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Production and Characterization of Adsorbent Materials from Sewage Sludge by Pyrolysis

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The conventional sludge disposal options include landfill, application to farmland and forestry and incineration. However, since in the last decade sewage sludge and industrial sludge are being generated in increasing amounts due to the rapid urbanization and industrialization, a growing interest has been devoted in developing cost effective and renewable disposal alternatives. Among them, the manufacture of adsorbents to remove metals from water and wastewater appears to be promising, also considering the high cost of commercial carbons.
In this paper copper, zinc and cadmium removal from wastewater using adsorbents produced from pyrolysis of sewage sludge is investigated in comparison with commercial adsorbents. The kinetic of the pyrolytic process was studied, and the adsorbents produced under different pyrolysis conditions were characterized. The adsorption capacity of the pyrolyzed material were estimated in batch tests performed in an activated sludge reactor. Results show that the adsorbent materials obtained by sewage sludge pyrolysis increased organic matter removal in activated sludge systems, and limited the inhibition effects of heavy metals. In addition, a chemical activation of the sludge before the pyrolysis resulted in an increase of the adsorption capacity of the obtained adsorbent.

1. Introduction

The management of sewage sludge is one of the critical issues facing society today: the amount of generated sewage sludge in Europe (about 10.9 million tons of dry sludge for EU-27 in 2005) has been continuously increased in the last decades, due to the increase in the percentage households connected to the municipal treatment plants and the major environmental limitations in water disposal (Kelessidis and Stasinakis, 2012). Surplus sludge produced during the biological treatment of industrial and municipal wastewater requires expensive disposal procedures (Aytimur et al., 2008) often including advanced treatment (Stoller et al., 2010): the cost of sludge disposal accounts up to about 50% of the overall cost of wastewater treatment. In addition, due to the potentially high metal content, their uncontrolled disposal may induce soil and groundwater pollution (Di Palma et al., 2003). Conventional methods include landfilling, composting for farmland use and incineration (Martin et al., 2004). Alternative disposal technologies such as solidification/stabilization and thermal treatment are currently being developed (Velghe et al., 2012). Among the thermal treatment, pyrolysis allows the reduction of the volume of solid residue, and increases the resistance to natural lixiviation of the heavy metals present in the pyrolysed carbonaceous matrix (Inguanzo et al., 2002). In addition, the process produces useful gas and oil fraction (tar) with a high energetic value and a solid residue (char) that could be used as cheap carbon-based material. It is well known, in fact, that several organic wastes can be used as a precursor of activated carbon (Amutio et al., 2012; Borsodi et al., 2011; De Filippis et al., 1994), the final properties of the obtained product depend not only on the characteristics of the used raw material but also on the activating agent used (Oyedun et al., 2012) and the conditions of the activation process (Seggiani et al., 2005). Basing on those considerations, pyrolysation under controlled conditions and/or with some chemical treatment can be adopted to convert sewage sludge into activated carbon (Chen et al., 2002; Karayildirim et al., 2006).

Usually, a preliminary chemical activation is required in order to increase the surface area of carbon materials (Rozada et al., 2003), though this step is not attractive, since often results in the production of a high amount of acid wastes (sulphur and metal compounds), that is not environmentally acceptable due to the potential risk of water and air pollution.

The aim of this work was to set up a low temperature pyrolysis process to obtain a carbon based adsorbent from sewage sludge, and test the product in both a conventional activated sludge treatment and a model system, to enhance the organic matter degradation and the removal of heavy metals from wastewater (Rozada et al., 2005).

The high cost of commercial activated carbons, estimated as more than 3.0 US$/kg (Ahmaruzzaman, 2011), stimulates in fact the development of effective low cost adsorbents for the removal of metals from wastewater (Velghe et al., 2012). Therefore, the use of activated carbon from sewage sludge to remove contaminants from wastewater could offer both a management option and valorization of sewage sludge.

2. Materials and methods

2.1 Sludge characterization

The mechanically dehydrated sludge was collected at a conventional activated sludge reactor from a municipal wastewater treatment plant located in Roma (Italy).

Before the pyrolysis tests the sludge slurry was filtered and dried for 24 h at 110 °C in a laboratory oven crushed to particle size less than 0.1 mm and characterized. The Cu, Zn and Cd content was determined following 3050b USEPA method by a Philips PU 9299 FAAS. The elemental analysis was carried out in EA Eurovector analyzer.

Thermogravimetric analysis was carried out up to 950 °C by a STA 780 Series thermal analyzer, under N_2 atmosphere.

