Adsorption of Metal Ions from Carwash Wastewater by Phosphoric Acid Modified Clay: Kinetics and Thermodynamic Studies

Bassey Sam Enoh* Wetpan Christopher
Department of Chemistry, Faculty of Natural Sciences, University of Jos, Plateau State, Nigeria
* E-mail of the corresponding author: enohb@unijos.edu.ng

Abstract

The adsorption kinetics and the thermodynamic parameters for the removal of metal ions from carwash effluent using phosphoric acid modified clay were investigated in this study. Kinetic parameters were determined by analysing the modified second-order and intra-particle models. In the second order kinetics, Cd^{2+} had adsorption capacity q_e of 7.5mg/g with the regression coefficients of linearization (R^2) of 1.0 followed by Ni^{2+} with q_e of 1.36mg/g with R^2 of 0.949. For the intra-particle kinetics, Cd^{2+} had Kid of 1.0 with R^2 of 0.959, while Pb^{2+} had Kid of 0.144 with R^2 of 0.997. Adsorption generally increases with temperature and time. At 240minutes, all Cd^{2+} had been removed from solution, same at 50°C with trend of removal following the order $Cd^{2+} > Pb^{2+} > Cr^{3+} > Ni^{2+.}$ ΔH^o ranged from -1.4KJ/mol for Cr^{3+} to -6.0KJ/mol for Cd^{2+} indicating physical adsorption. ΔS^o ranged from 12..7J/mol for Cd^{2+} to 100J/mol for Cr^{3+} while ΔG were negative for all metal ions indicating that the adsorption was spontaneous and feasible.

Keywords: Carwash wastewater, adsorption, phosphoric acid modified clay, kinetics and thermodynamics

1.0 Introduction

Water is considered an important and scarce commodity in many countries around the world. Water is the source of life and is the basic condition for human survival. However, the severe water contamination and insufficient water source are nowadays two thorny problems. Rapid industrialization, unplanned urbanization and unskilled utilization of natural water resources have led to the destruction of water quality in many parts of the world. In many developing countries, groundwater provides drinking water for more than one-half of the nation's population, and is the sole source of drinking water for many rural communities and some large cities (Lohdip, 2011). However, due to industrial, agricultural and domestic activities, a variety of chemicals can pass through the soil and potentially contaminate natural water resources and reservoirs.

Industrial effluents are contaminated with highly toxic, non-biodegradable and carcinogenic heavy metals, such as Pb, Cr, Cd, Zn etc which are generated by industries such as electroplating, mineral processing, ternary, galvanization plants, paints formulation, porcelain enameling, nonferrous metal and vegetable fat producing industries including car wash centres(Meena et al., 2005; Pereira et al., 2010).

If not carefully managed, wastewater may produce both short- and long-term effects on human health and the ecological system. Even, a minor concentration of heavy metals can bio-accumulate and enter the food chain causing mental retardation, reduction in hemoglobin production and interference with normal cellular metabolism and consequently may damage nervous system. Strong exposure may cause gastric pain, nausea, vomiting, severe diarrhea, hemorrhage and even cancer in the digestive tract and lungs(Amuda and Ibrahim, 2006; Rajani, 2011). There are several methods for treatment of metal contaminated effluents such as chemical precipitation , coagulation–flocculation, reverse osmosis, ultra-filtration, electro-dialysis, flotation , ion exchange and membrane processes. They have their inherent advantages and limitations in application. Among the physicochemical treatment processes for pollutant removal, adsorption is highly efficient, inexpensive and easy to adapt (Bhattacharya and Gupta, 2006). Chemical adsorbents are used widely in the treatment of surface and ground water for the supply of potable water, and in industrial effluent treatment. They play an important role in the removal of heavy metals, natural organic matter, and synthetic organic compounds.

