Applying a Gouy–Chapman–Stern Model for Adsorption of Toxic Metals to Soils in Arsenic Affected Areas of Chhattisgarh

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ABSTRACT

An effective adsorption model was developed by S. Nir in 1978 for predicting adsorption to synthetic membranes and was also adapted by him afterwards to clay minerals. The main principles of the model are the solution of the electrostatic Gouy-Chapman equations while calculating the adsorbed amounts of the cations as the sum of those residing in the double-layer region and the cations that are chemically bound in a closed system. Thus, the equilibrium concentration in solution is influenced by the adsorption as the function of the amounts bound. The model was later developed and adapted for the adsorption of METAL cations, and, in most cases, the fit of calculated results to measured adsorbed amounts of cations was very good, after calibrating the model for the chemical tested, with only two adjustable parameters for each chemical. In the current work, we tested the applicability of this model for the adsorption of a monovalent and a divalent METAL cation by several soils, by considering the cation exchange capacities (CEC) and the specific surface areas (SSA) of the soils. For three out of four soils, a very good fit was obtained by using the required parameters for the calculations from previous studies of cation adsorption on clay minerals. The main advantage of the presented model over Langmuir and Freundlich adsorption isotherms is that no additional changes in the parameters were needed when the background concentration of salts in the suspensions was increased from 10 to 50 or 500 mM.

Keywords: heavy metal Phytoremidation, toxic metals, Gouy-Chapman, Electrostatic models

1. INTRODUCTION

Adsorption is described as the accumulation of count on the solid–liquid interface. Most of the adsorption in natural structures takes place within the dispersed phase that is composed predominantly of in METAL colloids (clays, metallic oxides, metallic hydroxides, and metal carbonates) and METAL colloidal be counted of detrital starting place as well as living microorganisms [2]. Adsorption processes are considered to be of very high importance due to the fact they decide the quantities of nutrients, metals, insecticides and other METAL chemical compounds retained on soil affecting the shipping and fate of nutrients and contaminants [2]. In addition to influencing the distribution of materials among the aqueous and the stable phase, adsorption also influences the electrostatic homes of suspended particles and colloids, influencing their tendency to coagulate or settle and the reactivity of the surfaces. Consequently, adsorption influences precipitation, dissolution, catalysis and redox strategies on the matrix [2].

Thus, the dedication of the quantities adsorbed to sorbents is crucial for the prediction of the environmental destiny of pollutants in soils [13-28]. Predicting the behavior of reactive solutes in a porous medium as soil calls for an accurate description of the sorption. In the case of an unmarried component Arsenic distribution in at any location inclusive of the Chhattisgarh soils is in all likelihood to encompass at the least three populations of concentrations, which may or might not be easily distinguishable. These include natural background, a diffuse anthropogenic influence, or anthropogenic background, and localized point sources. The relative proportion of each population varies strongly between these areas. Therefore, knowing the distribution of arsenic in these compared with their relative populations aids our understanding of the impacts of human activity on natural concentrations of arsenic in soils [1]. Significant land-use changes have occurred over the decades due to the migration of people to Chhattisgarh in search for more availability of natural resources and better economic opportunities. Adsorbed by the soil matrix, the retention can be estimated from relatively simple experiments. Utilization of bulk mineralogical data represented in the predominant phases in natural systems often has failed to predict reliably solute and contaminant behavior [3]. Electrostatic models used in mechanistic approaches may not be defensible for soil due to the complexity of the sorbents that do not conform with the essential assumptions of double-layer models [3]. Several additional limitations may be added as influences of soil METAL matter (SOM), dissolved METAL matter (DOM), formation of ionic pairs, etc. We tested whether, phenomenologically, the model can reproduce the adsorbed amounts of the monovalent METAL cation acriflavin (AF+) and the divalent METAL cation diquat (DQ+ +) on various natural soils.

Adsorption model A complete detailed review on the adsorption model employed, including all the mathematical aspects, appears in [3]. Our explanation for the model principles will be mainly qualitative. The model is based on the following main elements. Specific binding to the surface when a negatively charged particle, such as a clay platelet, is introduced into a solution containing cations and anions, migration of the ions occurs, and cations in suspension move toward the surface of the particle, being attracted by electrostatic forces. Fractions of those cations are specifically and chemically bound to the surface of the sorbent (cations in the Stern layer). Several mechanisms of binding may occur.

