

The Use of Compost – Red Gypsum Mixture as a Low Cost Alternative Adsorbent for Lead

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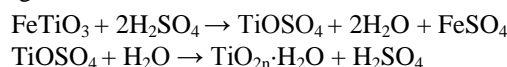
Abstract Red gypsum, a waste material which derives from the production of titanium dioxide with a high content of CaSO_4 and $\text{Fe}(\text{OH})_2$, was evaluated as a low-cost adsorbent mixed with green compost. Red gypsum is becoming interesting because of the widespread TiO_2 industrial production in many industrialized countries. The aim of this work was to evaluate whether a mixture of red gypsum and compost could be used as an adsorbing material to decontaminate waters polluted with heavy metals. Batch adsorption experiments were carried out with Lead as representative of heavy metals in polluted waters. Lead adsorption was studied to test the performance of the composite material as a function of the composition of the mixture. The evaluation of the adsorption capacity of the compost plus red gypsum mixture was based on the Freundlich and Langmuir equations. The results indicate that the composite material has a high adsorption capacity for Pb from aqueous solutions. The adsorption capacity grew following the addition of increasing amounts of red gypsum due to the increase in negative charges, which promoted the attraction towards the positively charged Pb ions. Pb adsorption may occur as a result of different mechanisms such as ion exchange, surface complexation and electrostatic interaction. The mixture compost - red gypsum showed a considerable capacity to remove Pb from aqueous solutions over a wide range of concentrations.

Keywords Adsorption, Red gypsum, Compost, Lead, Freundlich, Langmuir

1. Introduction

Water contamination by heavy metals arising from industrial activities is a problem for all industrialized countries. Galvanic industries, mining activities and textile productions are only some examples of the many industrial processes that can release heavy metals in wastewater. Worldwide industrialization seriously contributes to the release of heavy metal polluted streams. Unlike organic compounds, heavy metals are not biodegradable and can accumulate in living organisms, causing various diseases and disorders. They must thus be removed before they can be discharged into water bodies. Very strict regulations are enforced worldwide to prevent the discharge of toxic heavy metals into aquatic systems. The removal of heavy metals from wastewaters is thus an environmental issue of paramount importance [1]. Adsorption is one of the best techniques to clean-up heavy metals from aqueous solutions such as waste water, stormwaters, landfill leachates and acid mine drainage [2]. This technology is particularly appreciated for its consolidated affordability and public acceptance. One of the most important aspects of the adsorption processes is the possibility to use low cost

materials as adsorbents and simultaneously promote waste recycling [3]. Among these possibilities, compost is particularly interesting because it can act as “bio-adsorbent” resulting from the aerobic biological degradation of organic waste [4, 5]. The utilization of compost in agriculture is a diffuse practice to improve the physical properties and fertility of the soil and at the same time is a practical sustainable and efficient option in the general problem of waste management. Other waste materials that can act as adsorbents are also being studied and their use in decontaminating polluted waters can play a very important role in solving the problem of their final destination [6, 7]. Red gypsum is a waste material that derives from the production of titanium dioxide, a widespread industrial activity in many industrialized countries. The most important producers of pigments based on TiO_2 are located in Asia and North America. Asia-Pacific is also the principal sales market for titanium dioxide with 40% of total global demand. The production of titanium dioxide by the sulphate method in which ilmenite (FeTiO_3) is treated with sulfuric acid 98% for its dissolution, resulted in the production of an acidic effluent [8]. Red gypsum is mainly constituted by $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and has also a high concentration of iron hydroxides according to the simplified following scheme:



This acid solution, after TiO_2 precipitation, is neutralized

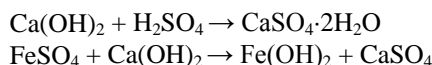
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with lime or limestone, generating large amounts of a waste product: red gypsum, so called because of the red color imparted by the iron hydroxides. This by-product is then separated by filtration.



The final disposal of large amounts of red gypsum generates costs that impact on industrial competitiveness. Thus, the evaluation of the adsorption properties of this material is a viable option of valorization of this kind of waste that should be considered.

