

Effect Of Ph Of Anolyte In Electrokinetic Remediation Of Cadmium Contaminated Soil

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Abstract

This paper investigate the effect of anode solution pH on electro osmosis process of electrokinetic remediation of cadmium contaminated soil at wide range of pH (pH 3-12). Deionized water is used in anode as well as cathode compartment and pH of anodic solution is maintained by 1N HCL and 1N NaOH solution. The results shows that there is increase of electro osmotic flow as gradual increase of pH in anode compartment. However, the voltage gradient is not significant affected by change in pH in soil specimen. The result shows resemblance with previous investigations. .

INTRODUCTION

Cadmium is a poisonous element which can be transferred easily in hydrosphere and can be accumulated in human and animals. It may be toxic or even lethal if accumulated in excessive quantities. In nature, cadmium is always concomitant with zinc. The cadmium contamination is observed due to discharge of waste water and waste residues which are produced by the exploitation, smelting and piling of lead-zinc based mines. In 1989, the copper metallurgy industries had discharged 88 tons of cadmium in China [Zheng et al. 2002].The exploitation of some lead-zinc mines have also caused the pollution of the rivers and soils. The higher cadmium concentration is observed in urine of the inhibitor on to [Lin 1997]. In Daye city, Hubei province, the farmland near a copper metallurgy factory was also contaminated by cadmium with the maximum and average concentration of 99.5 mg/kg and 51.11 mg/kg respectively. Also, the cadmium concentration in the drainpipe sludge observed as 2630mg/kg [Chen et, al 2003].

The current practice for remediation of cadmium contaminated sites usually involves excavation, soil washing, phytoremediation etc. which are time consuming and costly processes. Recently, attention has been focused on developing cost effective, in situ treatment technologies for remediating cadmium contaminated sites. Electrokinetic remediation is one such in situ technology that has significant potential for effectively and economically removing cadmium from soils.[Reddy et al. 1997].

Electrokinetic remediation occurs when an electric field is applied to the saturated polluted soil by means of electrodes inserted in the soil mass. The pore fluid is used as the conductive medium [Acar et al. 1996]. The major advantages of this technique are: (a) a unique applicability to low permeability soils (clays, silts) because these soils have greater ability to adsorb pollutants. (b) a high degree of control of flow direction , unlike soil flushing [Li et al. (1996), Ho et al. (1995), Dzenetis et al. 1997].(c) The capability of removing a wide range of contaminants especially heavy metals, and (d) a low electric power consumption. Laboratory experiments have shown that it is possible to achieve high removal of heavy metals such as As, Cr, Cd, Fe, Hg, Ni ,Zn, NO₃⁻ and organic

compounds like phenol, toluene, ethanoic acid, benzene as well as radionuclide like uranium thorium, strontium, are possible with this technique.

The pH is important parameter in Electrokinetic process because soil surface properties (cation exchange capacity, adsorption capacity, sign and magnitude of zeta potential) as well as speciation and dissolution of the pollutants are generally pH dependent [Pamuku et al. 1992].

Geochemical reactions, including precipitation / dissolution, sorption, redox reactions are highly dependent upon pH generated by the process of complexation reactions. The advance of the acid front from anode towards cathode assists in desorption and dissolution of metal precipitation. However, formation of the high pH zone near the cathode results in immobilization to precipitation of metals hydroxides.

When heavy metals enter into basic conditions, they get adsorbed onto the soil particles or precipitate as hydroxides, oxy hydroxides, etc. In acidic conditions, these ions get desorb, solubilize and migrate [Chen et al. 2002]. In order to remove the heavy metals from soils, different liquids other than water can be used as purging agent. The cathode reaction should be depolarized to avoid the generation of hydroxides and their transport in the soil [Acar and Alshawabkeh 1993]. In order to enhance the Electrokinetic remediation process a favorable pH condition is necessary [Reddy et al. 2003].