The neutralization of negatively charged sites on the sorbent surface may arise from the binding of a monovalent cation to one monovalent site, or from the binding of a divalent cation to a divalent site on the surface, and so on. Such divalent site is formed of two monovalent sites

on the surface. Those reactions are mainly electrostatic and should be considered for both, METAL and in METAL cations. For the case of METAL cations, we must also consider adsorption over the CEC of the sorbent, as was observed in several studies, leading, in some cases, to a charge reversal of the particle [3-4].

Such adsorption cannot be described merely by coulombic charge –charge interactions. [3-4]. There was introduced the possibility for monovalent METAL cations to form charged complexes containing two monovalent METAL cations and one monovalent surface site. Divalent METAL cations may also sorb above the CEC [4, 10] showing that charged complexes in that case arise from the binding of one divalent METAL cation to one monovalent site. Thus, for each cation, we may define two different binding coefficients: (1) the coefficient for the formation of a neutral complex denoted as K_i; and (2) the coefficient of the formation of a charged complex denoted as $\bar{K}_i$. For in METAL cations that do not form charged complexes, $\bar{K}_i = 0$. **Table 1** shows the binding coefficients of the METAL cations used in this study solution of the electrostatic equations. When dealing with charged particles in suspension, it should be recalled that, irrespective of the origin of the surface charge, electrical neutrality requires that an equal amount of charge of opposite sign must accumulate in the liquid near the charged surface. Several models can be developed to describe such behavior in suspensions. The Gouy–Chapman equation arises from the combination of Poisson's law and Boltzmann's distribution, and the main assumptions involved in this equation are [5, 11]: (a) The charge is uniformly spread on the surface; (b) The charge in the solution is built up by unequal distribution of point charges; (c) The solvent is considered as a continuous medium with invariant properties (dielectric coefficient, density, temperature); (d) Ions and surface are only involved in electrostatic interactions; (e) The surfaces are flat and infinite, and the distance between the surfaces is also infinite. The GCS model used for this study solves numerically the electrostatic Gouy–Chapman equation for the relevant suspension in each experiment or sample.

2. MATERIAL AND METHOD

2. 1. Sampling area

The studied area lies between 20º70' to 22º29' N latitudes and 81º29' to 88º29' E longitude. The physiography is directly related with the different landforms terrain under a broad physiographic classification. The area falls under Chhattisgarh plane of peninsular India. Depending upon the variations in physiographic position and topography of the area, present investigation reveals that the soils are narrow to very deep, taxonomically classified as typicChromuters, Andic Ustocrepts and typicUstorthents, belonging to Hyperthermic family.

Soil samples and rock samples were collected from surface and outcrops of representative parts. These soils samples were passed through 2-mm plastic sieve using an agate mortar and pestle to ensure that trace metal contamination did not originate from the grinding process.

These soil samples were weighed and digested in a hot oven using modified EPA method 3052 [6]. Quality assurance samples (a blank, a duplicate, spike and a standard reference material (SRM) NIST, SRM-1648 for Urban Dust sample) were included for every 20 samples in the digestion following a quality assurance plan [7]. Arsenic concentrations in the digestates were analyzed on a Chemito 201 AAS with hydride generation and a Zeeman background

correction using EPA SW 846 method 7060 A [6]. The total mapped area was approximately 500 km^2.

3. RESULT AND DISCUSSION

Previous studies, involving the wide spread distribution of Arsenic in the area and its effect of groundwater contamination by Pandey *et al.* (2002), sporadically affecting the water quality of the major river namely the Sheonath River flowing through this region had already been conducted. It should also be highlighted that this arsenic affected region is a major catchment area of river Shivnath which also is a major tributary of the Mahanadi River. Mahanadi Basin is spread over an area of 141,589 km^2, which is nearly 4.3% of total geographical area of the country. The basin lies in the states of Chhattisgarh (75,136 km^2), Orissa (65,580 km^2), Bihar (635 km^2) and Maharashtra (238 km^2). The basin has been divided into four regions, geographically. They are the Northern Plateau, the Eastern Ghats, the Coastal Plain, and the Erosional Plains of Central east India. The first two are hilly regions. The coastal plain is the central interior region of the basin, traversed by the river and its tributaries. The main soil types found in the basin are red and yellow soils, mixed red and black soils, laterite soils and deltaic soils. Cultural area in the basin is about 8.0 Million ha, which is 40% of the total Culturable area of the country

This study on soil shows that contamination level in the soil has reached a level, which is much higher than the safe level of 5 mg kg^{-1} [4-7] and hence is a cause of concern (**Table 1**). These levels have been compared with the soils of the near-by areas of Chhattisgarh like Durg and Raipur District, whose catchments area do not fall in the Rajnandgaon district, have shown a very small mean level, which could be taken as a background value. Compared to all the above factors, this area is quite enriched by arsenic, particularly the Chowki Block. This necessitates to a descriptive and regular monitoring of the entire catchment area of the river Shivnath and study its effect on the Mahanadi river system and the Mahanadi Delta Plain (MDP).

