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STATASTICAL ANALYSIS FOR THE BATCH ADSORPTION STUDY OF Cr (VI) ON SELECTED AGRICULTURAL SOILS

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Abstract

Correlation and regression analysis, ANOVA, multiple comparison by Scheffe's post hoc test are used in the current study to figure out the influence of 13 soil parameters present in various agricultural soils in a batch adsorption study of Cr (VI). The soil parameters namely pH, electric conductivity (Eh), Ca, CaO, organic carbon (OC), organic matter (OM), cation exchange capacity (CEC), available nitrogen, sulfur, potassium (K) and Sodium (Na) etc were estimated for all the soil samples as they play a vital role and influences the adsorption affinity of metal ions on the soils. Among the 48 soil samples lowest pH was found in range of pH was 4.86 - 7.94, the CEC values ranged between 0.696meq/100g to 5.99meq/100g. The adsorption affinity of Cr (VI) on various agricultural soils was carried out in a batch adsorption study with experimental conditions, the Cr (VI) adsorption was found to be in the range of 37.78% to 98.725%. Statistical analysis using correlation and regression analysis along with one way ANOVA were used to identify the influence of soil parameters on adsorption of Cr (VI) has been carried out. A significant positive correlation was observed between soil parameters and adsorption of Cr (VI) at 10ppm at 0.01 levels. The parameters $CaCO_3$ and P_2O_5 had shown significant negative correlation.

Keywords:

Adsorption
Cr (VI)
Agricultural Soils
Batch study
Correlation and Regression analysis
ANOVA
Scheffe's post hoc test.
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1. Introduction

Heavy metals are natural components of the earth's crust and the natural concentrations of these heavy metals in soil tend to remain low (1). The biggest concern of today's environment is soil pollution, and it is a growing risk due to the potential negative impacts on human health and the surrounding environment (2). Certain metals are toxic even at a very low concentration and their accumulation in soil at alarming rate is an issue of concern. Adsorption plays a key role for the accumulation of heavy metals. The most important

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interfaces involved in the absorption of heavy metals in the soils are predominantly inorganic collides such as mineral clay content, hydroxides, various metal oxides, metal phosphates and carbonates.

In the field of agriculture the major contributors of metal pollutants are the chemical fertilizers and pesticides. The fertilizers like nitrogen and potash contains relatively low heavy metal content as compared to phosphoric fertilizers which contain considerably high amounts of toxic heavy metals. The raw materials along with the manufacturing processes of the compound fertilizers contribute to the heavy metal concentrations. In fertilizers, the heavy metal contents are high in the amounts in the order of phosphoric fertilizer > compound fertilizer > potash fertilizer > nitrogen fertilizer (3, 4).

The soil components that govern the adsorption of heavy metals in general are phyllosilicates, humic materials, aluminosilicates, carbonates, and other minerals with variable charges such as oxides of Al, Fe, Mn and Ti (5). The physicochemical properties also influence adsorption phenomenon in presence of clay minerals, pH, and quantity of organic fractions involved, water content and temperature of soil along with the properties of metal ions (6,7,8,9).

At the most modern times pollution by heavy metals mainly Cr (VI) is of foremost concern as it is non-biodegradable and at towering concentrations recognized to be toxic, carcinogenic and teratogenic, unless lethal. Chromium exists in two stable forms in aquatic system, Cr (VI) and Cr (III). Cr (III) may also have toxic effect but its concentration is usually well below water quality standards due to the low solubility of chromium hydroxide in the pH range of natural waters.

The soil quality can be evaluated by estimation of Physico-chemical parameters such as pH, electric conductivity, bulk density, soil texture, organic carbon, organic matter, calcium, calcium oxide, calcium carbonate, magnesium, magnesium oxide, cation exchange capacity (CEC), potassium, sodium etc. likewise, as the mobility, adsorption/desorption of heavy metals are also influenced by Physico-chemical properties of soils. Hence, it is requisite to focus upon the Physico- chemical properties of soil before the study of adsorption of heavy metals in soils.