Clay minerals are natural materials well known for their role in retention and persistence of organic and inorganic compounds in soil. Clay minerals are being modified through different processes to alter their charge and surface properties tailored for specific purposes. Modified clays in general include pillared layered clays, organoclays, and nanocomposites, acid and salt-induced, thermally and mechanically induced modified clays. Pillared organoclays and nanocomposites constitute a novel class of materials, mainly one kind of modification of expanding 2 : 1 clay minerals(Basak et al. 2012). Acid modified natural bentonites are the subject of many studies and papers (Bergaya and Lagaly, 2001; Carrado and Komadel, 2009; Madejová et al., 2009; Amari et al., 2010). The first step in modifying the clay mineral structure with acid is a separation of exchangeable cations from protons. The second step is flushing Al, Mg and Fe from octahedral and tetrahedral sheets, in the way that SiO4 groups of tetrahedral sheets remain mostly intact. Increasing of the specific surface area is an important physical change (Taylor et al., 1989; Rhodes and Brown, 1992; Christidis et al., 1997;

Komadel, 2003) which is a function of the structure and removal of octahedral sheets (Madejová et al., 1998; Komadel and Madejová, 2006, Tyagi et al., 2006).

The abundance of world reserves of bentonite makes it impossible to estimate the quantity of these resources in a global context. The main consumers of these materials are petroleum companies, which employ the clay as thixotropic agent for use in drilling wells; industries that work with iron ore pellets uses clay as binding agent; paint and varnish industries, among others also uses clay and Nigeria has a large deposits of this raw material(Ahmed, 2012).

This paper reports the adsorption of Cr^{3+}, Ni^{2+}, Pb^{2+} and Cd^{2+} from Carwash wastewater by phosphoric acid modified clay. Kinetics and thermodynamics of the adsorption are presented here.

2. Materials and Methods

The clay samples were obtained from Kerang, Mangu Local Government Area of Plateau State of Nigeria. The clay samples were purified by sedimentation in accordance with stokes law and the 200mesh fractions were further treated with 0.05moles/dm^3 of HCl and 1mole/dm^3 of NaCl solutions. 16g of dry clay were treated with 2.5moles/dm^3 of phosphoric acid at 80°C for 2hours, filtered and dried at 105°C.Carwash effluent was obtained from the Rukkuba Road central carwash stream early in the morning before the start of the days' activity. The water was collected in a previously wash and sterilized polyethylene bottles and were stored in refrigerators.

Analyses of wastewater for metal ions before and after adsorption were done using the ICP-OES Atomic Adsorption Spectrophotometer. Adsorption was done by adding 2g of clay adsorbent to 100cm^3 of the wastewater. Time was fixed at 60, 120, 180 and 240minutes while the temperature was fixed at 25, 30, 40, and 50°C respectively.

The quantity of metal ions adsorbed at a time t was calculated from the equation:

$$q_t = \frac{(C_o - C_t)V}{M} \text{---------------------------------} (1)$$

while the percent metal ion removed were calculated using the relationship

$$\%\ \text{metal ion removal} = \frac{(C_o - C_t)}{C_o} \times 100 \text{------------------------------} (2)$$

according to Vijayakumar et al.,(2012).

Thermodynamic parameters such as Gibb's free energy change ΔG, enthalpy change ΔH and entropy change ΔS were evaluated from the following equations:

$$\Delta G = -RT\ln Kc \text{------------------------------} (3)$$

$$\Delta G = \Delta H - T\Delta S \text{----------------------------------} (4)$$

$Kc = C_{ae}/C_e$, where C_o, C_t, C_{ae}, and C_e are the initial metal ion concentration (mg/l), concentration after time t and concentration of metal ion on the adsorbent and equilibrium concentration of metal ions in solution after adsorption all in mg/l. V is the volume of wastewater used and M the mass of adsorbent. The the pseudo second order kinetics were tested using the equations: $t/qt = 1/(k_2q_e2) + t/q_e$ ----------------------------- (5)
where qt and q_e = adsorption capacity ($mg.g^{-1}$) at time *t* and at equilibrium; t = time (min); k_2 = rate constant of pseudo second order adsorption ($g.mg^{-1}.min^{-1}$) while the intra particle kinetic was tested using the equation:

$$q_t = k_{id}t^{1/2} \text{-----------------} (6)$$

3. Results and Discussions

3.1 Effect of Time and Temperature: When adsorption is involved, thermodynamic and kinetic must be used to know more details about its performance and mechanisms. Kinetic performance of a given adsorbent is also of great significance for the pilot application. From the kinetic analysis, the solute uptake rate, which determines the residence time required for completion of adsorption reaction, may be established.

The percentage adsorption of the different metal ions at different times and temperatures are shown in tables 1and 2 respectively.

