# CADMIUM, LEAD, ARSENATE, AND PHOSPHATE SORPTION ON RED MUD AND GYPSUM MIXTURES

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## ABSTRACT

Red mud (RM) and gypsum (G) are mining by-products that have potential to be used as soil amendments in contaminated areas. They can be used in natura or be subjected to a pretreatment in order to change their properties aiming for a better sorption performance. This work evaluated cation (Cd and Pb) and anion (As and P) adsorption on RM, comparing it with G and a mixture of both by-products at different proportions: 100% G, 75% G + 25% RM, 50% G + 50% RM, 25% G + 75% RM and 100% RM. After the adsorbent preparation, adsorption of Cd, Pb, As, and P was carried out using nitrate salts for cations and sodium as the accompanying cation for anions (ionic strength of 30 mmol $L^{-1}$). Following adsorption, samples were reacted with 30 mL of $Ca(NO_3)_2$ and NaCl solutions to promote desorption of previously adsorbed elements. After 72h of reaction, samples were centrifuged and the supernatant collected for analyses. The adsorbed concentrations of Cd and As increase with increasing RM proportion in the mix with G, with the highest Cd adsorption occurring for the mixture 25% G + 75% RM. Decreasing the proportion of G mixed with RM decreased Pb adsorption significantly, but did not affect P adsorption. Lead showed the highest Kd value followed by P, As, and Cd for RM containing G; for RM without G the decreasing order was P<Pb<As=Cd. Lead and Cd had the highest and As and P the lowest desorbed amount upon increasing the proportion of RM in the mixture with G. Effectively adsorbed percentages of P and Pb were the highest followed by As and Cd.

## INTRODUCTION

- The use of by-products as soil amendments or adsorbents for sorption of contaminants is attractive because it provides double benefits to the environment, i.e., reduces the harmful effects of the contaminant to the ecosystem, thereby improving the environment for plant development, and deliver value-added products through beneficial use of residues (Costa et al., 2012; Lombi et al., 2002).
- Red mud and gypsum can be used as adsorbents or soil amendments in their native form, as well as after one or more pretreatments.
- Pretreatment of a by-product might be necessary for its reuse or can be performed in order to improve the by-product´s performance with respect to a particular purpose.
- Pretreatments may be economically feasible particularly if they improve the by-product´s ability to remediate soil contamination, i.e., if they are not required to correct undesirable characteristics for reuse.

**Gypsum (G)**

- Gypsum here refers to phosphogypsum, which is a by-product formed during the processing of phosphate ore into fertilizer with sulfuric acid, which results in the production of phosphoric acid .

