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Rice Husk Ash Based Composites, Obtained by Toxic Fly Ash Inertization, and their Applications as Adsorbents

Alberto Bosio, Nicola Rodella, Laura E. Depero, Elza Bontempi*

INSTM and Chemistry for Technology Laboratory, University of Brescia, Brescia, Italy
elza.bontempi@unibs.it

Rice husk ash (RHA) was recently employed as stabilizer, for municipal solid waste incineration (MSWI) fly ash. Indeed, this ash contains large amount of heavy metals, as Pb and Zn. MSWI fly ash contains also soluble salts (mainly NaCl) in 10-20% mass amount. These salts can be recovered after inertization procedure, by material washing.
RHA, that is combined with other by product materials, as flue gas desulfurizing residues and coal fly ash, shows good capability in heavy metals inertization, and the technology transfer was financed by EU Commission, in the frame of LIFE+ project (LIFE11 ENV/IT/000256).
The obtained composites are characterized by using chemical and structural techniques.
In this work first results about the employ of the obtained composites in the field of absorption of Methylene Blue are reported and discussed.

1. Introduction

Water and wastewater treatment represent one of the most serious issues in the field of environmental protection policy. Water pollution due to organic dyes contamination, especially deriving from several industrial processes, is an important aspect of wastewater treatment. Many conventional or non-conventional processes, such as biological, physico-chemical, filtration treatment or advanced oxidation (AOP) were tested for dyes degradation (Rehman et al., 2012). Also adsorption, which is quite simple and favoured by the availability of adsorbents, is a widely adopted technique. Problems connected to adsorption processes are the cost of adsorbent materials, their pre-treatments and their eventual regeneration treatment (Sharma et al., 2010). Hence the demand of low cost adsorbent materials.
Another topic related to the environmental management is the solid waste disposal. In European context, during last years, one of the most widespread processes has been represented by incineration treatment. Municipal solid waste incineration (MSWI) results in a high reduction of the global waste volume and produces thermal energy but it can also create environmental problems connected to process by-products (bottom ash and fly ash). Fly ash management and landfill disposal are particularly difficult in terms of environmental pollution and volumes to be stored (Bontempi et al., 2010). MSWI fly ash is classified as dangerous waste and it can contains high amounts of heavy metals (Pb and Zn in particular). Due to these problems, many alternative reuses for fly ash were proposed, such as in construction industry. Several attempts to reemploy MSWI fly ash were also carried out in the field of absorption in pollution control (Rafatullah et al., 2009).
In order to reduce the danger level of MSWI fly ash, it can be treated by solidification-stabilization methods. These processes allow to incorporate the hazardous fraction into an inert matrix.
A stabilization process for MSWI fly ash was recently developed at University of Brescia and the produced inert material was named COSMOS RICE. In this process, rice husk ash (RHA) is employed as stabilizer (Bosio et al., 2013b). RHA is a rich in amorphous silica by-product deriving from rice husk combustion.
Besides MSWI fly ash and RHA, COSMOS RICE material is composed by two other by-products: flue gas desulfurization residues and coal fly ash. COSMOS RICE project is inserted in the LIFE+ program of European Commission (LIFE11 ENV/IT/000256). In the COSMOS RICE stabilization methodology, rice husk ash employed is equal to the 9% on total weight.

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As inert, COSMOS RICE composite is suitable to be reused for further purposes. In this work, COSMOS RICE was tested as adsorbent material for degradation of Methylene Blue water solutions. Thus, batch tests were realized to determine equilibrium properties of Methylene Blue sorption on COSMOS RICE and experimental data was analyzed with Freundlich and Langmuir isotherm models.

2. Materials and methods

2.1 Fly ash inertization

Fly ash from municipal solid waste incinerator (MSWI) was stabilized by adding rice husk ash (RHA). The process also involved the addiction of desulfurization fly ash and carbon fly ash. Water is also added to allow a good mixing of the employed fly ash (Bontempi et al. 2012). The obtained material, as reported by Bontempi et al. (2012), is characterized by high stability regarding the release of heavy metals in water (Pb and Zn in particular).