Table 1: Effect of Time on the Percentage adsorption of metal ions by Phosphoric acid modified clay from carwash wastewater

Time (mins)	Percentage Adsorption			
	Cr^{3+}	Ni^{2+}	Pb^{2+}	Cd^{2+}
60	64.7	57.1	74.1	93.3
120	76.5	64.3	79.8	95.0
180	91.2	85.7	92.9	96.7
240	97.1	93.9	100	100

From the results, the percentage of metal ions adsorbed increased with increase in time. In the first hour, more than 50% of the metal ions were adsorbed and the subsequent increase in time did not show very high adsorption. According to other researchers, in the first 30minutes to 1 hour, the adsorbent still had a vast number of unoccupied sites unto which the adsorbate particles could adsorb. As a result, there was a high probability of adsorption for every migrating and diffusing molecule of adsorbate. As so many adsorbate particles adsorbed within this time, the number of unoccupied sites decreased and the adsorbent surface started approaching saturation leading to less adsorption at higher times (Ejikeme et al, 2011; Okoye et al, 2012). In multi component metal ions, the preference of metal ions followed the trend Cd^{2+}> Pb^{2+}> Cr^{3+} >Ni^{2+} for time studies.

Table 2: Effect of Temperature on the Percentage adsorption of metal ions by Phosphoric acid modified clay from carwash wastewater

Temperature (°C)	Percentage Adsorption			
	Cr^{3+}	Ni^{2+}	Pb^{2+}	Cd^{2+}
25	64.7	57.1	74.1	93.4
30	79.4	85.7	81.1	94.0
40	94.1	92.8	89.4	95.4
50	96.6	100	98.8	100

Similarly, in the temperature studies, 93.3% of Cd^{2+} ions were removed at 25°C while only 74.1% and 57.1% of Pb^{2+} and Ni^{2+} respectively were removed at the same temperature. For all the metals, adsorption increases with increase in temperature with almost all the metal ions being removed at 50°C. There is a clear dependence of adsorption on temperature for all the ions tested. This could be possible because the mobility of adsorbate ions in the solution increase with increase in temperature and therefore the affinity of adsorbate for the adsorbent are higher at high temperatures. The trend of adsorption followed that of the time studies. Fig 1 and 2 shows the variation of percentage adsorption with time and temperatures respectively.

3.2 Kinetics Studies

The kinetics study was carried out by testing the pseudo second order and the intra-particle equations. When the second order equation was tested by plotting q_t/t against t, straight lines were obtained for all the metal ions. Cd^{2+} had the highest qe value of 7.5mg/g with R^2 value of 1.00 while Ni^{2+} had qe value of 1.36mg/g with R^2 of 0.949. All the metal ions tested had R^2 values greater than 0.9 indicating very high correlations as shown in table 3. The rate constant of pseudo-second order adsorption (k_2) obtained for Cd was found to be lower than that computed for Pb^{2+}, Ni^{2+} and Cr^{3+}. This indicates that the uptake of Cd^{2+} onto phosphoric acid modified clay from aqueous solution was more rapid and favourable. Also, Cd ion had the adsorption capacity of 7.5mg/g followed by Ni ion with 1.36mg/g. The value for Cd ion is higher than the 1.79mg/g reported by Torab-Mostaedi et al (2010) for Cd^{2+} while the 1.36mg/g for Ni ion is lower than the 2.34mg/g reported by same author.

Similarly when the intra-particle diffusion was tested by plotting q_t against $t^{1/2}$, Cd^{2+} had the highest intra-particle diffusion constant K_{id} of 1.0 with R^2 of 0.959, while Pb^{2+} had k_{id} of 0.144 with R^2 of 0.997. Given that the correlation coefficients for both the second order and the intra-particle diffusion for all the metal ions are all above 0.9, the kinetics of this adsorption could be said to be both second order- intra-particle diffusion. When intra-particle diffusion is involved, the kinetics of adsorption process on porous materials such as clay is controlled by three consecutive steps (Mohan et al., 2001; Baniamerian et al., 2009): transport of the adsorbate from the bulk solution to the film surrounding the adsorbent, diffusion from the film to the proper surface of adsorbent, and diffusion from the surface to the internal sites followed by adsorption immobilization on the active sites. According to Tomic et al.,(2011), acid when treated with clay caused an exchange of Al^{3+}, Fe^{3+} and Mg^{2+} with H^+ ions which led to a modification of the smectite crystalline structure including flushing of the exchangeable cations with H^+.