The aim of this work was to evaluate whether a mixture of red gypsum and compost could be used as an adsorbing material to decontaminate waters polluted with heavy metals. The materials were used after had been mixed thoroughly in batch experiments. Lead has been selected as representative of heavy metals in polluted waters, because it is almost totally absent in the materials used. High concentration of lead in waters deriving from several industrial activities is a major health and environmental concern since lead is dangerous even at low concentration and tends to bio-accumulate in the food chain [9].

2. Materials and Methods

A Compost and red gypsum (RG) were derived from the Archives of Italian Institute of Soil Chemistry. The main characteristics of compost and red gypsum were determined in accordance with Chemical Methods of the Soil Science Society of America [10].

Batch sorption experiments were carried out at constant values of pH (7.4) and solid/liquid ratio (1:10). A metal solution (20 mL) at different concentrations from 1 to 50 mg/L was added to 2 g of compost - red gypsum mixtures. Compost includes putrescible garden organics, woody garden organics and trees residues. The compost and red gypsum were dried at 45°C for 48 h and then ground to pass a 2 mm sieve. The mixtures were prepared by mixing compost with increasing amounts of red gypsum to obtain final materials with 10, 20 and 30% of red gypsum. The Pb solution was prepared from a NIST standard solution of 1000 mg Pb per liter in MilliQ water. Suspensions were shaken for 12 h at 20±0.5°C. Preliminary sorption experiments, showed no significant variation in Pb concentration for periods longer than 4 h. This time was considered adequate to obtain a lead distribution near the equilibrium. After equilibration, the suspensions were centrifuged at 7000 xg to separate the solution phase from the suspensions and Pb concentrations in the supernatants were determined. The amount of Pb adsorbed per mass of the different adsorbing materials was calculated by the difference between the quantity added and that recovered in the equilibrium solution, according to the equation:

$$q = \frac{V (C_i - C_e)}{m}$$

where,

q = The amount of Pb adsorbed per unit mass (m) of the adsorbent expressed as mg g⁻¹

C_i = The initial Pb concentration (mg L⁻¹)

C_e = The Pb concentration at equilibrium (mg L⁻¹)

V = The volume of Pb solution added (L)

All experiments were conducted in triplicate, and the mean values are reported in the text. The maximum standard deviation was ±2.3%.

Pb concentration was determined using ICP-OES (Varian AX Liberty) with a method for the generation of hydrides [10]. Quality assurance and quality control were performed by testing a standard solution every 10 samples. A certified reference material (SQC001) was used to control the quality of the analytical system. The detection limit for Pb was 0.005 mg L⁻¹. The recovery of spiked samples ranged from 95 to 101% with an RSD of 1.93 of the mean.

3. Results and Discussion

The main characteristics of compost and red gypsum are reported in Table 1. Both the materials contained negligible Pb amounts.

Table 1. Selected chemical properties and elemental contents of green compost and red gypsum

Green compost		Red gypsum	
pH	7.79	pH	7.9
EC (mS cm ⁻¹)	975	EC (mS cm ⁻¹)	1672
Humidity (%)	48	Ca (% d.w.)	17.9
TOC (% d.w.)	23	Si (% d.w.)	0.73
N (% d.w.)	1.06	TiO ₂ (% d.w.)	0.43
P ₂ O ₅ (% d.w.)	0.39	P ₂ O ₅ (% d.w.)	0.04
K ₂ O (% d.w.)	0.4	K (% d.w.)	0.02
MgO (% d.w.)	0.98	Mg (% d.w.)	0.21
Mn (mg kg ⁻¹ d.w.)	284	Mn (% d.w.)	0.38
Fe (mg kg ⁻¹ d.w.)	2580	Fe (% d.w.)	3.4

The experimental data of adsorption are described by the adsorption isotherms. In the case of a solid-liquid interaction, they represent the amount of solute adsorbed per unit weight of the adsorbent material and the concentration of solute remaining in solution at equilibrium.

The adsorption process of Pb on the composite material can be analyzed according to the shape of the isotherms. Inspection of the isotherms obtained (Figure 1) showed that they were “L type” according to the Giles classification [11].