Bruell et al. (1992) have observed an increase in pH at cathode in Electrokinetic remediation of dissolved organic compounds. Eykholt and Daniel (1994) have studied the Electrokinetic remediation of kaolinite contaminated with copper, and reported that the pH of the soil sample influences the electrokinetic process. Electrokinetic flow is observed higher of higher pH of solution without any contaminants.

Pamuku et al. (1997) and Pamuku and Wittle (1992) reported that pH control at anode and cathode should create suitable environment for metal ions to remain in solution as single species

Shapiro and Probstein (1993) investigated that electro-osmotic flow is ceased before a high removal efficiency was reached, but that they could increase the flow towards the cathode by using a basic purge solution to limit the H^+ ions producing by the anode.

Copper is generally removed at higher pH in the wood preservation soil [Ottosen et al. 1997] and at lowest pH=4 no removal was obtained in soil [A.B. Ribeiro et al 1997].

Ottosen et al. (2001) was observed that copper was mobilized at a higher pH in both calcareous and non calcareous soils.

Acar and Alshawabkeh (1993) have stated that zeta potential decreases linearly with the logarithm of the pH of the soil medium which results in the reduction of electro-osmotic flow and also found that at high initial ionic conductivity and low initial soil pH, a little electro-osmotic flow occurs.

Gent and co-workers (2004) have documented the electrokinetic removal of cadmium and chromium through the field experiments. They observed that after four months of treatment, 78% of the soil volume had been cleared of the chromium (initial chromium concentration 180-1100 mg/kg) and 70% of the soil volume had been cleared of the cadmium (initial cadmium concentration 5-20 mg/kg) contamination.

Hamed and Bhadra (1997) investigated the influence of variation of current density and pH on electrokinetics. They varied the current density in range of $0.123\text{mA}/\text{cm}^2$ to $0.615\text{mA}/\text{cm}^2$ and pH in range 2 to 10. It was observed that increasing the current density

reduced the time needed for the acid front generated at the anode to reach the cathode. Increase in the pH increased the electro-osmotic flow and a sharp increase in electro-osmotic flow was noticed at pH 10-12. Increasing the current density increased the energy consumption for the same ideal case.

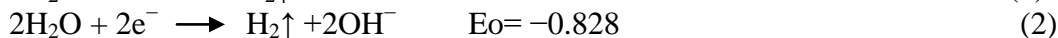
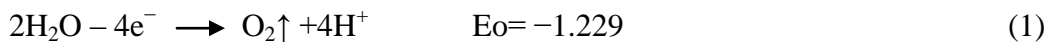
Importance of pH on the removal of organic and inorganic contaminants from the soil. Some of the enhancement techniques such as controlling the pH at the cathode compartment need to be explored in detail to further improve the removal efficiency of metal ions from soil by electrokinetics remediation technique.

It is gleaned from the literature that pH plays an important role in electrokinetic remediation of metals contaminated soils. Therefore, In present paper it is aimed to observe the effect of pH on the contaminant transport during the electrokinetic treatments of soil. Simplifying conditions are assumed. The influence of the hydraulic gradient is neglected in this study because it is restricted to low permeability clays. Under these assumptions, the two major Electrokinetic phenomena involved are electro-osmosis and electro-migration. All laboratory tests were performed at room temperature and deionized water is used to prepare cadmium contaminated soil as well as for different pH as anolyte solution.

BACKGROUND:

Electrokinetic remediation is an in situ technique in which a low direct current is applied across the soil medium to remove the contaminants. The important mechanisms by which the contaminant transport takes place are electro-osmosis and electro-migration.

Electro-osmosis is the movement of water from the anode to the cathode as a result of dipolar water molecules interacting with double diffuse layer when an electric potential is applied [Electrokinetic's is a feasible method to remove heavy metals like copper, chromium, and arsenic from CCA contaminated soils]. Electro-migration is the movement of positively and negatively charged ionic species towards the electrodes of opposite sign. Electrolytic reactions take place at the electrodes when a direct electric current is applied across the soil sample. The primary electrode reactions are shown below by Eqs. (1) and (2).