Table 3: Kinetic Parameters for the adsorption of metal ions by Phosphoric acid modified clay from carwash wastewater.

Second Order Kinetics				
	Pb2+	Cd2+	Cr3+	Ni2+
K_2(g/mg/min)	22	20	48	100
q_e(mg/g)	0.28	7.5	0.52	1.36
R^2	0.995	1.00	0.992	0.949
Intra-particle Diffusion Kinetics				
Kid (mg.g^{-1}.$min^{-0.5}$)	0.144	1.0	0.068	0.047
R^2	0.997	0.959	0.986	0.938

3.3Thermodynamics of the Adsorption: The results of the thermodynamic studies are shown in table 4. For all the metal ions tested, the equilibrium constant Kc had values greater than 1.0 for all the temperatures tested indicating the preference of the metal ions for the clay surface than the wastewater. Also, the free energy ΔG^o for all the metal ions at all temperatures was negative indicating that the adsorption between the metal ions and the clay occurs spontaneously. The increased negative values of ΔG^o for all the metal ions could imply that adsorption will be more favourable at lower temperatures. Similarly, the enthalpies of adsorption ΔH^o for all the metal ions were negative for all temperatures. This implies that the adsorption phenomenon is exothermic. Generally, the adsorption process in a solid–liquid system is a combination of two processes: (a) The desorption of the water molecules previously adsorbed from the clay surface and (b) adsorption of the adsorbate species onto the clay.

In an exothermic process, the total energy absorbed in bond breaking is less than the total energy released in bond making between adsorbate and adsorbent, resulting in the release of extra energy in the form of heat. Therefore ΔH^o will be negative. The magnitude of ΔH^o may also give an idea about the type of sorption. The heat evolved during physical adsorption is of the same order of magnitude as the heats of condensation, i.e., 2.1–20.9 kJ mol-1, while the heats of chemisorption generally falls into a range of 80–200 kJ mol-1(Chowdhury and Saha, 2010). The ΔH^o for the present study ranged from -1.4 kJ mol^{-1} for Cr^{3+} to -6.4KJmol^{-1} for Cd^{2+}, therefore, as seen from Table 4, the adsorption of heavy metal ions by phosphoric acid modified clay is purely physical adsorption. The entropy change for the various metal ions ranges from 12.7J$mol^{-1}$for Cd^{2+} to 100Jmol^{-1} for Cr^{3+}. A positive value of ΔS^o reflects the affinity of the adsorbent towards the adsorbate species. Positive value of ΔS^o also suggests increased randomness at the solid/solution interface with some structural changes in the adsorbate and the adsorbent. The adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate ions/molecules, thus allowing for the prevalence of randomness in the system. The positive ΔS^o value also corresponds to an increase in the degree of freedom of the adsorbed species (Chowdhury and Saha, 2010).

Table 4: Thermodynamic Parameters for the adsorption of metal ions by Phosphoric acid modified clay from carwash wastewater.

Metal ion	T(K)	Kc	ΔG(KJ/mol)	ΔH(KJ/mol)	ΔS(J/mol)
Cr^{3+}	298	1.84	-1.50	-1.4	100
	303	3.86	-3.40		
	313	16.0	-7.20		
	323	3.26	-3.17		
Ni^{2+}	298	1.34	-0.71	-2.8	30
	303	6.0	-4.51		
	313	13.0	-6.66		
	323	27.0	-8.86		
Pb^{2+}	298	2.85	-2.60	-2.2	66.6
	303	4.3	-3.68		
	313	8.4	-5.46		
	323	84.0	-11.90		
Cd^{2+}	298	14.0	-6.54	-6.4	12.7
	303	16.6	-7.08		
	313	19.0	-7.65		
	323	29.0	-9.02		

4.0 Conclusion

In conclusion, the adsorption of metal ions from car wash wastewater by phosphoric acid modified clay is feasible, spontaneous and exothermic. The removal of metal ion from solution increases with time and temperature and followed the order the trend Cd^{2+}> Pb^{2+}> Cr^{3+} >Ni^{2+}. This is correlated by the high R^2 values obtained. The adsorption followed the second order, intra-particle kinetics. The work has clearly demonstrated the practicability of using modified clay for wastewater remediation.