2.2 Activated carbon production and characterization

Pyrolysis of dried and crushed sludge was undertaken in a fixed bed vertical furnace (45 mm i.d., 550 mm length) under N_2 atmosphere. At the beginning of each semi-batch experiment 15 g of dried sludge were loaded in the reactor and 500 mL/min of N_2 was fluxed to realize inert atmosphere. Then, the reactor was heated up to the desired temperature and held at this temperature for a selected time. Pyrolysis vapors where quenched in water-cooled traps placed immediately at the bottom of the reactor till a temperature of 30 °C. At the end of the pyrolysis test the solid residue (char) was cooled to room temperature under an inert atmosphere. Selection of temperature and duration of the pyrolysis were based on the profiles previously obtained from thermogravimetric analysis.

The char obtained at different temperatures was analysed. The adsorption capacity was estimated by adsorption measurements of two standard test substances: iodine and methylene blue. The iodine number was obtained in accordance with the ASTM D4607-86. The adsorption kinetic with methylene blue was determined using 5 mg of the sample placed in 35 mL of stock solution prepared by dissolving 20 mg/L of methylene blue in distilled water and the residual concentration, C_f (mg/L), in solution was measured after different stirring times. The methylene blue concentration was determined in a Sequoia Turner spectrophotometer model 340 by measuring the light absorbance at a wavelength of 613 nm. Similar test was performed for a commercial activate carbon (Aquacarb 207EA, Sutcliff Carbons LTD).

2.3 Evaluation of the adsorption properties and efficiency in activated sludge systems

Experiments on activated sludge and in a combined system of activated sludge (AS) and sludge-based char (AS-PC) were performed in the presence of mineral nutrients and metabolic end products (mixed liquor). As an acclimation reactor, a 10 L lab scale activated sludge reactor fed with a synthetic wastewater (COD = 300 mg/L, added as sucrose, and the necessary amount of mineral nutrients) was used. The reactor was inoculated with the aerobic sludge (SST = 3120 mg/L, SSV = 2750 mg/L, TOC = 43.93 mg/L) coming from a municipal wastewater treatment plant, and operated at a mean sludge residence time of 10 days.

The adsorption properties of the produced chars were estimated in batch tests: 10 mg/L sample (char or commercial activated carbon) were added to 150 mL of the mixed liquor from the acclimation reactor and 50 mL of the previously described synthetic wastewater with the addition of weighted amount of the selected metal (2 mg/L of copper chloride or 20 mg/L of cadmium chloride or 40 mg/L of zing sulfide; all supplied Carlo Erba Reagents, Milano, Italy). The slurry obtained was stirred for 24 h at room temperature. Sample of the liquid fraction were withdrawn at selected times and after filtration the residual TOC (Analyzer 5000-A Shimadzu) and metal concentration were measured.

3. Results and discussion

3.1 Sludge and sludge-based sorbents characterization

Table 1 shows the main characteristics of the sludge: the low value of fixed carbon and ashes and the high volatile matter content can be noted.

Table 1: Main characteristics of the sludge as received

Proximate analysis	Value	Ultimate analysis (% wt dry basis)	
Humidity, % wt.	32.0	Carbon	36.7
Volatiles, % wt. dry basis	71.9	Hydrogen	6.1
Fixed Carbon, % wt. dry basis	14.8	Nitrogen	4.3
Ashes, % wt. dry basis	13.3	Sulfur	0.9
		Oxygen (by difference)	38.7
		Carbon/Hydrogen	6.02
		Carbon/Nitrogen	8.53
		Carbon/Oxygen	0.95

Figure 1a shows the thermogravimetric analysis of sewage sludge: the mass loss percentage and the temporal derivative of the mass versus temperature are reported. As the figure shows, the pyrolytic reactions mainly take place from 200°C to about 500°C, the mass loss was lower, but non-negligible, in the range between 500°C and 950°C.

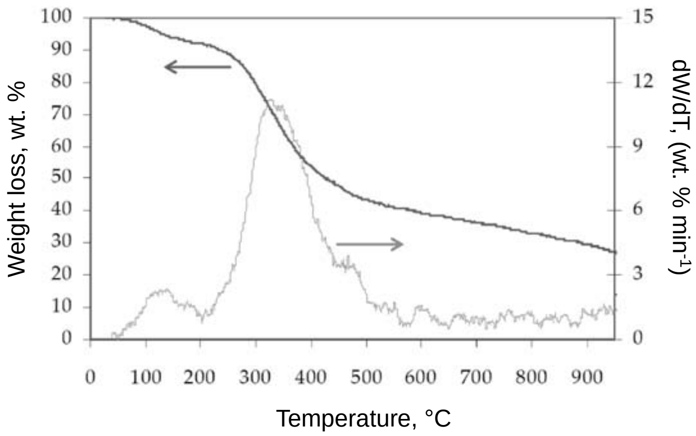

Figure 1: TGA and DTG curves of the dried sludge in nitrogen

The observation of the temporal derivative of mass curve reveals that two reactions occur between 200 °C and 600 °C: the former between 100 and 350 °C that can be attributed by the decomposition of structural carbohydrate; the latter between 350 and 500 °C, that is the weight loss influenced by the decomposition of proteins (Kristensen, 1990).