Oxidation takes place at the anode producing hydrogen ions (H^+) and liberating oxygen gas while reduction occurs at the cathode producing hydroxyl ions (OH^-) and liberating hydrogen gas. The type of electrolytic reactions occurring at the electrodes depends on the availability of chemical species and the electrochemical potential of these reactions. Although, other secondary reactions may occur at the cathode because of their low electro chemical potentials. The water reduction half-reaction ($\text{H}_2\text{O}/\text{H}_2$) is dominant during the early stages of the electrokinetic process [The amount of current applied, which in turn affects the pH of the soil medium and hence effect the removal efficiency. Copper was desorbed from the soil and mobilized at pH values of approximately 4.0.

].The rates of acid and base production during electrolysis depend upon the current density. Based on Faradays law of equivalence of mass and charge, the rate at which ions are produced at the electrodes is expressed as:

$$J = \frac{1}{(Z) * (F)} \quad (3)$$

Where, J is the molar flux ($\text{mol}/\text{cm}^2 \text{ s}$), I is the current density (A/cm^2), Z is the ionic valence, and F is the Faradays constant ($96,485 \text{ C}/\text{mol}$ electrons).

Material and Methods

The experiments were performed on clayey soil using deionized water as the purging solution in Anode and cathode reservoir. The pH was varied between 3 to 12. The cadmium concentration was kept as $13\text{mg}/\text{Kg}$ and the applied voltage was 36 volt. In all the tests, the voltage gradient applied across the electrode was $1 \text{ VDC}/\text{cm}$ and the moisture content was kept at 35% for test duration of 72 hours as presented in Table 1.

Table 1 Parameters value

Tests	Designation	Cd conc. (mg/Kg)	Voltage (mV)	Moisture content %	pH of Anolyte	Time duration (days)
1	EK Cd-I	13	36	35	3	3
2	EK Cd-II	13	36	35	4	3
3	EK Cd-III	13	36	35	5	3
4	EK Cd-IV	13	36	35	6	3
5	EK Cd-V	13	36	35	7	3
6	EK Cd-VI	13	36	35	8	3
7	EK Cd-VII	13	36	35	9	3
8	EK Cd-VIII	13	36	35	10	3
9	EK Cd-IX	13	36	35	11	3
10	EK Cd-X	13	36	35	12	3

The properties of the test soil used are shown in below Table 2. From table 2 it is seen that soil is alkaline in nature having high carbonate content. The particle size distribution analysis indicates that the soil contains approximately 15% clay-size particles. The soil has higher organic content (6.25 %) due to long term of cultivation activity. Soil has high buffering capacity, low conductivity high swelling and hence high adsorption capacity.

Table 2. Properties of the soil used

Property	Value
Particle Size Distribution	
Gravel (%)	6.60
Sand (%)	18.4
Silt (%)	60.0
Clay (%)	15.0
<i>Atterberg Limits</i>	
Liquid Limit (%)	45
Plastic Limit (%)	17
Specific gravity	2.62
Maximum Dry Unit Weight (kN/m ³)	18.68
Optimum Moisture Content (%)	14.4
Cation exchange capacity (USEPA) (meq/100 g)	22
pH	8.36
Organic Content (%)	6.25
CaCO ₃ (%)	2.5
Soil classification (USCS)	CL
Cd concentration	Not traceable

Test Procedure:

About 1.8 Kg of dry soil was used for each test. Cd(NO₃)₂.4H₂O was used as a source of cadmium. The cadmium solution of known concentration was prepared in deionized water and then added to the soil, mixed thoroughly with steel spatula. The contaminated soil was then placed in oven and dried. Dried soil was crushed and mixed with 700mL of deionized water to attain a moisture content of 35%. This soil was placed in Electrokinetic cell in layers and compacted uniformly using hand compactor. The anode and cathode electrode compartments were connected to the electrokinetic cell as well as reservoirs containing deionized water. A voltage gradient of 1.0VDC/cm was applied to the soil sample. The electric current, voltage across the electrode, and electro osmotic flow per day were measured at a time interval of 3 hours throughout. Each test was terminated after 72 hours. Thereafter, the soil specimen was extruded from cell by using mechanical extruder and sectioned in to six sections. Each section was tested for pH, moisture content and residual cadmium concentration. The pH and Cd concentrations were measured with Orion Model, 920 A⁺ and the Atomic absorption spectrophotometer (PerkinElmer).

RESULTS AND DISCUSSION:*Electrical Current:*

Figure 1 shows the profile of electric current observed during the tests. In case of deionized water used for solution of different pH (2-12) , the current reached maximum

values in nearly six hours for solution of different pH except for pH 4 and 8 for which maximum current is achieved after 30 hours of experiment. It has been reported that the measured electric current is proportional to the dissolved species present in the solution (Acar and Alshwabkeh 1993). After 36 hours of test run, current suddenly dropped down due to crack formed at the section 2-3. The current flow remained constant up to 48 to 54 hours of experiments. The pattern of decreasing current over time is observed in similar pattern with the finding of other investigators. [Eykholt 1992, Grundl and Michalski 1996].

The pH of purging solutions also affects the current by changes in physico-chemical properties such as mineral dissolution chemical precipitation/dissolution etc. At low pH of influent solution current reaches its maximum value due to higher solubility of minerals and their migration [Hamed and Bhadra 1997].

