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Assessment of Pollution Potential of Soil and Groundwater in a Non-Engineered MSW Landfill Site

Kalyan Adhikari and Supriya Pal

***Abstract*—Assessment of pollution potential of soil and groundwater by MSW landfill leachate in an industrial city of the eastern India has been carried out through physico-chemical characterization of soil and groundwater, identification of priority contaminants, batch adsorption and isotherm studies of priority contaminants. The study region used to receive wastes for 8-10 years in an area of 1000m × 500m before it was abandoned 3 years ago. Cr^{6+} has been taken as priority contaminant in the leachate because of its presence in the MSW dump site soil as seven times higher (10.16 mg/Kg) than the CCME standard. Hydrogeologically the dump area underlies potential unconfined aquifer with easterly flow direction of the groundwater. Depth of water table (0.91-5.92 m) suggests a thin zone of aeration which increases the possibility of the contaminant to reach groundwater. Batch equilibrium study revealed that the intermediate soil zone possess good resilience with respect to Cr^{6+} transport in the subsurface. Freundlich isotherm model provided the best fit (R^2=0.9837, RMSE=0.89) to Cr^{6+} batch adsorption results. Multiple binding of Cr^{6+} was facilitated by the presence of higher concentration iron in the in-situ soil.**

***Index Terms*—Adsorption, chromium, groundwater, in-situ soil, isotherm, MSW dumpsite.**

I. INTRODUCTION

The most common and convincing method to manage the municipal solid waste is the burial in an engineered landfill. In India, most of the urban areas dump their solid waste in open fields either little away from the locality or in the vicinity of the locality. The open waste dumps, apart from odors, rodent and aesthetic nuisance are prone to generate leachate in different stages of interaction under various physico-chemical condition in the subsurface. Once the refuse is very well decomposed, the rate of oxygen diffusion into the landfill may exceed the rate of microbial oxygen depletion [1], [2]. It is quite critical to extrapolate the long term impact of landfill because different parts of a single landfill may undergo different phases of decomposition at the same time. Furthermore, decomposition continues for several years, even after the landfill stops receiving waste.

Groundwater contamination by landfill leachate has been widely reported [3]-[6] around the world. Leachate quality, quantity and their variation with time are not only the controlling factors but also the physicochemical characteristics and mineralogical components of soil or rock in the unsaturated and saturated zone are equally important in assessing soil and groundwater pollution.

The objective of the study was to assess the pollution potential of soil and groundwater in a MSW waste dump site and its proximities through physico-chemical characterization of soil and groundwater, identification of priority contaminants, batch adsorption and isotherm studies of priority contaminants.

A MSW open dump located in the Durgapur city, West Bengal, India was operative for 8-10 years before it was abandoned three years ago. The approximate area covered by the waste dump is 1000m × 500m. There are villages in the proximity of eastern boundary of the waste dump site. As the MSW dump site is entirely unprotected in terms of leachate generation and migration of leachate in the sub-surface, there are possibilities of formation of contaminant plume in the groundwater beneath the dump. The rural people, living in the proximity of this MSW dump site, may become the victim by consuming this contaminant laden groundwater.

II. MATERIALS AND METHODS

A. Sampling of Soil

The entire landfill area was subdivided into five equal grids (A, B, C, D, E) from which 11 nos. of soil samples were collected by augur boring to predetermined depth. The soil samples were taken to laboratory for physico-chemical analysis.

B. Sampling of Groundwater

14 number of groundwater samples were collected from dug wells in the close proximity of MSW dumpsite. Out of 14 samples only one sample was collected from the only unlined dug well (L-12) present within landfill. The water samples then analyzed for the parameters like pH, TDS, Cr, Pb, Fe and Zn, respectively by using standard methods as described in APHA [7]. Effort was also made to measure depth of water table to prepare the water table contour map of the MSW dump site.

C. Soil Analysis

500 gm of each soil sample was oven dried for three days at temperature of less than 60 ^{0}C, so that biomass and volatiles are retained ([8], Puget Sound). For heavy metal analysis, 100gm of oven dried soil sample was added to 100 ml of 0.1 N HCl, 100 ml of (1:9) phosphoric acid, 100ml of 0.1 N nitric acid and 200ml of distilled water and digested for 2hours; then 50 ml of concentrated HNO_3 was added to the suspension and digested for further 30 minutes. The digested suspension

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was transferred to 200ml of distilled water and then filtered through 0.47µm filter paper. The filtrate was analyzed for Cd, Cr, Cu, Pb, Ni, Zn and As in the ICP following the method stated in APHA [9].