2.2 Characterization techniques

A QE65000 Ocean Optics UV-Vis spectrophotometer was utilized to perform absorbance measurements on Methylene Blue solutions. Halogen and deuterium lamps were used. Each UV-Vis measurement was carried out on 3500 μL of sample solution.

2.3 Batch adsorption tests

Batch adsorption tests were performed to determine COSMOS RICE material adsorption capacity. Methylene Blue solutions at different concentration, 4 mg/L, 5 mg/L, 7.5 mg/L and 10 mg/L respectively, were produced. An arbitrary amount of COSMOS RICE (0.2 g) was added to 200 mL of each Methylene Blue solution. Methylene Blue solution pH value was equal to 7.0 for each solution. After the addiction of COSMOS RICE powder, pH values increased to 8.5. Batch tests were carried out for 2 days at room temperature with constant stirring. UV-Vis absorbance measurements on Methylene Blue solution were executed at appointed times. Methylene Blue concentration was then estimated by measuring the area under the pick located from 500 nm to 750 nm. The visible spectra of Methylene Blue solution are reported in Figure 1. A proper calibration plot was produced in the range of 1 mg/L to 10 mg/L to determine dye concentration.

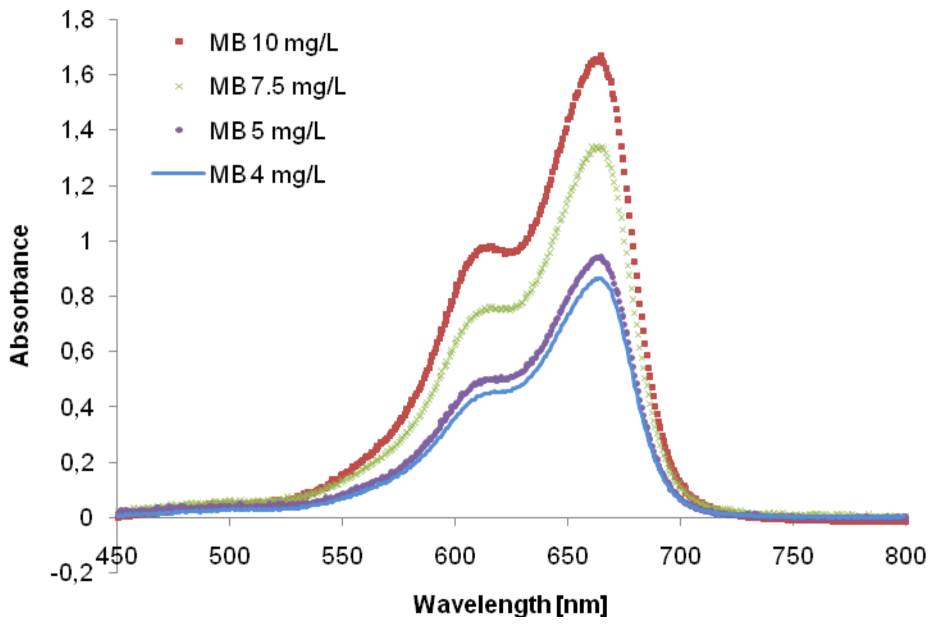

Figure 1: Visible absorbance spectra of Methylene Blue solutions at different concentrations.

3. Results and discussion

3.1 Adsorption kinetics

The effect of contact time on the residual Methylene Blue concentration during batch adsorption tests is reported in Figure 2. The abatement of dye is evaluated by the percentage removal efficiency *R(%)*, calculated as Eq(1),

$$R(\%) = \frac{C_0 - C}{C_0} \cdot 100 \qquad (1)$$

where C_0 is the initial Methylene Blue concentration and *C* is the concentration after the adsorption process (Chandrasekhar and Pramada, 2006).