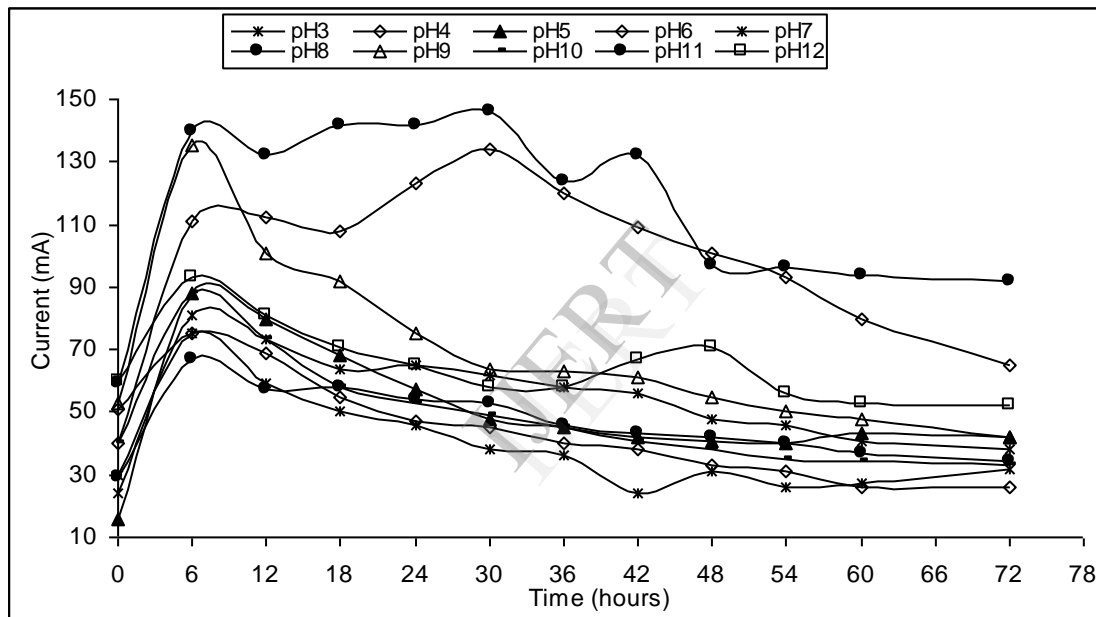


Fig.1 Variation of current with time at pH 3,4,5,6,7,8,9,10,11,12

Voltage

Figure 2. Presents the voltage across the electrodes for different pH of influent solution. In beginning of the experiments there is a slight increase in voltage except for solution with pH 4, 9 and 10 having low voltage. It is reported that lowering the pH across the soil sample would decrease the overall resistance in the soil. Thus, there is high voltage [Chung and Kang 1999] while some times dissolution and desorption mechanism was dominant in the soil system causing increase in resistance and voltage drop within the cell [Kim and Kim 2001] while at high pH voltage drop may be occurs as a result of precipitation of contaminant. The maximum value was attained as 37.5 volts across the cell for all tests. The result shows that the pH of influent affects the electric potential between the electrodes. Kim et al. 2002 reported that the resistance and voltage across the

soil sample decreased during the experiment, because dissolved and / or desorbed metal contaminants migrated and transported. After some time voltage maintained at constant level due to low of soil converts the metals in mobile fractions (exchangeable form) and their migration in soil sample continued throughout the test.

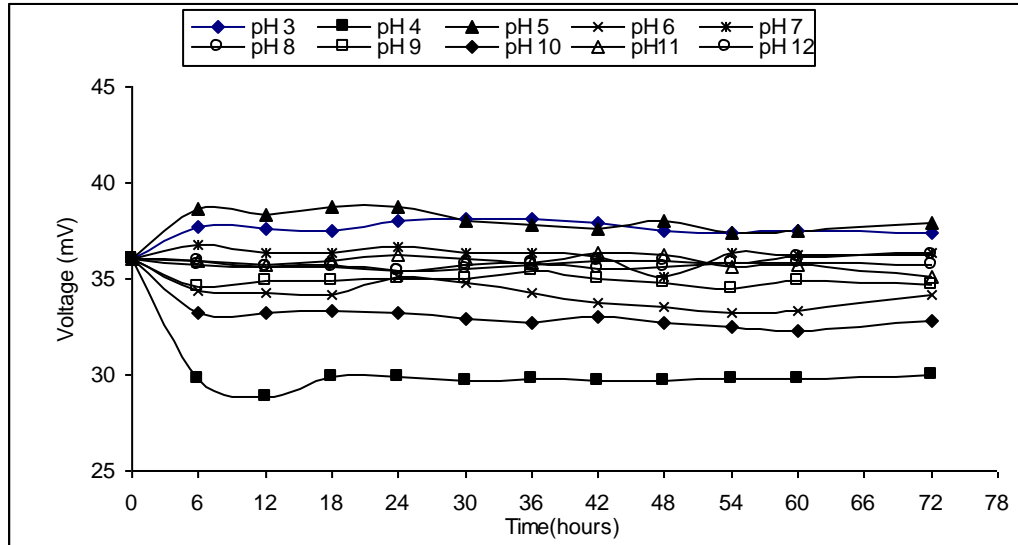


Fig.2 Variation of voltage with time at pH 3,4,5,6,7,8,9,10,11,12

Electro-osmotic Flow:

Fig .3 presents the variation of electro osmotic flow with time for all the experimental runs at different pH (3-12). Due to electro migration of ionic species and the electrolysis of water the surface charge of the soil particles (zeta potential) and pore fluid properties (dielectric constant and viscosity), changes with time influences the electro osmotic flow (Reddy et. al, 2002). As can be seen in fig. 1 that the current is observed high during first few hours due to which the electro osmotic flow was actually low. At start of the experiment, the higher conductivity of soil may reduce the thickness of diffuse double layer and ultimately inhibit the electro-osmotic flow [Reddy and Ala 2005]. After 24 hours, the electro osmotic flow increased due to reduction in conductivity by electro migration and / or due to the increase concentration and migration of H^+ and OH^- ions. However, the soil surface charge may become predominantly positive due to high alkalinity conditions developed which ultimately led to more negative zeta potential and resulted in the increase in the cumulative electro-osmotic flow. From figure 3 it is clear that accumulated electro-osmotic flow is gradually increased between pH 3-9, but from pH 10 – 12, there is a sharp increase in electro-osmotic flow which is also evident from the studies of different researchers (Jihad T. Hamed, Ashish Bhadra. 1997). This indicates that in clayey soil electro-osmotic flow is favoured by high pH of the influent. In addition zeta potential of soil is higher at high pH values further enhances the flow rate.