D. Batch Adsorption Experiment and Adsorption Isotherm

TABLE I: HEAVY METALS IN IN-SITU SOIL

Grid	**Cr (mg/Kg)**	**Cd (mg/Kg)**	**Pb (mg/Kg)**	**Fe (mg/Kg)**	**Cu (mg/Kg)**	**Ni (mg/Kg)**	**Zn (mg/Kg)**
A	7.60	0.475	8.65	6025	0.09	3.83	50.70
B	6.43	0.225	2.32	4732	0.09	3.80	6.85
C	11.87	0.400	4.25	9985	0.14	5.02	20.35
D	12.50	0.375	3.85	7895	0.13	4.55	11.18
E	12.38	0.425	4.07	11412	0.24	7.90	2.35
CCME Standard	1.4	1.4	70	---	63	50	200

Cr^{6+} was taken for batch adsorption because of its dominancy (Table I) in the landfill soil. Laboratory scale batch studies were conducted to investigate the adsorption phenomenon of landfill soil using Cr^{6+} as an adsorbate. Representative soil samples, used as an adsorbent, were prepared by mixing all the soil samples by coning and quartering method. Chromium solution of initial concentrations 1,2,4,5 and 10 mg/L with soil adsorbent dosage ranging between 15 to 120 g/L were taken in a series of 100ml capacity conical flasks. Although the adsorptive affinity of Cr^{6+} to soil surfaces notably increase in acidic environment [10], but in the present study pH was maintained at 7 to ensure natural onsite condition where average pH of the landfill soil sample was found to be 6.72. Each batch of 6 conical flasks including one blank were placed in an orbital rotary shaker at room temperature (25°C) and agitated at speed of 160 rpm for 6 hours. The flasks were taken out serially at different predetermined time intervals (30, 90, 180, 360 min) one after another from the shaker and the treated solution was filtered through 22µm filter paper. The residuals Cr^{6+}concentration of filtrate was analyzed spectrophotometrically using UV-VIS spectrophotometer at a wave length of 540nm in a 5cm cell following the procedure of USEPA, [8]. The standard curve and adsorbance value were used for estimating residual Cr^{6+} concentration. The percentage of Cr^{6+} adsorbed by the in-situ soil (landfill soil) calculated by eqn. no. 1.

$$\text{\% removal of } Cr^{6+} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

C_0 and C_e are initial and equilibrium concentrations respectively.

The adsorption isotherm experiments were carried out maintaining a fixed amount of adsorbent dosage with varying initial Cr^{6+} concentration ranging between 1-10 mg/L at constant solution pH level of 7 for each set of experiment as described above. The different adsorbent dosages (15-120 mg/L) were taken for different sets of experiments. After equilibrium, the solutions were filtered and analyzed for residual Cr^{6+} concentration. The equilibrium Cr^{6+} adsorption capacity, S (mg/Kg) was calculated by Eqn. no. 2.

$$S = \frac{(C_0 - C_e)}{M} \times V \tag{2}$$

where, V is the volume of solution is in ml and M is the mass of adsorbent (in-situ soil) in gram.

Langmuir and Freundlich isotherm models, described in Eq. 3 and 4, were applied to derive the isotherm constants.

Linear isotherm,

$$S = K_d C_e \tag{3}$$

Freundlich isotherm,

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

where, K_d(L/Kg) is the linear isotherm model constant; K_f (L/Kg) and n are Freundlich isotherm constants which were derived using nonlinear regression analysis.

III. RESULTS AND DISCUSSIONS

A. Soil Characteristics

The soil in the study area is silty clay in nature. Average pH (6.61), depicts that the soil in the dump site is little acidic to neutral. The overall specific gravity of the 11 soil samples ranged between 2.45 and 2.84. The wide variation of heavy metal contents (Table II) in the dump site may be due to poor sorting or no sorting at all of the rejects, while dumping. Uniform spreading during dumping of the materials was not practised. The solid waste comprises food-wastes, batteries, plastics, rubbers, papers, building materials, metals, scraps, e-waste and other wastes produced in the city. Apart from chromium, other heavy metal concentrations are within the standard as prescribed by CCME (1991) (Table I). Presence of Fe also shows high concentration (avg. 8010 mg/Kg, range: 2747-11413 mg/Kg).