Each abatement curve is characterized by a first step, with a contact time value of about 400 minutes, of high abatement efficiency. After that, the adsosbance kinetic appears to be slower, until equilibrium concentration values are reached. This is probably due to the fact that at the biginning, dye molecules arrive on the adsorbent boundary layer, than they diffuse quite rapidly into the adsorbent surface and more slowly in the micro-porous adsorbent structure (Chandrasekhar and Pramada, 2006).

In these experimental conditions, the optimum conctact time is about equal to 400 minutes, especially for low concentrated solutions.

The adsorption of Methylene Blue solution of 4 mg/L and 5 mg/L has a removal efficiency almost equal to 100% (in correspondence with a contact time of 2880 minutes). The removal efficiency for the 7.5 mg/L solution is higher than 90%. On the contrary, in the case of the MB solution concentrated at 10 mg/L, the removal efficiency is drastically reduced at about 75%.

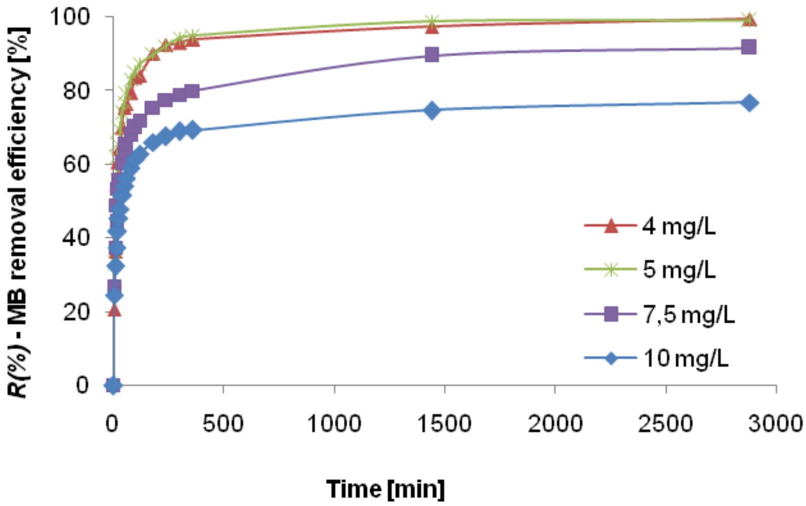

Figure 2: Methylene Blue removal efficiency R(%) versus contact time for each batch test.

To describe the adsorption process was employed the pseudo-second order model proposed by Ho and McKay (1998) and reported in Eq(2),

$$\frac{dq}{dt} = K_2 \cdot (q_e - q)^2 \qquad (2)$$

Where K_2 (g/mg min) represent the pseudo-second order rate constant, q_e (mg/g) is the Methylene Blue amount adsorbed at equilibrium and *q* (mg/g) is the amount adsorbed at the time t.

Eq(2) was integrated imposing the initial condition q(t = 0) = 0 and linearized to obtain the following Eq(3):

$$\frac{t}{q(t)} = \frac{1}{K_2 \cdot q_e^2} + \frac{t}{q_e} \qquad (3)$$

The plot of Eq(3), depicted in Figure 3, allows to calculate the constants K_2 and q_e for each Methylene Blue initial concentration adsorption process. K_2, q_e and R^2 (determination coefficient) values are reported in Table 1.