**Red mud or aluminum industry by-product (RM):**

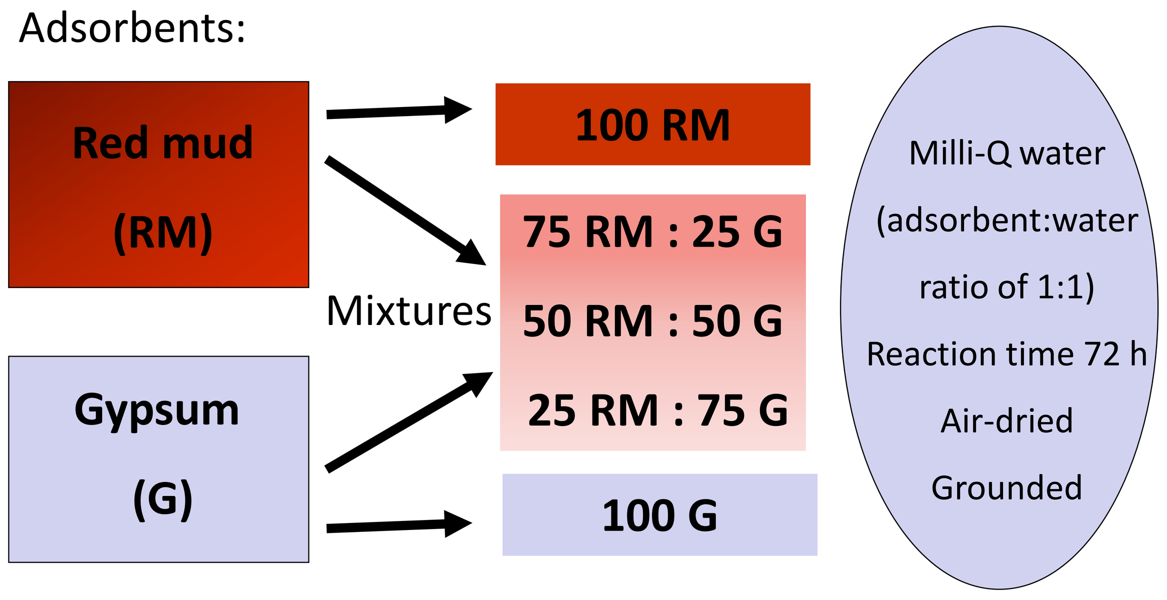
- Generated in large proportions - 1 t of alumina generally results in the production of 1-1.5 t of mud (Brunori et al, 2005)
- Oxide-rich mineralogy - hematite, goethite, maghemite, quartz, gibbsite (Costa et al., 2009 and 2012)
- High pH and Na concentration – pH ($H_2O$, 1:2.5) ~ 10.0 (Costa et al., 2009)
- Beneficial use as an adsorbent and soil amendment (Genç-Fuhrman et al., 2004; Ciccu et al., 2003; Gray et al., 2006; Costa et al., 2008)