B. Groundwater

Regional hydrogeology suggests groundwater generally occurs under unconfined to semi confined state. Regional flow is towards south-east [11]. The height of water table in study area and its' proximities varies between 76 and 114m. It is evident from the water table contour map that permeability of the formation increases towards south with decreasing head. The area of interest of the present study that is the MSW dump area falls under higher permeable region where velocity of groundwater is comparatively slower than the northern part of the study area.

TABLE II: PHYSICO-CHEMICAL ANALYSIS OF GROUNDWATER OF THE STUDY AREA

	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11	L12
pH	7.54	7.43	6.93	6.90	6.95	6.60	7.66	7.40	7.66	6.96	7.63	5.5
TDS	66	170	145	68.8	78.8	53.1	70	210	124	32.1	40.8	153
Cr	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Pb	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Fe	0.07	0.08	0.06	0.05	0.05	0.06	0.06	0.05	0.33	0.05	0.05	0.05
Zn	0.04	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

TABLE III: BATCH ADSORPTION STUDY RESULTS

C_o	**Contact Time (minutes)**											
	30			**90**			**180**			**360**		
	C_e	**% rem.**	q_e	C_e	**% rem.**	q_e	C_e	**% rem.**	q_e	C_e	**% rem.**	q_e
1	0.11	88.8	29.6	0.094	90.6	30.2	0.130	87.0	29.0	0.114	88.6	29.5
2	0.32	84.2	56.1	0.274	86.3	57.5	0.272	86.4	57.5	0.233	88.3	58.9
4	0.55	86.3	115.0	0.525	86.9	115.8	0.521	87.0	116.0	0.516	87.1	116.1
5	0.68	86.3	143.8	0.617	87.7	146.1	0.781	84.4	140.6	0.703	85.9	143.2
10	1.61	83.9	279.8	1.513	84.9	282.9	1.630	83.7	279.0	1.643	83.6	278.6

C_o and C_e are the initial and final Cr^{6+} concentrations in (mg/L), % rem=Percentage Removal, %r =[(C_o-C_e)/C_o] 100 and q_e=[(C_o-C_e)/M] V in (mg/kg)

Physico-chemical characterisation of groundwater (Table II) reveals that meteoric water during its subsurface journey has not undergone long interaction with the surrounding geological materials which is an indication of recharge zone. All parameters including heavy metals conform to the drinking water standard specified by WHO [12]. L12 (Table II) shows much reduced pH (5.5) in comparison to the other wells of the study area. L12 is a significant well as it is the only well which is located within the MSW dump area. The pH of L12 hints about acid phase of decomposition of landfill. Acid phase promotes heavy metal dissolution from the soil, but there is no indication of enrichment of heavy metals in groundwater (Table II). According to the age of land fill (8-10 years) the acid phase should get over by now but unplanned dumping with plastic and building materials might have temporarily mummified the decomposable wastes. Later on tilling activities for vegetable cultivation by poor local people rendered moisture availability to the waste and thereby facilitated the late decomposition. If acid phase continues, the increased rate of heavy metals dissolution from soils and its transport to groundwater in future cannot be ruled out. Presence of chromium in much higher concentration in the landfill soil may pose problem to groundwater in near future. Considering this aspect the soil resilience with respect to chromium has been studied through batch equilibrium studies.

C. *Batch Equilibrium Study*

Laboratory batch tests, involving initial chromium concentrations (1, 2, 4, 5 and 10 mg/L) in different adsorbent (in-situ landfill soil) doses (15, 30, 60, 120 g/L) for contact time of 360 minutes at pH of 7, demonstrate chromium adsorption increases up to 30 g/L adsorption dose and thereafter decreases. Table III shows results of batch adsorption study with the optimum soil dose of 30 g/L. There is no definite trend of change of percentage removal of chromium with contact time for particular initial concentration of chromium. In most cases maximum removal was over 80% at equilibrium. Maximum removal recorded as 90.6% with initial concentration 1 mg/L. Cr^{6+} adsorption isotherm results were plotted in Linear, Langmuir and Freundlich isotherm model as shown in Fig. 1 - Fig. 3 respectively, and Freundlich isotherm model (coefficient of determination, r^2=0.9837, RMSE=0.89) provided the best fit to the test results (Table III) as compared to the Langmuir isotherm (r^2=0.4114, RMSE=4.52) and Linear isotherm (r^2=0.9785, RMSE=1.057) models. The isotherm constants of Freundlich adsorption model were obtained as K_f=9.77 L/kg and $1/n$ = 0.89. The closer fitting of Freundlich isotherm model with the experiment batch adsorption results also indicates multiple binding and heterogeneity for Cr^{6+} adsorption in soil media [13].