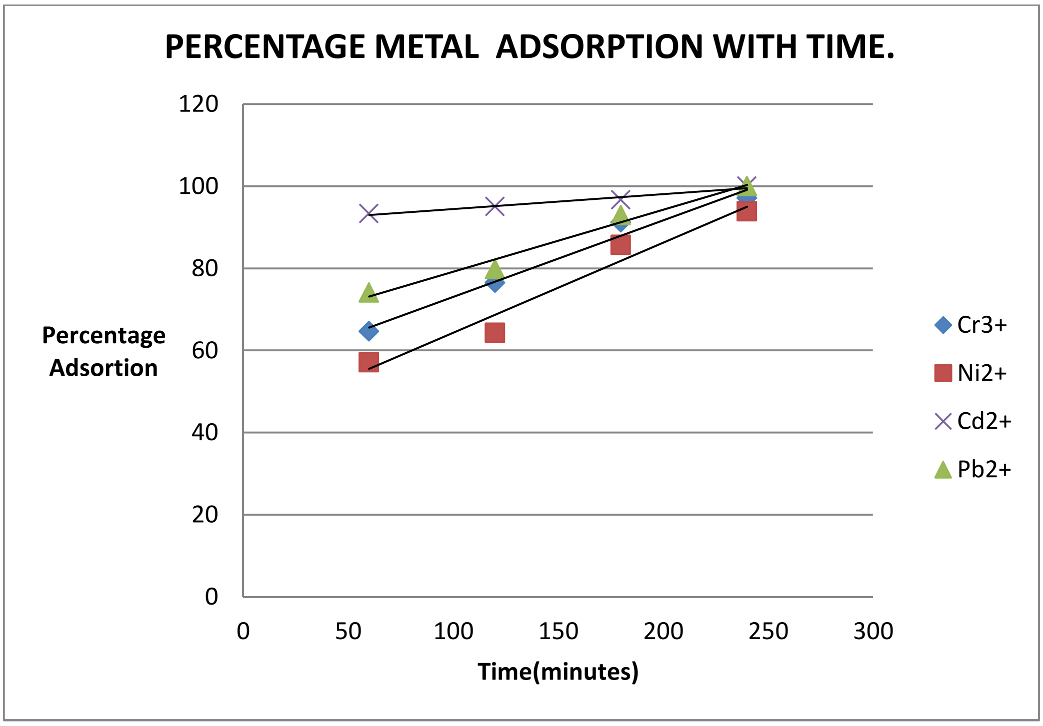

Fig. 1: Effect of Time in the adsorption of metal ions from car wash wastewater by phosphoric acid modified clay.