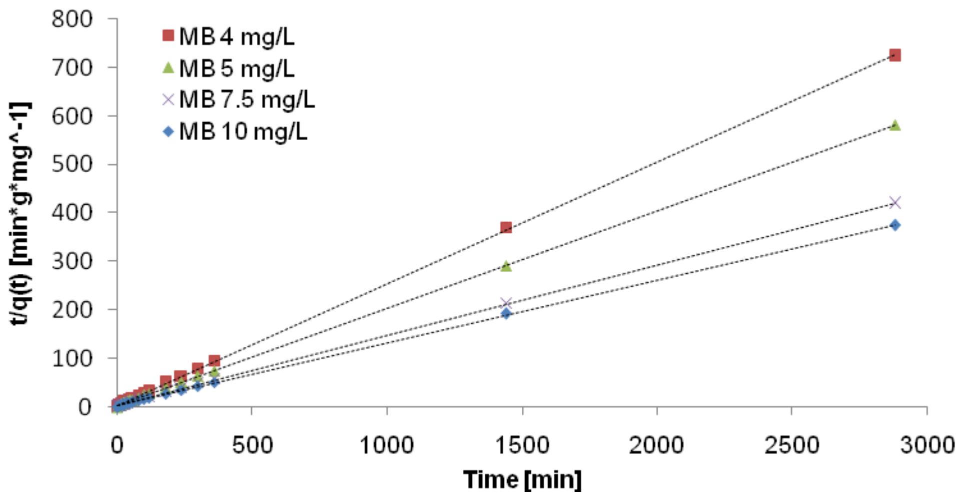

Figure 3: Linearized pseudo-second order plot for Methylene Blue on COSMOS RICE

Table 1: Kinetic constants for Methylene Blue sorption on COSMOS RICE.

Methylene Blue initial concentration [mg/L]	K_2 [g/(mg min)]	q_e [mg/g]	R^2 [-]
4	0.0137	4.00	0.999
5	0.0146	4.98	1.000
7.5	0.0055	6.70	0.999
10	0.0058	7.75	0.999

Observing Table 1, is possible to conclude that the pseudo-second order kinetic model approximates very well the sorption process of Methylene Blue onto COSMOS RICE material.

3.2 Adsorption isotherms

Equilibrium data were analyzed using Freundlich and Langmuir isotherm equations, Eq(4) and Eq(5), respectively,

$$q = K_f \cdot C_e^{1/n} \tag{4}$$

$$q = \frac{K_L \cdot Q_{max} \cdot C_e}{1 + K_L \cdot C_e} \tag{5}$$

where q is the amount of adsorbate per weight unit of adsorbent (mg/g); C_e is the equilibrium concentration reached at the end of the sorption process. K_f and n are the Freundlich constant related to the adsorption capacity and intensity of the adsorbent material (Vadivelan and Kumar, 2005). Similarly, K_L is the Langmuir constant and Q_{max} is the Langmuir maximum adsorption capacity (Bosio et al., 2013). These experimental constants were calculated from the intercept and the slope of the plot of linearized Freundlich and Langmuir equations (Eq(6) and Eq(7)).

$$\log(q) = \log(K_f) + {}^1/_n \cdot \log(C_e) \tag{6}$$

$$^1/_q = {}^1/_{Q_{max}} + {}^1/_{(K_L \cdot Q_{max} \cdot C_e)} \tag{7}$$

The plots of linearized Freundilich (A) and Langmuir (B) isotherm equations are reported in Figure 4. The linear interpolation was characterized by a determination coefficient R^2 equal to 0.981 for Freundlich model and to 0.938 for Langmuir isotherm. Thus, the sorption process is quite well represented by Freundlich model and this can mean that dye adsorption onto COSMOS RICE occurs as a non ideal phenomenon.

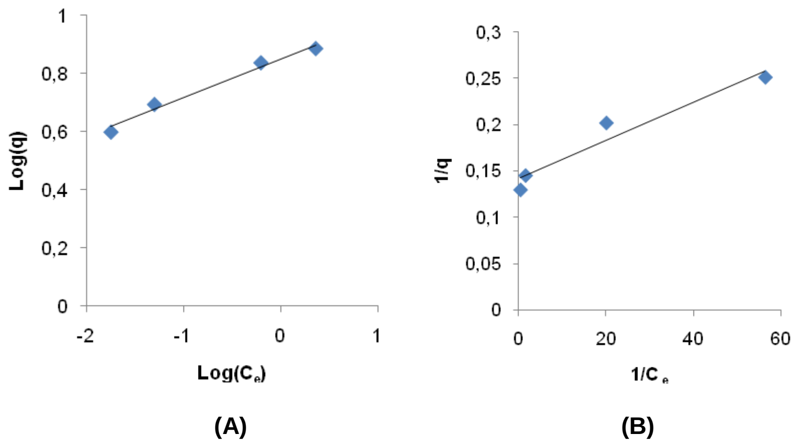

Figure 4: Linear fitting of equilibrium data with Freundlich (A) and Laugmuir (B) isotherm models.