A study involving 248 minor stations was fixed in a manner to provide a representative picture of the contamination levels of soil and to undergo assessment of various other effects, including vegetation study and health risks to the large population residing in the area. Sampling stations were spread between 20°30' N to 22°0 N and 80°30' E to 81°15 E. Overall, sampling and subsequent analysis of various stations in the area led the sampling zone to be demarcated into three broad zones, according to of the following geological-geographical features:

Zone-A: The Mineralized zone, considered as maximum contaminated zone the Chowki Block. Zone-B: Moderately contaminated and mineralized zone which includes Dongargaon and parts of Rajnandgaonblock. Zone-C: The unmineralised or less contaminated zone, which includes Mohla and Manpur blocks.

Elaborated studies showed that in Rajnandgaon district four blocks, mainly Ambagarh Chowki, Mohla, Manpur, and Dongargaon are having soil levels higher than the normal background concentration, i.e. the typical soil arsenic concentrations range between 0.1 and 40 mg kg^{-1} worldwide, with an arithmetic mean (AM) concentration of 5–6 mg kg^{-1} [5-7]. The samples have a low standard deviation and sample variance. Further sample analysis showed a lower Kurtosis and Skewness values, which testify a gaussian distribution of the contamination levels. A large number of samples, which were collected and analyzed, have contributed to this scenario where a gaussian distribution has been obeyed.

Metals associated with the aqueous phase of soils are subjected to movement with soil water, and may be transported through the vadose zone to ground water. The complex species in soil solution affect the transport of metals through the soil matrix relative to the free metal ions. Clay minerals, oxides and METAL matter exert a strong preference for some anions in compared to other anions, such as phosphate exhibiting specific adsorption through inner surface complexation phenomenon. Arsenate (AsO_4^{3-}) is adsorbed to oxides and soils through specific binding mechanisms [6-7]. The adsorption capacity for anions is, however, small relative to the cation adsorption capacity of soils. The adsorption capacity whether both, exchange and specific adsorption of a soil affects number and a kind of sites available, which in turn is correlated with various other soil properties, for instance anion adsorption is correlated with Fe and Mn oxide content, pH, redox potential, etc. These interactions guide the movement of metals in the soil water. In spite of this fact, it is essential to determine the arsenic level in the Rajnandgaon district because of the fact that an Arsenic poisoning episode is already underway in the parts of Rajnandgaon. In view of the arsenic poisoning reports [8], it's only a question of scientific vocabulary that the levels being reported in the report are called 'A high background concentration' or 'Soil contamination'. What is important is the soil Arsenic levels and its probable translocation to the various matrices of the environment, which water, air, food, etc. is needed to be studied. From this 'bio-availability focused approach' it is also important to find out that what is the soil Arsenic distribution characteristics (**Figure 1**), i.e. up to which depth the soil is contaminated and what sort of remediation strategy can be envisaged in the future. In general, arsenic concentrations in Chauki and particularly in Kauriakasa were higher than rest of the studied sampling areas. Arsenic concentrations varied significantly with Geological background and land-use. Soil arsenic concentrations in these areas showed a significant correlation with natural soil properties (clay content and total Fe). Knowledge of classical pedology can be employed to predict arsenic distribution in these areas. Land-use categories can serve as good indicators of arsenic distribution in these areas. Still more research is needed to better understand the temporal variation of arsenic in different compartments in all these areas so that better decisions can be made about land application of the waste and remediation of possibly contaminated soils.

Table 1. Mean soil arsenic concentration in mg kg^{-1} in the three different zones and corresponding. Summary statistics for in 4 major blocks (all concentrations in mg kg^{-1}) falling in this zone.