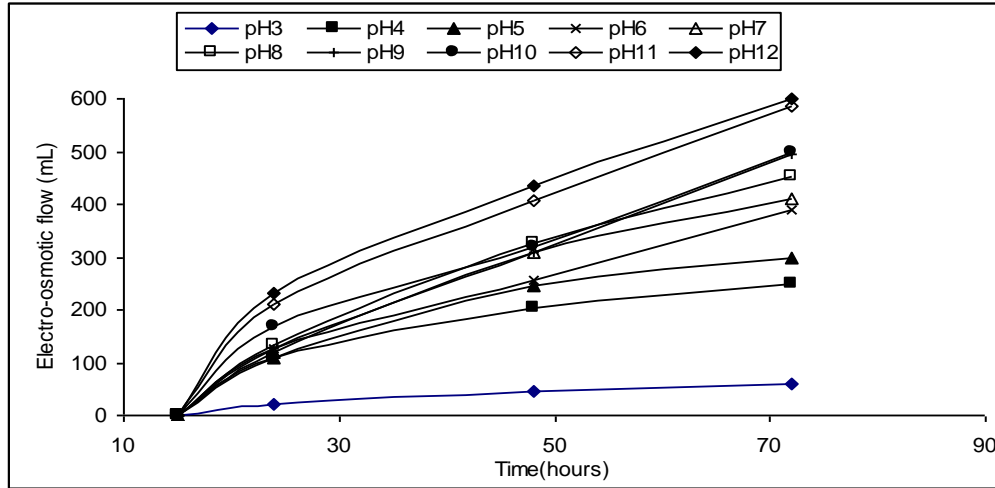


Fig.3 Variation of electro-osmotic flow with time at pH 3,4,5,6,7,8,9,10,11,12.

Moisture content:

In figure 4 the moisture content of the soil is presented at different pH (3-12). There is slightly changes occurs in moisture contents of different sections due to variation in electro-osmotic flow at different pH of anolyte solution which indicates that no significant changes are found except in pH 10-12 in which last compartment contains low value than previous one because precipitation of cadmium metal in cathode section. In middle section of soil specimens have comparatively low moisture content because of soil regions where the electro-osmotic flow was high, created a pressure so that the solution was pulled from regions where the electro-osmotic flow was lower. Same trend has been seen for all the tests. In most cases the cathode and anode section have high moisture contents because of direct contact with reservoirs.

