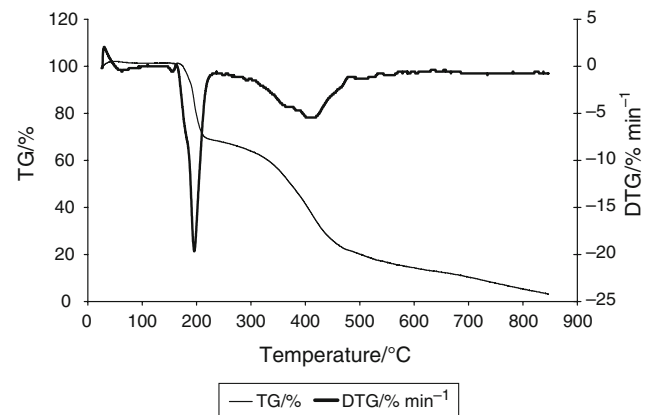**Fig. 2** TG (wt%) and DTG (%/min) of MG

decomposition of MG starts at lower temperatures adsorbed in HP-3 and RT-3 due to their dispersion on adsorbent surface.

Figure 4 shows DTA of MG adsorbed on HP-3 and RT-3 (400 mg MG/g of adsorbent). It could be observed as the first peak of MG decomposition was more endothermic
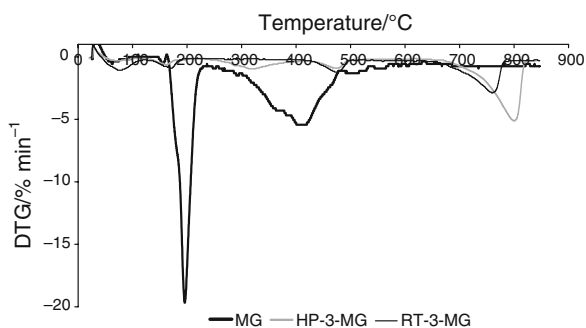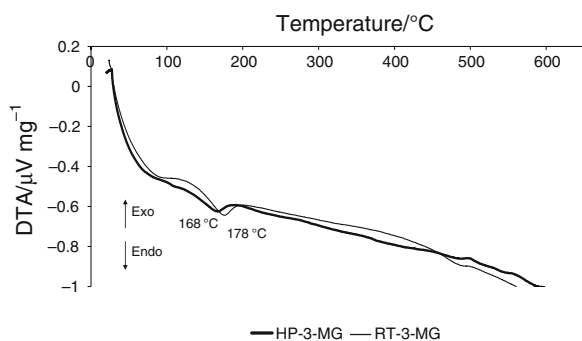
and displaced at higher temperatures for RT-3 than for HP-3. This result could be related with the higher affinity of RT-3 for MG observed with the Langmuir and Freundlich parameters.

Fig. 3 DTG (%/min) of MG and MG adsorbed on HP-3 and RT-3 (400 mgMG/g of adsorbent)

Fig. 4 DTA (μV) of MG adsorbed on HP-3 and RT-3 (400 mgMG/g of adsorbent)

Conclusions

(1) High removal of MG could be achieved using adsorbents obtained from pyrolysis of paper mill waste materials.

(2) The obtained Langmuir and Freundlinch fittings were reasonably good for the materials tested. HP-3 shows more adsorption capacity for MG (Q_0), whereas RT-3 shows more affinity for MG (K_L and $1/n$).

(3) Thermal decomposition of MG was greatly influenced by the presence of the adsorbent. DTA shows as the first peak of MG decomposition was more endothermic and displaced at higher temperatures for RT-3. This result could be related with their higher affinity for MG.

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