2. Research Method

In the present research work adsorption of Cr (VI) has been investigated on agricultural soil using 48 soil samples collected from 6 different locations from different mandals of Visakhapatnam Viz, Anakapalli, Bheemunipatnam, Makavarapalem and Bondapalli mandal of Vizianagaram district and the soil samples were coded according to their location namely AnM, AnG, AR, AB, VS, VR. 13 Physico - chemical properties of 48 soil samples were estimated with the standard procedures. Adsorption of Cr (VI) on selected agricultural soils samples was carried out with a known volume of (50ml) solution containing different ppm of metal ion was taken in a 250ml beaker to which dosage of 1g of agricultural soil (particle size below 500 microns.) was added. Adsorption of Cr (VI) was carried out at the stock pH of 3.1, 1g dosage at 24 hours contact time, the various concentrations of 1, 10 and 50ppm were varied initially. There was no adsorption observed. As the pH and contact time plays an important role on the adsorption, it was varied from pH 1 to 9, at 10 minutes of contact time with 1g dosage at 10 ppm of initial concentration. At the optimum conditions the batch adsorption studies were carried with all selected soil samples. Statistical analysis was carried out using correlation and regression analysis along with one way ANOVA to identify the impact of soil parameters on adsorption of Cr (VI).

3. Results and Analysis

3.1: Physico-Chemical Parameters

Among the 48 samples lowest pH was found in range of pH was 4.86 - 7.94 and the pH of all soil samples were within this range. The lowest EC value was found in sample VS6 (0.19) while the highest EC value was observed in AB3 (1.53). Calcium values ranged between 0.025mg/g to 0.176mg/g. Magnesium is found to be low in AnM7 sample (0.113mg/g) and was high in AB8 sample (0.312mg/g). The MgO were found to be in the range of 0.187mg/g to 0.517mg/g. The percent of $CaCO_3$ among 48 samples ranged from 4.5 to 15%. The range of percentage of organic carbon was ranged between 0.3% - 2%. The percentage of organic matter ranged between 0.5196% - 3.464%. The sodium values of all samples were in the range of 54 to 540mg/g. Potassium levels in soil samples ranged between 0.7mg/g to 7.9mg/g. The CEC values ranged between 0.696meq/100g to 5.99meq/100g in all 48 samples. Available sulphur ranged between 0.416mg/g to 22.49mg/g. The available nitrogen in all 48 samples ranged between 0.02497mg/g to 0.10267mg/g. The phosphates in soil samples were estimated as P_2O_5. The 48 soil samples were found with range of P_2O_5 between 0.003 to 0.025mg/g.

3.2: Adsorption of Cr (VI)

The Cr (VI) adsorption was in the range of 37.78% (VS2) to 98.725% (AB6). Among 48 samples, about 7 samples were reported with < 50% of Cr (VI) adsorption. The low percentage of adsorption was prevalent among 4 samples of VS and 3 samples AnG. Above 90% of adsorption was observed in samples VR1 to VR8, 5 samples of AR1 to AR8 and 6 samples of AB1 to AB8. The mobility and bioavailability in these soils was greater for Cr (VI) than Cr (III) was reported (10).

The physico chemical parameters present in the agricultural soil samples may have shown influence on the percentage adsorption of Cr (VI) i.e. 94.64% found to be the highest among all samples. In order to identify the factors responsible for influencing the adsorption capacity, Statistical analysis using correlation and regression analysis along with one way ANOVA to identify the impact of soil parameters on adsorption of heavy metals has been carried out.

3.3: Statistical Analysis

A two tailed correlation studies between soil parameters and selected metal species adsorption was carried out followed by regression analysis, ANOVA and multiple comparison by Scheffe's post hoc test (11).

3.3.1: Correlations Between Soil Parameters and The Adsorption of Cr (VI)

The adsorption of Cr (VI) at 10 ppm at pH 1 had shown significant positive correlation with parameters like pH, electric conductivity (Eh), Ca, CaO, organic carbon (OC), organic matter (OM), cation exchange capacity (CEC), available nitrogen, sulfur, potassium (K) and Sodium (Na). A significant positive correlation was observed between soil parameters and adsorption of Cr (VI) at 10ppm at 0.01 levels. The parameters Mg and MgO had shown significant positive correlation at 0.05 levels. The parameters $CaCO_3$ and P_2O_5 had shown significant negative correlation. These results were shown in table 1.