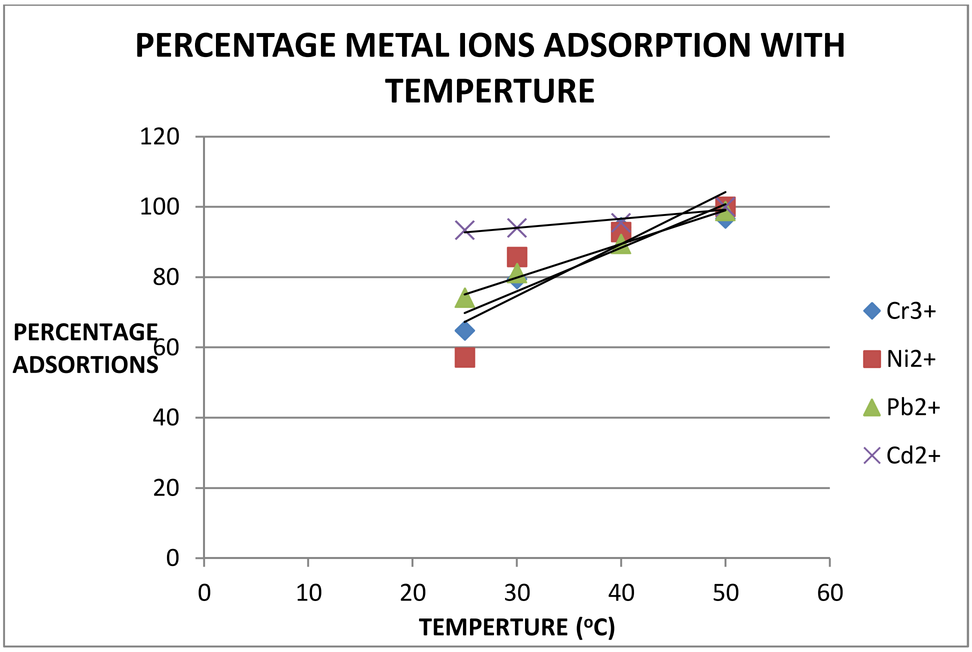

Fig. 2: Effect of Temperature on the percentage metal ion adsorbed by phosphoric acid modified Clay.

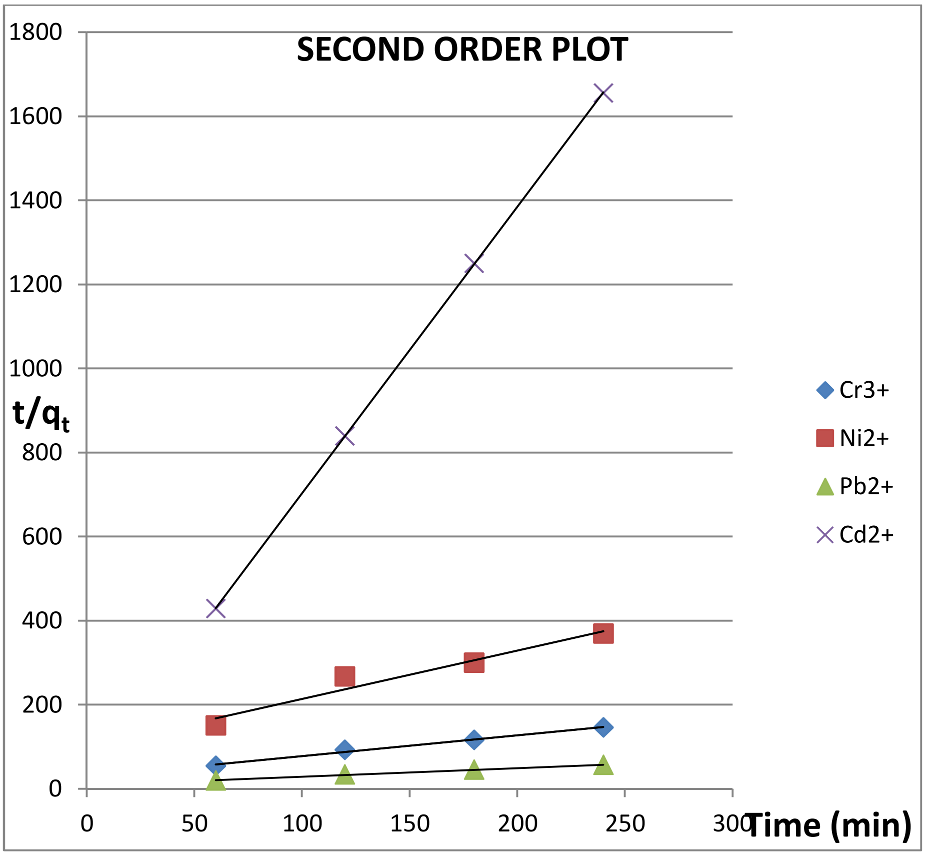

Fig.3: Second order plot for the adsorption of metal ion from car wash wastewater by phosphoric acid modified clay.