Sampling Zone	As (mg kg^{-1})	Range (mg kg^{-1})	Sampling area falling in the zone	AM[a]
Mineralised Zone (Zone A)	117.77	12.24-270.00	Chowki	140.29
Semi mineralised Zone (Zone B)	44.23	2.32-45.88	Dongargaon	24.42
			Mohla	7.92
Normal Zone (Zone C)	13.47	0.40-21.45	Manpur	6

[a]AM, arithmetic Mean. [b]GM, geometric mean;GSD, geometric standard deviation [c]CL, confidence Level
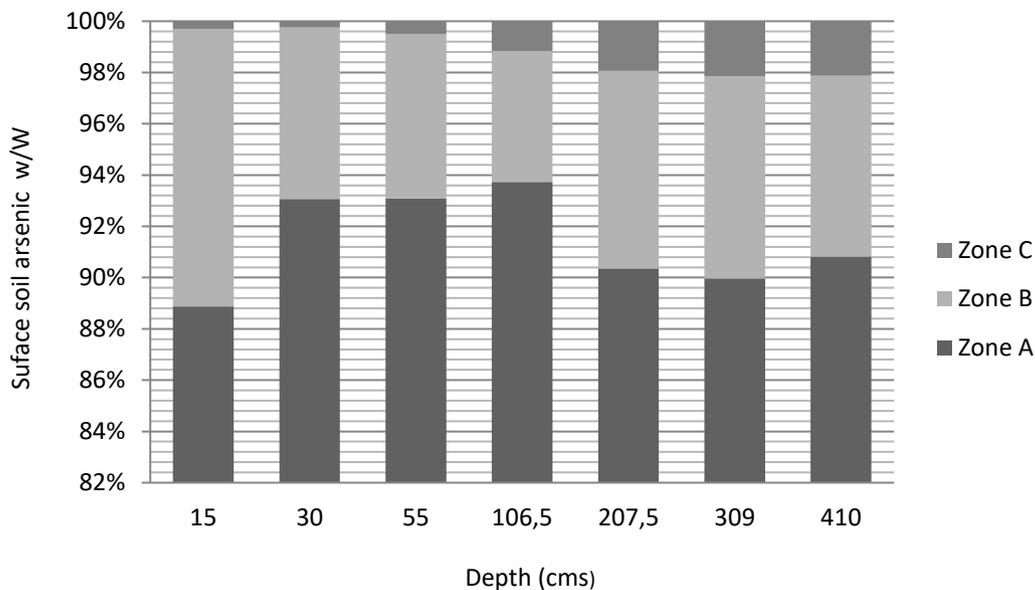

Fig. 1. Variation of Arsenic with depth in the three Zones (As values are in mg kg^{-1}).

Computational procedure A complex set of equations is obtained, the solution of which depends on the amount of charged sites and the area of each charged site in the sorbent (which, in cases where no three-dimensional matrix absorption is observed, refers directly to the CEC, SSA and the amount of sorbent in the system), the total concentration of all ions in the suspension (which is known from the experimental setup) and the binding coefficients of each ion (which might be obtained from the previous studies or from calibration experiments).

The solution of the equations is based on an iterative process that converges to one set of values yielding the surface potential of the sorbents, and the distribution of each of the ions among its various species and residence sites (neutral and charged complex, double layer, equilibrium solution, etc).

This is not a classic isotherm representation, but it helps to emphasize that when the total added amounts of both METAL cations were lower than the CEC of the soil (0.184 mol/kg), all cations were completely adsorbed. It also defines in the x-axis the independent variable that is the added concentration of the METAL cation. AF continued to sorb completely up to approximately 120% of the CEC. Similar results were reported for the adsorption of these cations on smectite clays [9-10]. The reported amounts of AF and DQ adsorbed increased up to saturation levels of about 135% and 105% of the CEC, respectively.

We compared the measured adsorption of AF to NirGalim soil, with the values evaluated from Freundlich and Langmuir isotherm. For the case of the Freundlich equation [11]. q ¼ KdC1 = n ð1Þ, where q is the adsorbed amount per unit mass of sorbents; Kd is known as Freundlich coefficient; C is the equilibrium concentration; and (1/n) is the nonlinearity coefficient. We evaluated the adjustable parameters from the measured results for the equilibrium concentration, yielding Kd = 0.549, and 1/n = 0.0815. Because the equilibrium

concentration is not known a priori, and the known parameter is the added initial concentration of the cation, Cini, we re-ordered Eq. (1) in order to account for the initial amount of the cation added in each experimental point.

4. CONCLOSUONS

Concluding remarks: As was stated in the Introduction, electrostatic models used in mechanistic approaches may not be defensible for soil due to the complexity of the sorbents that do not conform with the essential assumptions of the double-layer models [11-12]. However, we demonstrated the ability of the GCS model presented here to predict the adsorbed amounts of a monovalent and a divalent METAL cation on three different soils. This was achieved without making changes in any adjustable parameter, whereas all the binding coefficients of all ions were taken from the literature, and the relevant soil parameters were obtained from relatively simple soil analysis.

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