The adsorption of metal cations such as Pb, Cr, Cu, Zn, Cd and Ni was found to be negatively correlated with soil pH was attributed to formation of $(MOH)^{+}$ at higher pH was reported (12).

No correlation was observed with Cr sorption and soil organic matter content at pH 4.5 or 6.5. This was reported due to hexavalent form (CrO_4^{2-} or $HCrO_4^{-}$). The fraction of CrO_4^{2-} increases, decreasing $HCrO_4^{-}$ form as the pH shifts from 4.5 to 6.5. The adsorption decreases with increase in pH due to surface negative change on solid phase (13). A significant correlation between CEC and total Cr, Zn, Pb and Cd was observed at 0.01 levels though total Ni was found to be negatively correlated. The exchangeable metals also had shown significant correlation between Cr, Zn, Pb and Cd. No correlation was observed between CEC and Cu, a significant negative correlation was observed between CEC and exchangeable Ni at 0.01 level was reported (14).

Table: 1 Correlations between soil parameters and the adsorption of Cr (VI) (at pH 1) on various agricultural soil samples

	pH	EC mhos	Mg	MgO	Ca	CaO	$CaCO_3$	OC	OM	CEC	Available Nitrogen	Sulphur	P_2O_5	Potassium	Sodium	Cr (VI) 10ppm
pH	1	.291 * .040	.359 * .011	.359 * .011	.243 .089	.243 .089	.180 .212	.314 * .026	.328 * .020	.429 ** .002	.279 * .049	.111 .444	.082 .569	.323 * .022	.153 .289	.369 ** .008
EC mhos	.291 * .040	1	.433 ** .002	.433 ** .002	.217 .131	.217 .131	.046 .753	.412 ** .003	.436 ** .002	.519 ** .000	.083 .566	.077 .594	-.228 .112	.545 ** .000	.671 ** .000	.564 ** .000
Mg	.359 * .011	.433 ** .002	1	1.000 ** .000	-.044 .762	-.044 .762	.074 .612	.277 .051	.307 * .030	.479 ** .000	.240 .093	.147 .307	.015 .918	.398 ** .004	.383 ** .006	.355 * .011
MgoO	.359 * .011	.433 ** .002	1.000 ** .000	1	-.044 .762	-.044 .762	.074 .612	.277 .051	.307 * .030	.479 ** .000	.240 .093	.147 .307	.015 .918	.398 ** .004	.383 ** .006	.355 * .011
Ca	.243 .089	.217 .131	-.044 .762	-.044 .762	1	1.000 ** .000	-.061 .676	.307 * .030	.327 * .021	.344 * .015	.045 .755	.049 .734	-.272 .056	.073 .616	.513 ** .000	.392 ** .005
CaO	.243 .089	.217 .131	-.044 .762	-.044 .762	1.000 ** .000	1	-.061 .676	.307 * .030	.327 * .021	.344 * .015	.045 .755	.049 .734	-.272 .056	.073 .616	.513 ** .000	.392 ** .005
$CaCO_3$	.180 .212	.046 .753	.074 .612	.074 .612	-.061 .676	-.061 .676	1	.112 .439	.092 .526	-.151 .294	-.079 .585	-.224 .117	-.329 * .020	.105 .469	-.132 .360	-.144 .318
OC	.314 * .026	.412 ** .003	.277 .051	.277 .051	.307 * .030	.307 * .030	.112 .439	1	.994 ** .000	.525 ** .000	.317 * .025	.285 * .045	-.347 * .013	.415 ** .003	.417 ** .003	.586 ** .000
OM	.328 * .020	.436 ** .002	.307 * .030	.307 * .030	.327 * .021	.327 * .021	.092 .526	.994 ** .000	1	.566 ** .000	.321 * .023	.277 .051	-.341 * .015	.441 ** .001	.454 ** .001	.611 ** .000
CEC	.429 ** .002	.519 ** .000	.479 ** .000	.479 ** .000	.344 * .015	.344 * .015	-.151 .294	.525 ** .000	.566 ** .000	1	.441 ** .001	.417 ** .003	-.134 .353	.726 ** .000	.783 ** .000	.749 ** .000
Available Nitrogen	.279 * .049	.083 .566	.240 .093	.240 .093	.045 .755	.045 .755	-.079 .585	.317 * .025	.321 * .023	.441 ** .001	1	.352 * .012	-.100 .492	.233 .104	.231 .106	.364 ** .009
Sulphur	.111 .444	.077 .594	.147 .307	.147 .307	.049 .734	.049 .734	-.224 .117	.285 * .045	.277 .051	.417 ** .003	.352 * .012	1	-.036 .804	.132 .361	.192 .182	.606 ** .000
P_2O_5	.082 .569	-.228 .112	.015 .918	.015 .918	-.272 .056	-.272 .056	-.329 * .020	-.347 * .013	-.341 * .015	-.134 .353	-.100 .492	-.036 .804	1	-.226 .115	-.219 .127	-.144 .319
Potassium	.323 * .022	.545 ** .000	.398 ** .004	.398 ** .004	.073 .616	.073 .616	.105 .469	.415 ** .003	.441 ** .001	.726 ** .000	.233 .104	.132 .361	-.226 .115	1	.533 ** .000	.607 ** .000
Sodium	.153 .289	.671 ** .000	.383 ** .006	.383 ** .006	.513 ** .000	.513 ** .000	-.132 .360	.417 ** .003	.454 ** .001	.783 ** .000	.231 .106	.192 .182	-.219 .127	.533 ** .000	1	.627 ** .000
Cr (VI) 10ppm	.369 ** .008	.564 ** .000	.355 * .011	.355 * .011	.392 ** .005	.392 ** .005	-.144 .318	.586 ** .000	.611 ** .000	.749 ** .000	.364 ** .009	.606 ** .000	-.144 .319	.607 ** .000	.627 ** .000	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