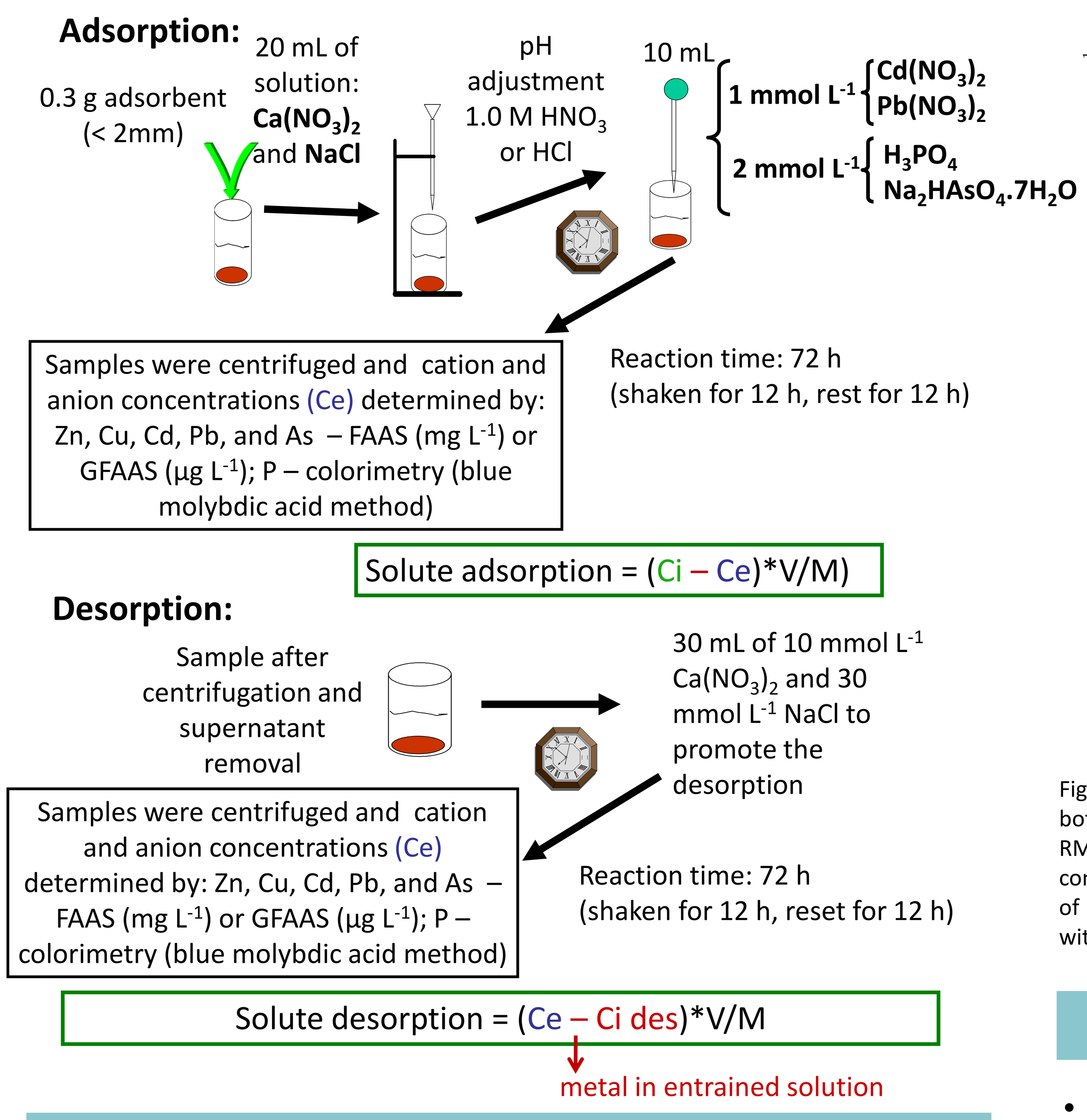
## OBJECTIVE

This work evaluated cation (Cd & Pb) and anion (As & P) adsorption on RM, comparing it with G and with mixtures of both by-products at different proportions: 100% G, 75% G + 25% RM, 50% G + 50% RM, 25% G + 75% RM and 100% RM

## MATERIALS AND METHODS

Adsorbents:




## RESULTS

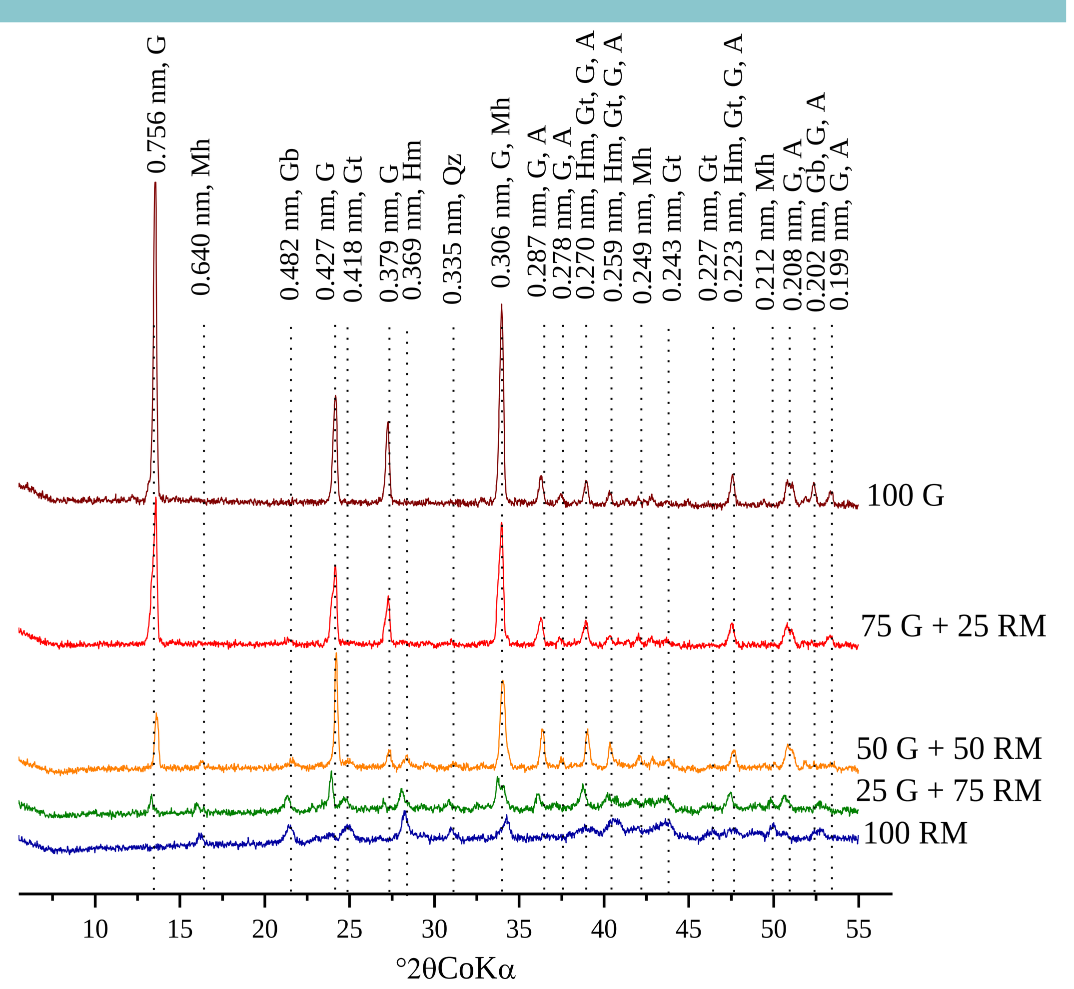



Fig. 1 X-ray diffraction of the gypsum (G), red mud (RM), and mixtures of both in different proportions: 100 g G (100 G), 75 g G + 25 g RM (75 G + 25 RM), 50 g G + 50 g RM (50 G + 50 RM), 25 g G + 75 g RM (25 G + 75 RM), and 100 g RM (100 RM). The numbers above the bands represent the d-spacing in nm with their minerals: A, anhydrite; G, gypsum; Gb, gibbsite; Gt, goethite; Hm, hematite; Mh, maghemite; and Qz, quartz.