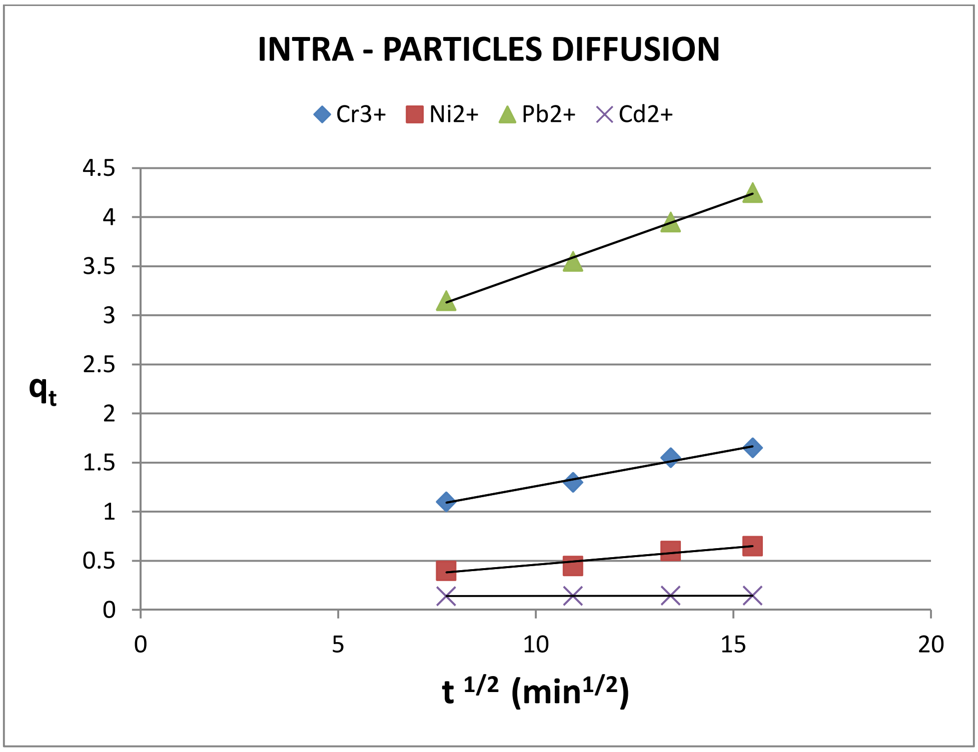

Fig. 4: Intra-particle plot for the adsorption of metal ions from car wash wastewater by Phosphoric acid modified clay.

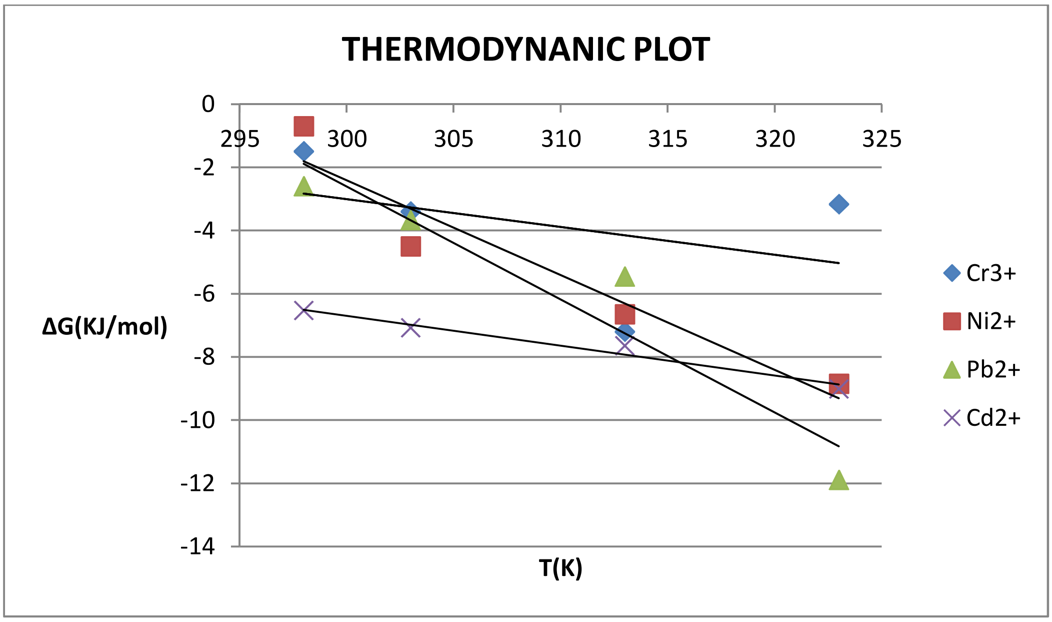

Fig. 5: Thermodynamic plot for the adsorption of metal ions from car wash wastewater by phosphoric acid modified clay.

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