Table 2 shows the estimated Freundlich and Langmuir isotherms parameters. Is possible to observe that, due to the *n* Freundlich parameter is higher than 1, the adsorption isotherm is favorable.

Table 2: Freundlich and Langmuir isotherms experimental parameters.

Parameter	Freundlich model	Langmuir model
K_f [(mg/g) (L/g)]	7.08	-
n	7.52	-
K_L [L/mg]	-	70.5
Q_{max} [mg/g]	-	7.09
R^2	0.981	0.938

The equilibrium curves of the sorption process of Methylene Blue on COSMOS RICE are represented in Figure 5. Both the Freundlich and the Langmuir isotherm was plotted using parameters reported in Table 2. Can be considered that, in correspondence to low equilibrium concentration values, experimental data are well fitted by both Freundilich and Langmuir model. At high equilibrium concentrations, Freundlich isoterm curve is closer to real data than Langmuir one.

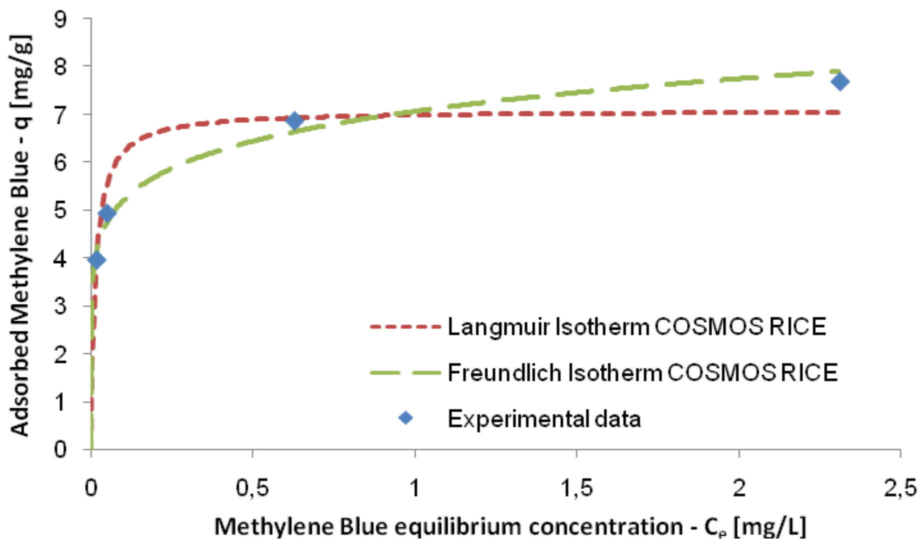

Figure 5: Equilibrium curve for the adsorption of Methylene Blue on COSMOS RICE.

The maximum sorption capacity of COSMOS RICE for Methylene Blue is slightly higher than 7 mg/g. This seems to confirm what emerged from the kinetic analysis.
Several experiments of Methylene Blue sorption an fly ash are present in literature. In order to make a comparison with COSMOS RICE, some maximum absorption values for Methylene Blue on different kinds of fly ash are reported in Table 3.

Table 3: Maximum adsorption capacity values of fly ash for Methylene Blue

Adsorbents	Adsorption capacity [mg/g]	Sources
Coal/lignite fly ash	3.07	(Rao and Rao, 2005)
Fly ash	5.57	(Kumar et al., 2004)
Coal fly ash	6.04	(Janos at al., 2003)
Coal fly ash	4.47	(Wang et al., 2005)

4. Conclusion

COSMOS RICE is an inert material produced by adding rice husk ash to municipal solid waste incinerator fly ash. Due to its inert properties, COSMOS RICE is suitable to be recovered and reused as secondary raw material in many fields. In particular, this work COSMOS RICE was employed as adsorbent material for Methylene Blue. It was determined that COSMOS RICE is characterized by good properties as adsorbent and the related adsorption process can be approximated by a pseudo-second order sorption model.

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