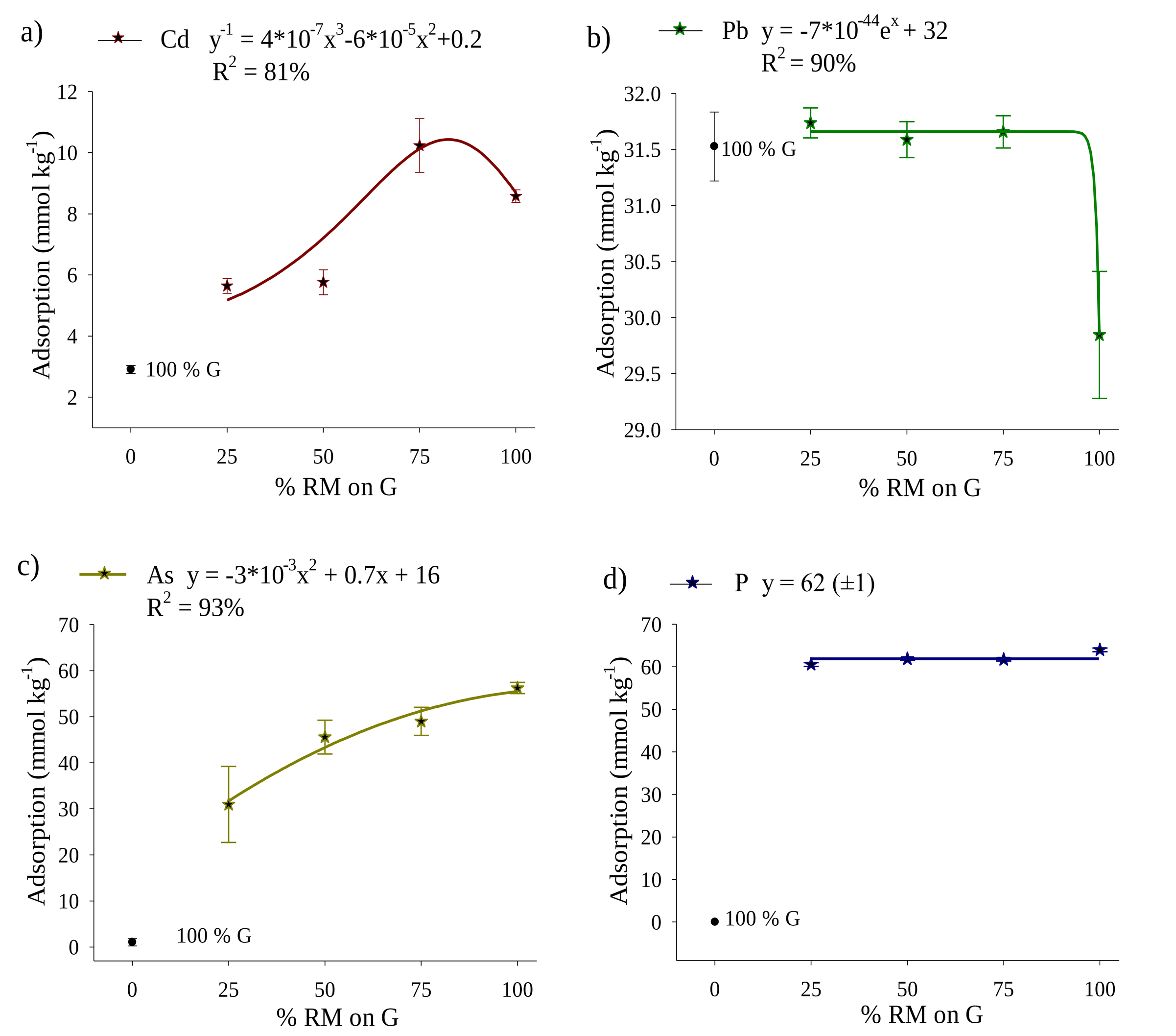



Fig. 2 Adsorption (mmol $kg^{-1}$) of Cd, Pb, P, and As on gypsum (G), red mud (RM), and mixtures of both in different proportions: 100 g G (100 G), 25 g G + 75 g RM (25 G + 75 RM), 50 g G + 50 g RM (50 G + 50 RM), 75 g G + 25 g RM (75 G + 25 RM), and 100 g RM (100 RM). Total concentration added in the adsorption of each element was 66.7 $mmol_c$ $kg^{-1}$ (33.3 mmol $kg^{-1}$ of Cd and Pb in 10 mmol $L^{-1}$ $Ca(NO_3)_2$, and 66.7 mmol $kg^{-1}$ of As and P in 30 mmol $L^{-1}$ NaCl) with adsorbent:solution ratio of 1:100 (10 g $L^{-1}$) at pH 5.5±0.2.