The effect of pyrolysis temperature on carbon yield is presented in Table 2: the char yield decreases from 41.25 % to 28.89 % increasing the temperature from 450 °C to 750 °C. Table 2 also shows that for all the pyrolysis temperatures the solid residue resulted enriched in carbon with a maximum at 500 °C. At the same time, as expected, increasing the pyrolysis temperature, a progressive decreasing of nitrogen (up to 0.95 % at 750 °C) and oxygen content was observed, corresponding to an increase of the amount of ashes.

The increased C/H and C/O molar ratios of the chars obtained at different temperatures with respect to the original sludge are indicative of a dehydrogenative polymerisation and dehydrative polycondensation during heat treatment, with significant loss of aliphatic hydrogen due to polycondensation reactions.

Table 2: Elemental analysis, char yield and C/H, C/O and C/N weight ratios of sludge carbon-based materials obtained at different pyrolysis temperature

	Temperature of pyrolysis				
	450°C	500 °C	550 °C	650 °C	750 °C
Char yield, % wt.	41.25	40.03	32.30	29.59	28.89
Ash, % wt.	32.26	32.90	41.30	44.80	48.96
Carbon, % wt.	42.24	43.78	40.81	40.50	42.25
Hydrogen, % wt.	2.45	2.08	1.97	1.76	1.39
Nitrogen, % wt.	2.85	2.69	2.37	2.17	0.95
Sulfur % wt	0.99	1.11	1.21	1.28	1.38
Oxygen, % wt.	19.21	17.43	12.35	9.49	5.09
Carbon/Hydrogen	17.21	21.01	20.75	23.07	30.48
Carbon/Nitrogen	14.82	16.25	17.18	18.64	44.60
Carbon/Oxygen	2.20	2.51	3.30	4.27	8.31

Moreover, the relatively high quantities of heteroatoms in carbonized sludge, especially oxygen and nitrogen derived from microorganisms, show that numerous functional groups would be present. Furthermore, the oxygen percentage decreases when the temperature increases, as a consequence the amount of acidic surface functional groups is expected to decrease in the organic fraction and the samples would become more basic. Finally, with increasing carbonization temperature, nitrogen content decreases because of the loss of volatile species. The organic nitrogen present as amine functionalities in the material carbonized at low temperature is gradually converted into pyridine-like compounds which should result in an increased basicity of the surface (Rio et al., 2005).

Table 3 reports the Cu and Zn amounts in the original material and in the pyrolytic residue: as expected, the concentrations of both metals resulted increased after the thermal treatment.

Table 3: Copper and zinc amount in dried and pyrolysed material

Metal (mg/kg)	Dried sludge	Pyrolysed sludge at 500°C
Copper	282.92	546.97
Zinc	688.49	3172.46
Cadmium	n.d.	n.d.

3.2 Adsorption and removal tests

The adsorption characteristics of the produced char at 450, 550 and 650 °C were determined using the iodine number and the methylene blue adsorption test. The iodine number gives information about the internal area of the activated carbon and it is representative of small molecules that are mainly adsorbed in pores with d>1nm (Rozada et al., 2005). The results obtained gave values of the iodine number of 98.2 138.7 and 127.4 mg/g respectively, significantly lower than the values of the commercial activated carbon (900-1050 mg/g). The results of methylene blue tests are reported in Figure 2 where a comparison with a commercial activated carbon is also reported.

As shown in the figure the sludge-based sample that gives the best results is that obtained at the temperature of 550 °C. These results can be justified considering that temperature of 450 °C could be too low to produce a fully developed porosity, while temperature higher than 550 °C can reduce the amount of active carbon due to the increase of ashes.

Furthermore, as expected the commercial activated carbon shows a removal rate higher than the sludge-based adsorbent reaching the equilibrium concentration quickly and assuring a methylene blue removal of 83.7 %. However the difference between the final equilibrium concentrations obtained with sludge-based carbon produced at 550 °C and the commercial activated carbon was negligible. In fact the sludge-based carbon ensured a methylene blue removal of 77.3 %.