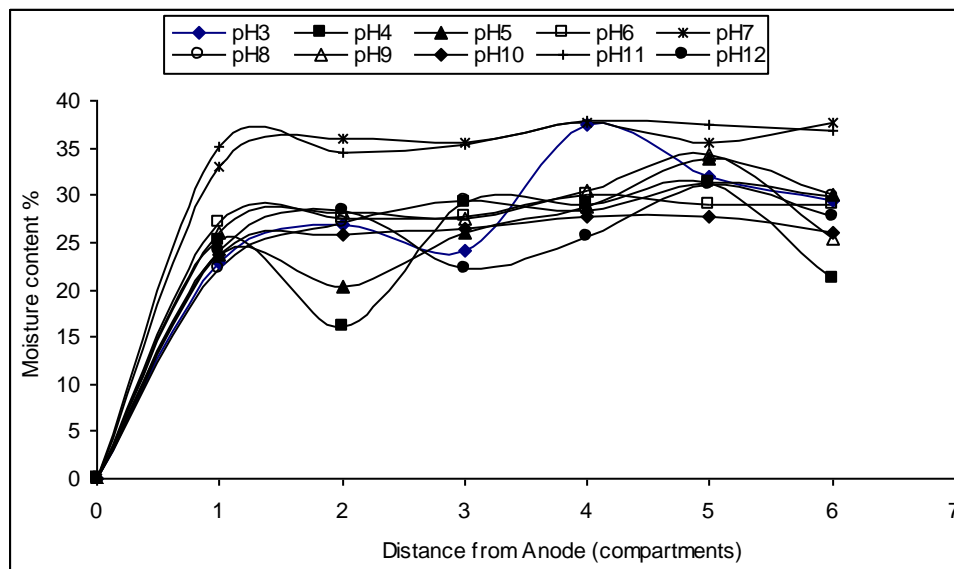


Fig 4 Variation of moisture content with distance at pH 3,4,5,6,7,8,9,10,11,12

Soil pH:

It is essential to measure the pH changes across the soil during the removal of toxic metal since pH is a major variable in chemical equilibrium and desorption / precipitation reaction. Final soil pH profile along the length of the cell in all experiments are presented in figure 4. It is observed that pH value is much lowered at the anode end of soil sample which cause dissolution of carbonates and hindrance the ion migration in experiment .In all case the pH values are found to be nearly 7 which is comparatively lower than the initial value of soil except in test 9. It can be seen that the pH 10-12 produced the highest cumulative flow and the test had the lower pH in the soil adjacent to the cathode rather than previous sections. It is important to note here that if there is a high electro-osmotic flow towards the cathode, the pH should be lower near the cathode because of opposite migration of OH^- ions towards the anode [Reddy et al 2002].

The test with pH 3 produces small amount of electro-osmotic flow, has allowed greater OH^- penetration, because the soil section of cathode contains highest pH (8.92) in all tests. The results indicate that the pH of influent has minor effect on the pH of electrokinetic remediate soil sample.

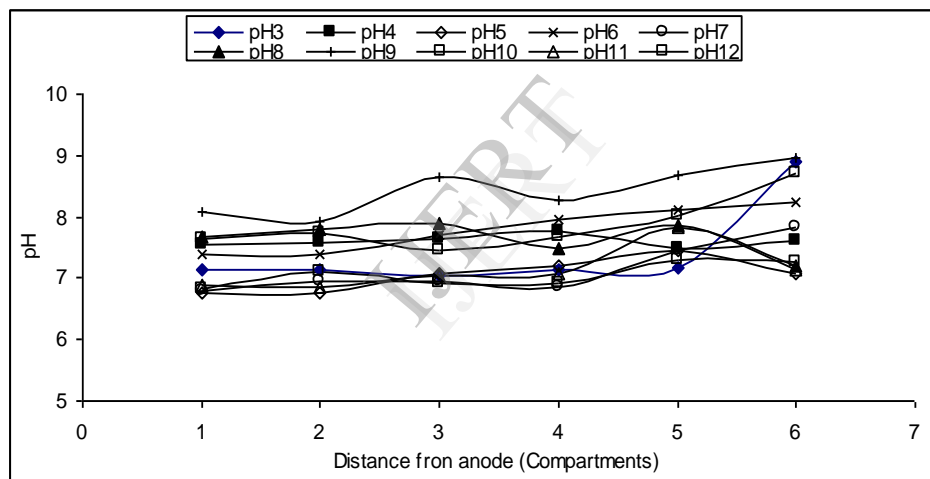


Fig.5 Variation of pH with distance at 3,4,5,6,7,8,9,10,11,12

Conclusions:

Based on above study it is concluded that increasing the influent pH from anode increase the electro osmotic flow. However, it does not affect electric potential across the cell. Due to high pH near cathode, the flow rate is high making less moisture content near cathode after the electrokinetic experiment high pH.

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