In the case of L type isotherm the availability of adsorption sites decreases with increasing Pb adsorption and saturation occurs when a monolayer on the surface of the adsorbent material has been completely covered. This kind

of isotherm indicates that the interactions adsorbent surface-solute are stronger than those solute-solute and surface-solvent interactions.

In the experimental conditions adopted, the amount of Pb adsorbed seemed to reach saturation, which indicates that the Pb ions filled all the available sites on the surfaces of the adsorbent materials. The addition of increasing amounts of red gypsum to the compost changed the adsorbing properties of the material and produced a significant increase in the amount of adsorbed Pb depending on the percentage of red gypsum added. The shapes of the isotherms in figure 1 were similar (L type), but the maximum of sorption increased. These findings indicate that new adsorbing sites in the composite material were available for Pb.

The evaluation of the adsorption capacity of the mixture

compost - red gypsum was based on the Freundlich and Langmuir equations, which are commonly used for investigating the sorption of heavy metals on soils or other different adsorbing materials.

The Freundlich isotherm is described by the following equation:

$$q = K C_e^{1/n}$$

where

q is the amount adsorbed per unit mass of the adsorbent (mg g^{-1})

C_e the equilibrium concentration of the adsorbate (mg L^{-1})

K and n are the Freundlich constants related to adsorption capacity and intensity, respectively.