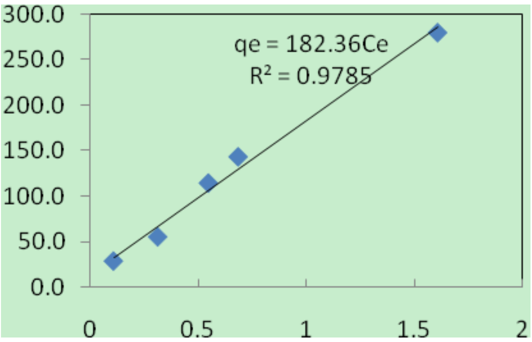

Fig. 1. Linear for Cr^{6+} adsorption.

When $1/n$ value is in the range of $0.1<1/n<1$, the adsorption process is favourable [14]. In the present investigation the high value of 1/n clearly indicate that the retardation factor is relatively high and the soil has relatively high Cr^{6+} attenuation capacity. The maximum amount of Cr^{6+} adsorbed in soil was found to be 466.6 mg/Kg (q_e=9.77 $Ce^{0.89}$) at pH (7). Cr normally forms insoluble precipitates with hydroxide [15]. Fe^{2+} associated with iron oxides/ hydroxide minerals in soils can reduce Cr^{6+} which results in precipitation (higher partition co-efficient). Experimental data for Cr^{6+} adsorption onto iron oxy hydroxide and aluminium hydroxide minerals [16], [17] indicate that adsorption increases with decreasing pH over the pH range 4-10. Such adsorption behaviour reveals that oxide show a decrease in the number of positively charged surface sites with increasing pH. Presence of high concentration of Fe in the soil of the present study has played a significant role in overall retardation of Cr^{6+} in the in-situ soil. Experimental data and peripheral evidences vividly explain that the insignificant concentration of Cr^{6+} ions in groundwater within the landfill and its proximities where as the concentration of the same in the landfill soils was approximately seven times above the standard limit as specified by CCME.

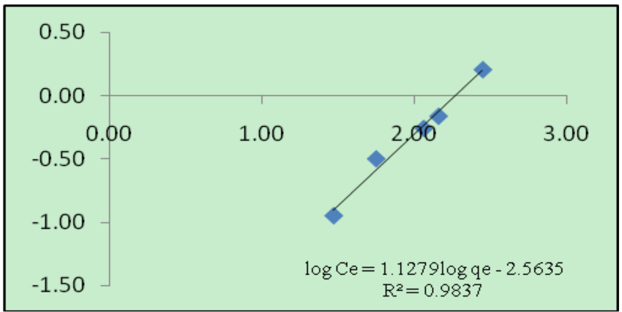

Fig. 2. Freundlich isotherm for Cr^{6+} adsorption, plot of log C_e against log q_e.

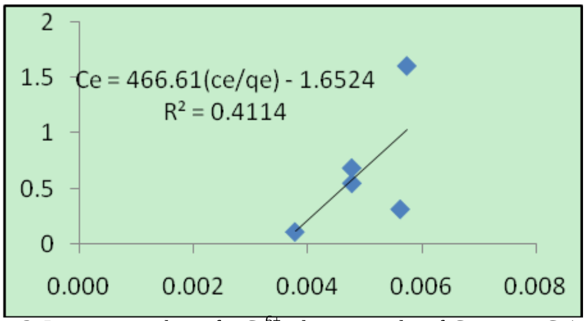

Fig. 3. Langmuir isotherm for Cr^{6+} adsorption, plot of C_e against C_e / q_e.

IV. CONCLUSION

Activities like tilling of soil for cultivation promotes infiltration of rain water which facilitates in producing leachate from MSW landfill. The pH (5.5) of the water sample (L12) collected from within the landfill area indicates acid phase of decomposition of the landfill. Although concentrations of Cr^{6+} (6.425 – 12.5 mg/kg) is very high in the in-situ soils but surprisingly groundwater under the landfill and in its proximities contain only 0.01mg/l of Cr^{6+}. Laboratory batch tests for Cr^{6+} with adsorbent as in-situ soil established the best fitted isotherm model is the Freundlich model with K_f =9.77 L/kg and 1/n=0.89. The experimental results and derived values of the coefficients indicate high Cr^{6+} attenuation capability of in-situ soils. The resilience of soil with respect to Cr^{6+} has further increased by precipitation mechanism in the presence of higher Fe^{2+} content in the in-situ soil.

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