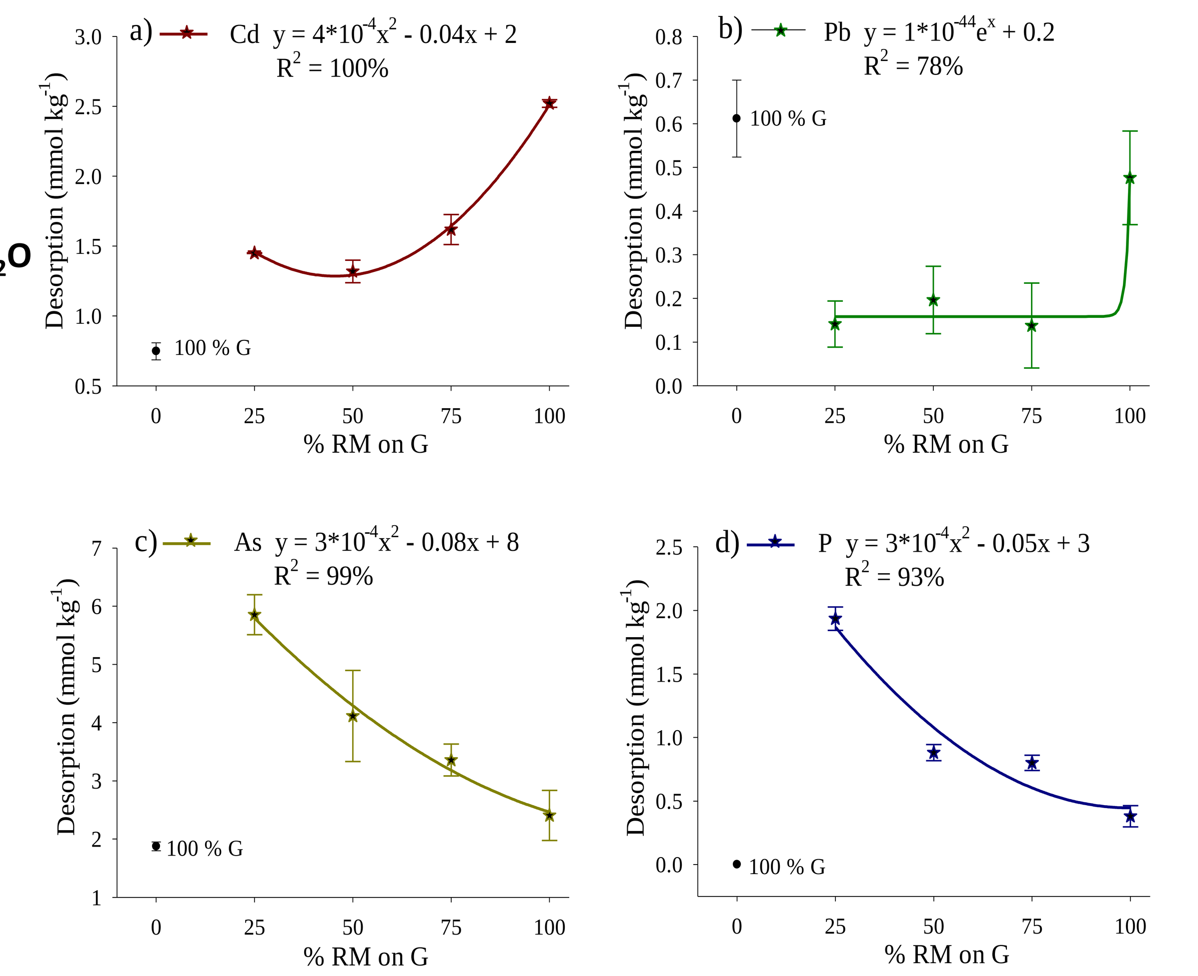



Fig. 3 Desorption (mmol $kg^{-1}$) of Cd, Pb, P, and As on gypsum (G), red mud (RM), and its mix of both in different proportions: 100 g G (100 G), 25 g G + 75 g RM (25 G + 75 RM), 50 g G + 50 g RM (50 G + 50 RM), 75 g G + 25 g RM (75 G + 25 RM), and 100 g RM (100 RM). Total concentration added in the adsorption of each element was 66.7 $mmol_c$ $kg^{-1}$ (33.3 mmol $kg^{-1}$ of Cd and Pb in 10 mmol $L^{-1}$ $Ca(NO_3)_2$, and 66,7 mmol $kg^{-1}$ of As and P in 30 mmol $L^{-1}$ NaCl) with adsorbent:solution ratio of 1:100 (10 g $L^{-1}$) at pH 5.5±0.2.

## CONCLUSIONS

- The adsorbed concentrations of Cd and As increased with increasing RM proportion in the mix with G, with the highest Cd adsorption occurring for the mixture 25% G + 75% RM.
- Decreasing the proportion of G mixed with RM decreased Pb adsorption significantly, but did not affect P adsorption.
- Lead showed the highest Kd value followed by P, As, and Cd for RM containing G; for RM without G the decreasing order was P<Pb<As=Cd.
- Lead and Cd had the highest and As and P the lowest desorbed amount upon increasing the proportion of RM in the mixture with G.
- Effectively adsorbed percentages of P and Pb were the highest followed by As and Cd.

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