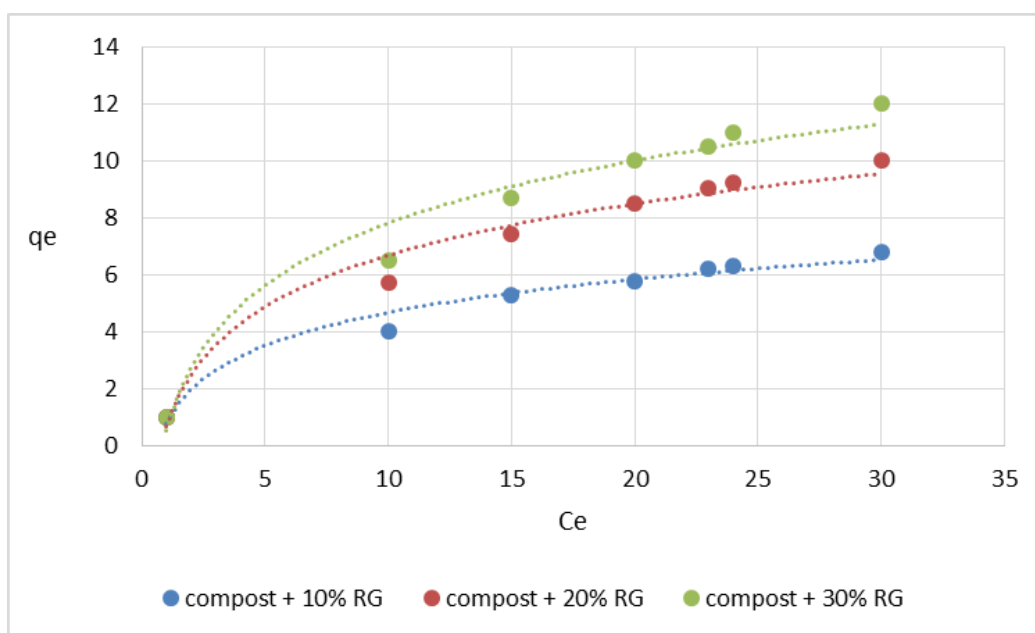


Figure 1. Pb adsorption isotherms on the mixtures compost + red gypsum

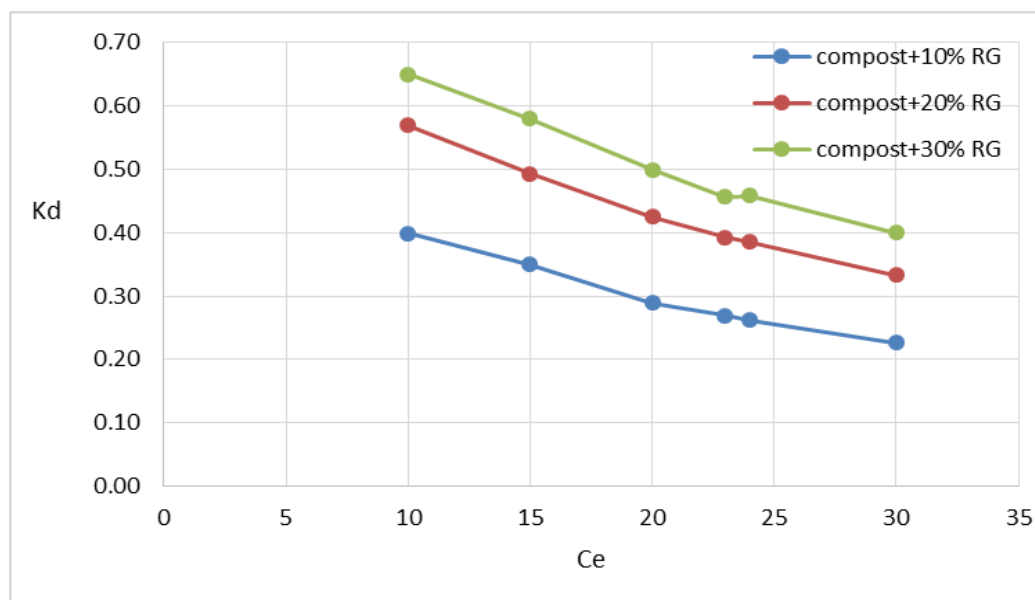


Figure 2. Effect of increasing percentage of red gypsum in the composite material on the distribution coefficient (K_d)

Deriving the logarithmic form:

$$\log q = \log K + 1/n \log C_e$$

The Freundlich constants, K and n , were estimated by linear regression analysis from the experimental adsorption data obtained for Pb. If $1/n > 1$, the adsorption can be considered as chemisorption, while for $1/n < 1$ the adsorption is a favorable physical process [12, 13, 14].

The mean values of the Freundlich parameter are shown in Table 2.

Table 2. Freundlich parameters of the different composite materials

Material	Log K	1/n	R ²
Compost + red gypsum 10%	0.2716	0.554	0.985
Compost + red gypsum 20%	0.2517	0.515	0.987
Compost + red gypsum 30%	0.1351	0.48	0.977

The data conformed well to the Freundlich equation, showing R^2 values around 0.98 and $1/n$ values < 1.0 , suggesting uniform sorption surface coverage. This result and the L shape of the isotherms suggested the use also of the Langmuir equation to evaluate the adsorption process.

The Langmuir equation can be expressed as:

$$q = \frac{q_{\max} * K C_e}{1 + K C_e}$$

where

q (mg g⁻¹) = The amount of Pb adsorbed per unit of weight of the adsorbent

C_e (mg mL⁻¹) = The equilibrium Pb concentration

q_{\max} and K = Adjustable parameters linked to the maximum and to the energy of adsorption.

The Langmuir isotherm model is based on some assumptions, which limit its applicability to simple systems. In fact, the adsorbent must be characterized by a finite number of active sites per unit area, and all the sites should have the same adsorption energy and bind a single adsorbate molecule, to form a monomolecular layer of substance. Despite these constraints, the Langmuir equation is able to describe suitably all those adsorption processes that tend to reach saturation and it has been used for many years to describe soil adsorption processes, where these conditions are not met. The Langmuir equation has also been used to describe heavy metal adsorption on unconventional adsorbents, such as red mud, fly ash, etc., without assigning an exact chemical configuration to the complex adsorbing surfaces [6]. Thus, although this model has some theoretical limitations, since the bonding energy at the sorption sites cannot be considered uniform, it enables the adsorption maxima to be compared for different materials. The Langmuir equation provides a quantitative evaluation of the effects of increasing the amounts of red gypsum on the sorption capability of this composite material. Data from the Langmuir equation are reported in Table 3.