3.3.2: Regression Analysis

Regression analysis was carried out between the soil parameters such as pH, EC mhos, Mg, MgO, Ca, CaO CaCO3, OC, OM, CEC, available nitrogen, sulphur, P2O5, potassium, sodium and percentage adsorption of individaul heavy metal species in the batch adsorption studies. The soil parameters MgO and CaO are removed from the equation due to highly correlated with other 13 parameters.

3.3.3: Adsorption of Cr (VI) On Various Agricultural Soil Samples

The regression equation for Cr (II) = 16.6 + 0.96 pH + 9.17 EC mhos - 5.4 Mg + 125 Ca - 0.330 CaCO3 - 40.6 OC + 29.7 OM - 2.89 CEC + 73.6 Available nitrogen + 1.47 Sulphur + 444 P2O5+ 4.69 Potassium + 0.0074 Sodium.

Predictor	Coef	SE Coef	T	P
Constant	16.58	15.27	1.09	0.285
pH	0.961	3.062	0.31	0.755
EC mhos	9.171	4.898	1.87	0.069
Mg	-5.40	35.29	-0.15	0.879
Ca	124.93	48.62	2.57	0.014
CaCO3	-0.3300	0.5991	-0.55	0.585
OC	-40.58	32.58	-1.25	0.221
OM	29.74	19.93	1.49	0.144
CEC	-2.891	3.374	-0.86	0.397
available nitrogen	73.61	97.24	0.76	0.454
Sulphur	1.4686	0.2450	5.99	0.000
P2O5	444.3	295.2	1.50	0.141
Potassium	4.695	1.388	3.38	0.002
Sodium	0.00739	0.02034	0.36	0.718