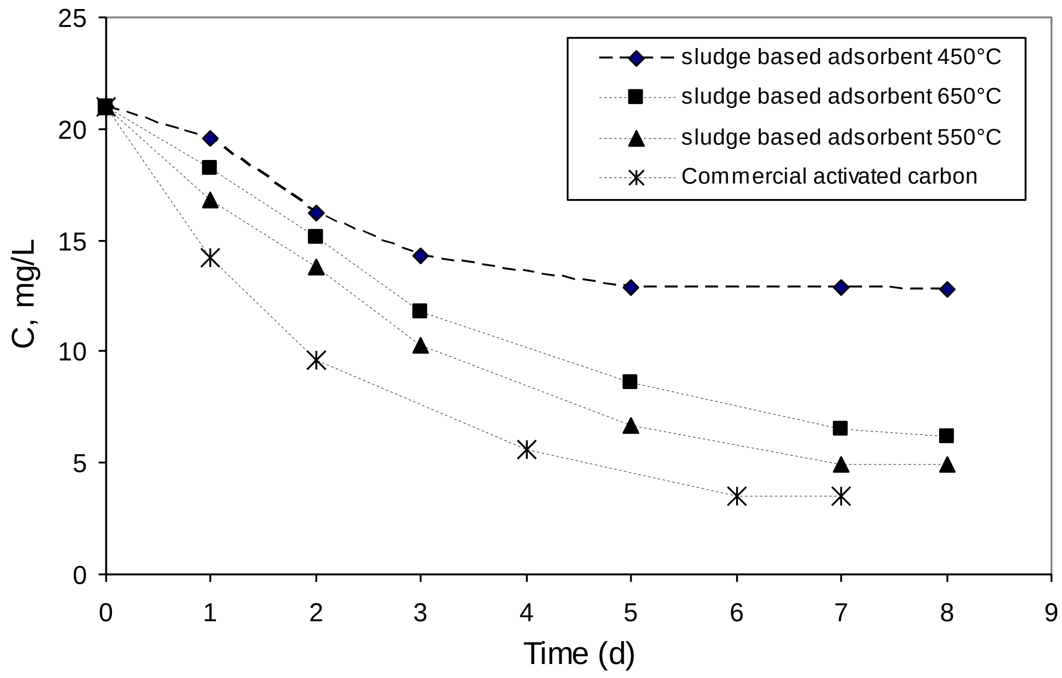

Figure 2: Methylene blue adsorption test

On the basis of the previous characterization, the adsorption performances towards carbon substrate and metal removal were evaluated only on char obtained at 550 °C. Table 4 shows that the sludge-based adsorbent exhibited a positive effect on the removal rate of organic matter. It ensured, in fact, a lower TOC concentration in the reactor: after 3 h of treatment a reduction in the range of 30-50 % with respect to the control was observed, while only a slight reduction was observed at the end of the 24 h tests.
The sludge-based adsorbent shows also a quite good metal removal performances, reducing all the selected metals concentration that in some cases is more than 50 % with respect to the control.
It is interesting to note that although the sludge-adsorbent material is characterized by an high content of copper and zinc, this material still maintains adsorption characteristics toward these metals.
These results can be attributed to both the formation of attached biomass, and the adsorption of metal onto the adsorbent material, thus reducing metal concentration in the solution at the end of the tests.

Table 4: Copper and zinc amount in dried and pyrolysed material

	TOC residual at 3h (%)	Metal residual at 3h (%)	TOC residual at 24 h (%)	Metal residual at 24h (%)
Wastewater + Zn	61	73	27	30
Wastewater + Zn + C.A.	39	43	20	14
Wastewater + Zn + Char	42	29	22	21
Wastewater + Cu	45	71	7	20
Wastewater + Cu + C.A.	18	50	6	13
Wastewater + Cu + Char	22	58	4	16
Wastewater + Cd	76	78	54	48
Wastewater + Cd + C.A.	58	57	27	24
Wastewater + Cd + Char	42	40	22	23

4. Conclusion

The work shows that the pyrolysis of sewage sludge is a possible alternative for the production of carbon-based adsorbent. Although the tests conducted on pyrolyzed material exhibited a iodine number and a methylene blue sorption capacity lower than that of commercial activated carbon, the adsorption capacity determined in activated sludge systems is quite good. The experimental results showed, in fact, that the

use of the sludge-based adsorbent can improve the quality of the effluent in terms of both substrate and selected metals removal. In particular, the addition to an activated sludge reactor of the material produced by pyrolysis at 550 °C determined an increase of TOC removal after 3 h from 67% to 85%.
A more detailed study of the method of production and characterization of sludge carbon-based material would be necessary in order to improve the properties of final product.

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