Table 3. Langmuir parameters of the different composite materials

Material	q_{\max} mg/g	K ml/mg	R ²
Compost + red gypsum 10%	8.77	0.1033	0.981
Compost + red gypsum 20%	14.9	0.0682	0.995
Compost + red gypsum 30%	19.6	0.0522	0.996

In order to evaluate the best fit, values of correlation coefficients (R^2) of the different models are generally considered [15, 16, 17, 18]. The Freundlich equation accounts for a multisite adsorption for heterogeneous surfaces and is characterized by the heterogeneity factor $1/n$. The Langmuir equation assumes that the surface of the adsorbent is energetically homogeneous. Although the composite material is characterized by heterogeneous surfaces, the R^2 values of the Langmuir model were found to be better than that of the Freundlich model for all the adsorbents tested [13, 14, 19].

To evaluate the favorability of the adsorption, the separation factor, R_L , based on the Langmuir equation, was calculated:

$$R_L = \frac{1}{1 + K C_0}$$

Where K is the Langmuir constant and C_0 is the highest initial Pb concentration (mg L⁻¹). The value of R_L indicates the type of adsorption either to be favorable ($0 < R_L < 1$) or unfavourable ($R_L > 1$) [20, 21, 22, 23]. Values of the dimensionless constant R_L were found to be within the favorable limits [24] for all the isotherms as they ranged from 0.16 (compost + R.G. 10%) to 0.79 (compost + R.G. 30%). The data showed that the affinity of the adsorbents for Pb ions increased with increasing the amount of RG added.

The higher adsorption capacity of the materials following the addition of increasing RG amounts could be explained by an increase in the surface sites available for adsorption.

This effect can be highlighted by using the distribution coefficient K_d defined as the ratio of Pb concentration in the solid phase and in solution at equilibrium (Figure 2).

Increasing the amount of added red gypsum the distribution coefficient K_d of lead tended to increase at all the equilibrium concentrations. The constituents of red gypsum increased negative charge on the surface and it promoted the attraction towards the positively charged Pb ions. The result indicates that all the composite materials are characterized by a high adsorption capacity for Pb from aqueous solution.

By plotting K_d values versus the initial concentration C_i , it is possible to obtain the equilibrium constant K_e as the intercept of the obtained straight lines reported in Table 4 together with the corresponding R^2 . The free energy of adsorption reactions (ΔG) on the composite materials can be calculated according to the equation:

$$\Delta G = -RT \ln K_e$$

Where R = gas constant ($0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1}$) and T = temperature in Kelvin (K)

Also these data are reported in Table 4.

Table 4. $\ln K_e$ and ΔG of the adsorption on the composite materials. ΔG is expressed as KJ mol^{-1}

Material	Equation C_i vs K_d	R^2	$\ln K_e$	ΔG
Compost + red gypsum 10%	$y = -0.0065x + 0.4792$	0.9281	0.5905	-1.463
Compost + red gypsum 20%	$y = -0.0088x + 0.6753$	0.9331	0.8392	-2.079
Compost + red gypsum 30%	$y = -0.0095x + 0.7681$	0.9313	0.8641	-2.140

This quantity represents the decrease in free energy of the system in the transfer of one mole of Pb from the solution to the solid phase of the adsorbent and can be considered as being representative of the strength of the adsorption. The adsorption linkages may be influenced by lateral interactions between Pb on adjacent sites. These interactions become important when a certain number of the surface sites have been occupied [25].

The values of Gibbs free energy describes the spontaneity of adsorption process, since the values are negative, the adsorption can be considered thermodynamically favored.

The results obtained confirm the positive effect of increasing quantities of RG in the composite materials on the lead adsorption.

We can reasonably assume that Pb interactions with the composite material under study may be considered as the sum of reactions of Pb ions with the two main components: humic-like substances of compost and CaSO_4 of red gypsum.

However the composition of the solid phase is more complex than the quantitatively sum of individual contributions of the mixed materials, and the adsorption process cannot be merely described as the interactions of two separate surfaces in equilibrium with the same liquid phase. The relative contribution to the overall adsorption depends on both the actual concentration of the Pb in solution and its affinity for the surface adsorption sites. In the presence of soluble humic-like substances deriving from compost, lead adsorption depended on the composition of solution where different aqueous complexes were formed.