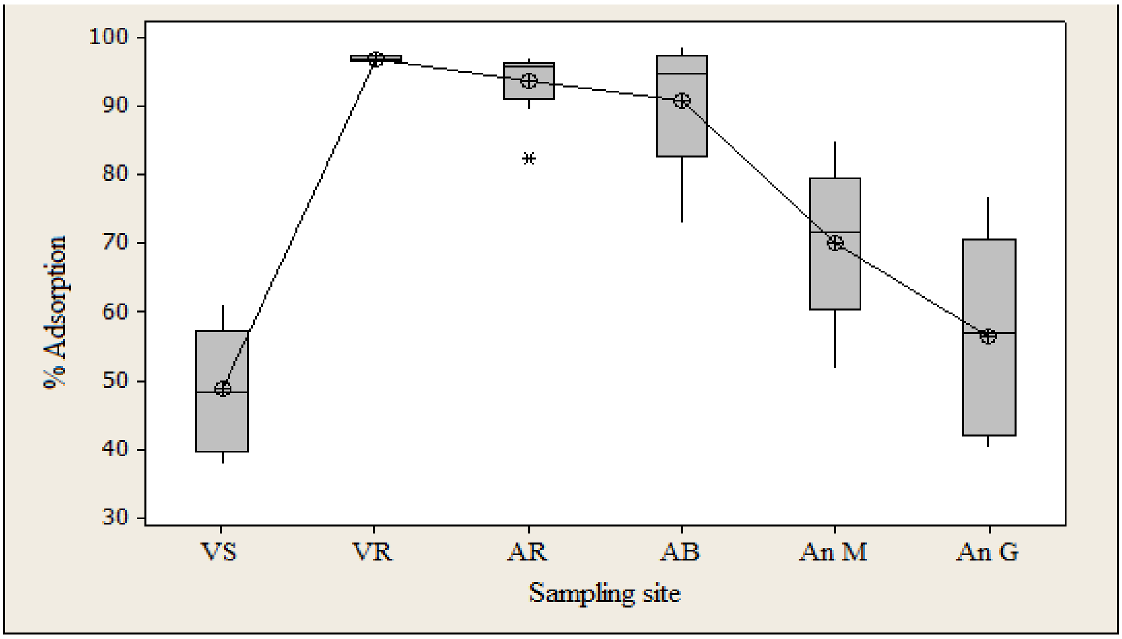
R-Sq = 84.4% P-Value: 0.000

It was concluded from the above equation that there was a significant linear relationship between the soil parameters with percentage adsorption of Cr (VI) on various soil samples. From the above R-square value (84.4%) and its corresponding P-value (0.000) there was a significant influence of soil parameters and percentage of adsorption. Further, out of 13 soil parameters, three parameters such as Ca, sulphur and potassium had shown significant impact at 5% level.

Sample code	N	Mean	SD	F-Value	P-Value	Decision
VS	8	48.6817	8.84573	38.662	0.000	Significant
VR	8	96.9559	.57116			
AR	8	93.5932	5.10803			
AB	8	90.9157	9.49227			
AnM	8	70.1653	11.63130			
AnG	8	56.4910	14.11825			

With regard to the Cr (VI) at pH1, the average percentage adsorption for VR sample code was significantly higher than the average percentage adsorption of remaining five soil samples, followed by AR and AB as per the significant P-value of the ANOVA test at 5% level of significance. The diagrammatic representation was shown below (figure 1).

Figure 1: Percentage adsorption of Cr (II) for Various agricultural soil sampling sites



Multiple Comparisons

Dependent Variable: % adsorption
Scheffe

(I) Sample Code	(J) Sample Code	Mean Difference (I-J)	Sig.
VS	VR	-48.27428 *	.000
	AR	-44.91149 *	.000
	AB	-42.23401 *	.000
	AnM	-21.48359 *	.004
	AnG	-7.80931	.735
VR	VS	48.27428 *	.000
	AR	3.36279	.991
	AB	6.04026	.891
	AnM	26.79069 *	.000
	AnG	40.46496 *	.000
AR	VS	44.91149 *	.000
	VR	-3.36279	.991
	AB	2.67748	.997
	AnM	23.42790 *	.001
	AnG	37.10218 *	.000
AB	VS	42.23401 *	.000
	VR	-6.04026	.891
	AR	-2.67748	.997
	AnM	20.75043 *	.005
	AnG	34.42470 *	.000
AnM	VS	21.48359 *	.004
	VR	-26.79069 *	.000
	AR	-23.42790 *	.001
	AB	-20.75043 *	.005
	AnG	13.67428	.157
AnG	VS	7.80931	.735
	VR	-40.46496 *	.000
	AR	-37.10218 *	.000
	AB	-34.42470 *	.000
	AnM	-13.67428	.157

*. The mean difference is significant at the .05 level.