The adsorption mechanisms by which the lead ions are adsorbed onto the investigated materials are various and comprise ion-exchange, precipitation, hydrogen bonding, and chemical interaction between Pb and the surface functional groups of humic-like matter in the compost.

Positively-charged heavy metal cations have been shown to dominantly associate with humic-like substances in compost [26], forming multi-ligand complexes with a variety of organic functional groups on the surfaces of biosolids.

At the basic pH of this composite material, the high deprotonation of polyanions of the humic-like fractions of compost produces a relevant diffuse negative charge resulting in an electrostatic repulsion between the negative

charges on humic acid and a change in molecular shape with a more open configuration. This allows a fast diffusion of Pb^{2+} ions, which form a strongly-bound metal-humate complex with deprotonated carboxylic acid and phenol groups with prevailing electrostatic bonds [27].

The reactions that occur by adsorption of ionic species on the charged surfaces of the composite materials involve the formation of two types of complexes: outer and inner sphere.

Outer sphere complexes are formed mainly due to electrostatic interactions between Pb ions in the solution and the hydroxyl groups of the surface, positively charged when protonated and negatively if completely dissociated. In general, the Pb adsorbed species is an ion hydrate, and is easily exchangeable with other hydrated ions capable of giving similar complexes. This type of indirect interaction, mediated by the water molecules that surround one of the charged species, is typical of non-specific adsorption and is characterized by low binding forces.

Inner sphere complexes involve the formation of covalent chemical bonds between the Pb ions and the oxygen atoms of the functional groups of the humic-like substances in the composite materials. The Pb species adsorbed are not hydrated, and may only be exchanged by other ions capable of forming this type of complex. This type of direct interaction between the metal ions and charged groups on the surfaces, implies a high bond strength, and is typical of specific adsorption. In the range of Pb concentrations used in this experiment the removal of Pb from an aqueous solution may take place with these two different mechanisms due to the properties of the two parts that make up the composite material. In addition, considering the properties of red gypsum although the ion exchange is the main process in Pb ion retention on the surface of calcium sulphate, also the formation of sparingly soluble Pb compounds (surface precipitation) is possible.

4. Conclusions

Studies regarding the use of unconventional adsorbents for metal retention are of increasing interest in the latest years. Using available, low-cost, efficient adsorbents is one of the most important aspects of successful adsorption processes. Compost has been successfully used for adsorbing organic and inorganic contaminants [28, 29, 30] and gypsum is considered as an affordable adsorbent for contaminated waste water [31, 32]. The compost plus red gypsum mixture showed a considerable ability for the removal of Pb from aqueous solutions over a wide range of concentrations. The results obtained showed that the composite materials are characterized by an interesting overall adsorption capacity as revealed by the values of adsorption maxima, which compare well with adsorption capacity of other low cost sorbents for heavy metals. The simultaneous presence of compost and red gypsum is likely to produce an articulated porosity in the composite material. The mesopores could facilitate the transport of lead to the smallest pores, and the

micropores produce a significant increase in the specific surface area and therefore of the adsorbing capacity.

Due to the heterogeneous nature of this composite material, the Pb adsorption may occur as a result of different mechanisms such as ion exchange, surface complexation, and electrostatic interaction. Not all the kinds of reactions involved in the adsorption can be identified from adsorption data. As previously stated [33] complete understanding of the sorption mechanism can only be achieved by using spectroscopy techniques such as extended X-ray absorption fine structure EXAFS, or resonance anomalous X-ray. For example, the characteristics of the composite material also suggest the possibility of the formation of ternary metal-bridged complexes in which Pb is bonded to both inorganic and organic reactive surfaces, thus increasing the total Pb adsorption [6]. The composite material used in this work was obtained by the mechanical mixing of compost and red gypsum, further researches should be carried out to optimize the preparation of this bio-inorganic material in order to increase its capacity to remove heavy metal and to deepen the knowledge of mechanisms involved.

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