4. Conclusion

Statistical analysis using correlation and regression analysis along with one way ANOVA carried out to identify the impact of soil parameters on adsorption of heavy metals. At pH 1, 1 g dose of soil sample, at 10 minutes of contact time the adsorption of Cr (VI) was found to be high in AB5 sample (98.72%). The adsorption of Cr (VI) at 10ppm at pH 1 had shown significant positive correlation with parameters like pH, electric conductivity (Eh), Ca, CaO, organic carbon (OC), organic matter (OM), cation exchange capacity (CEC), available nitrogen, sulfur, potassium (K) and Sodium (Na). Positive significant correlation was observed between parameters like Ca, CaO, available nitrogen and sodium at 0.05 levels. Sulfur had shown positive significant correlation at 0.01 levels. Box plot had shown a comparison for percentage of adsorption of Cr (VI) and area vise (sampling Location) by the Mean of 8 samples collected from 6 of the locations mention.

References

1. Nanos, N., Rodríguez Martín, J.A., Multiscale Analysis of Heavy Metal Contents in Soils: Spatial Variability in the Duero River Basin (Spain), *Geoderma* Vol. 189–190, pp. 554–562, 2012.
2. Yanez, L., Ortiz, D., Calderon, J., Batres, L., Carrizales, L., Mejia, J., Overview of Human Health and Chemical Mixtures: Problems Facing Developing Countries, *Environmental Health Perspectives*, Vol. 110, pp. 901-909, 2002.
3. Boyd R.S., Heavy Metal Pollutants and Chemical Ecology: Exploring New Frontiers, *J. Chem. Ecol.*, Vol. 36, No. 1, pp. 46–58, 2010.
4. Chao Su, LiQin Jiang, WenJun Zhang., A Review on Heavy Metal Contamination in the Soil Worldwide: Situation, Impact and Remediation Techniques, *Environmental Skeptics and Critics*, Vol. 3, No. 2, pp. 24-38, 2014.

5. Violante, A., Cozzolino, V., Perelomov, L., Caporale, A.G., Pigna, M., Mobility and Bioavailability of Heavy Metals and Metalloids in Soil Environments, *Journal of Soil Science and Plant Nutrition*, Vol. 10, No. 3, pp. 268–292, 2010.
6. Weber, J.B., Applied Plant Science, Vol. 5, No.1, 1991.
7. Stevenson F. J., Humus Chemistry. Genesis, Composition and Reactions. *Wiley-Intersc. Publ. New York*, 1992.
8. Dube, A., Zbytniewski, R., Kowalkowski, T., Cukrowska, E., Buszewski, B., Adsorption and Migration of Heavy Metals in Soil, Polish Journal of Environmental Studies, Vol.10, No. 1, pp. 1 – 10, 2001.
9. Jenny perez Holmberg, Competitive Adsorption and Displacement Behaviour of Heavy Metals on Peat. (http://www.wet.chalmers.se). 2006.
10. Girish, C., Nanthi, B., Megharaj, M. and Zuliang, C., Sorption and Mobility of Chromium Species in a Range of Soil Types, *19th World Congress of Soil Science, Soil Solutions for a Changing World* pp. 239 – 242, 2010.
11. Student, The Probable Error of a Mean, *Biometrika*, Vol. 6, No. 1, pp. 1-25, 1908.
12. Bansal, M., Singh, D., Garg, V. K. and Rose, P., Use of Agricultural Waste for the Removal of Ni Ions from Aqueous Solution, Equilibrium and Kinetic Studies, *Int. J. Civ. Environ. Eng*., Vol. 1, No. 2, pp 108–114, 2009.
13. Sherene. T., Mobility and Transport of Heavy Metals in Polluted Soil Environment, Biological Forum — *An International Journal*, Vol. 2, No.2, pp. 112-121, 2010.
14. Dawaki. U. M., Dikko. A.U., Noma. S. S. and Aliyu. U., Heavy Metals and Physicochemical Properties of Soils in Kano Urban Agricultural Lands, *Nigerian Journal of Basic and Applied Science*, Vol. 21, No. 3, pp. 239-246, 2013.