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ORIGINAL ARTICLE **OPEN ACCESS**

Removal of Zn(II) and Pb(II) from aquatic medium using potato peel as an adsorbent: Adsorption Isotherm and Kinetic study

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ABSTRACT
Heavy metal pollution is becoming a serious threat to ecosystem and human health through polluting water, soil and air in some parts of the world. In this study we investigated the adsorption isotherms and the adsorption kinetics of the adsorbent prepared from potato peel. The adsorbent used was characterized by SEM and FTIR to determine the surface morphology and the functional groups present on the surface of adsorbent. The effects of different conditions, for example contact time, sorbate concentration, solution pH, and temperature, on sorption were investigated. The adsorption data followed Langmuir model with R^2= 0.954 and 0.972 for lead and zinc respectively, and similarly the Fruendlich isotherm model also holds good for both the metals with R^2= 0.892and 0.974 for lead and zinc respectively.
***Keywords**: Heavy metal pollution, **Zn(II)** , **Pb(II)**, SEM, FTIR*

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INTRODUCTION

The toxic heavy metals are introduced to the environment from various industries in such a quantity that cause risk to human health. Metal plating facilities, mining operations, battery manufacturing, production of pigments and paints etc are the main sources of heavy metals in water. These heavy metals may enter into the human body directly or indirectly through food chain. Zinc and lead are prior toxic pollutants in industrial wastewater and ultimately become common ground water pollutants. The presence of heavy metals in drinking water is associated with different types of diseases like physical, muscular, neurological degenerative processes, Parkinson's diseases, muscular dystrophy etc [1-4]. Hence, different techniques have been developed and employed so far over the years to remove heavy metals from the waste water so that it can be reutilized for other purposes. Different conventional technologies like ion exchange, membrane separation, electro-coagulation, Nanoparticles, dialysis and filtration have been discussed to remove the heavy metals like zinc and lead from the wastewater but due to operation and capital cost the efficiency is of limited use [5-11]. To overcome these limitations the phenomena of adsorption has been employed and varieties of cheap materials have been used as absorbents to remove the Zn(II) and Pb(II) from wastewater. Some of the low cost absorbents include wheat bran, tea waste, coconut shell and coconut husk, zeolites, sea weeds etc and different biological materials were also used as good absorbents by different workers [12-18]. Different studies have evaluated the effectiveness of different agriculture based material which includes orange peel for the adsorptive removal of Pb(II) from aqueous solution with batch experiments. Banana peel has been used to extract copper and lead ions from water. These wastes require a little bit processing before use, are rich in nature, and are a by-product or a waste from an industry or agricultural operation. They are low-priced, easily available and have little economic value [18-24]. The natural materials are available in bulk quantities and acquire large surface area and high cation exchange capacity that are necessary requirement for an adsorbent. In the present study potato peel are selected as adsorbent for removal of Zn(II) and Pb(II).

MATERIAL AND METHODS

Potato peels were obtained from the kitchen wastes. The collected waste of potato peel were washed several times first with the tap water then rinsed with double distilled water to clean dust and soluble impurities and was dried in sunlight for one day and subsequently in oven at 90°C and finally ground to powder using laboratory grinder. Powdered biomass was pre-treated with acid in order to remove all the pigments and then washed with distilled water and again dried in oven at 90°C to get a constant weight followed by sieve through mesh to obtain fine grind powder of 0.2 mm. The adsorbent was kept in desiccators till the time of use.

pH metric measurements were made on decibel DB 1011 digital pH meter fitted with a glass electrode, which was previously standardized with buffers of known pH in acidic and alkaline medium. The reaction kinetics was studied with the help of Systronics spectrophotometer (166) over the wavelength range of (180 to 990 nm).

The entire chemicals used were of analytical grade obtained from sigma aldrich and solutions were prepared in distilled water. A stock solutions of 1000 ppm of Zn(II) and Pb(II) were obtained by dissolving $ZnCl_2$ and $Pb(NO_3)_2$ in deionized water respectively and the working solutions of 5, 10, 20, 50 and 100 mg/L were prepared daily by serial dilution. Britton-Robinson Buffers were prepared in the range of 3.0 to 8.0 in order to adjust the pH of the working solution.

Adsorbent characterization

To study the physiochemical characteristics of the adsorbents in order to find out their adsorption capacities different characterization techniques were employed and the outlines of these techniques were given:

Infrared spectra

The infrared spectral assignment of potato peel adsorbent was obtained by KBr disc method using Fourier Transform Infrared Spectroscopy (FTIR), 4100 JASCO, and Japan (Fig.1).The surface functional groups were ascertained by FTIR in the treated potato peel before Zn(II) and Pb(II) adsorption (Fig 1). The FTIR spectra were recorded in the range of 400 and 4004 $cm^{-1,}$ in FTIR spectrum (Model). Characteristic cellulose peaks in the region of 1000 to 1200 $cm^{-1}$was shown in FTIR.

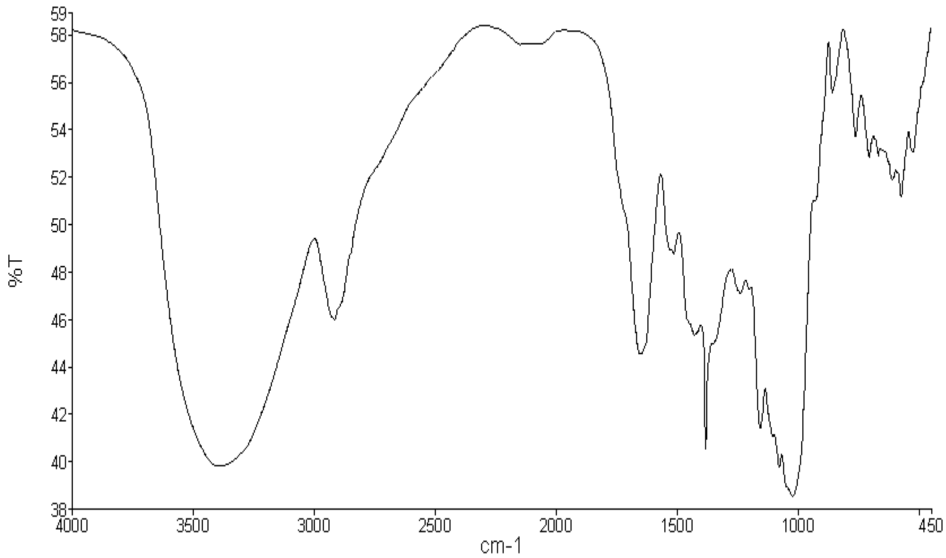

Fig:1IR Spectra of powered potato peel.

Surface topography (SEM)

The surface morphology of the adsorbent was examined by scanning electron microscopy (SEM). The surface of powdered potato peel was studied by SEM ZEISS. The samples for SEM were prepared by lightly sprinkling the powder on a double adhesive tape stuck to an aluminum stab. The stubs were then coated with gold to a thickness of about 300 A^0 under an argon atmosphere using a gold sputter module in a high-vacuum evaporator. The coated samples were then randomly scanned using a scanning electron microscope ZEISS: SEM and photomicrographs were taken (Fig. 2 (a & b).

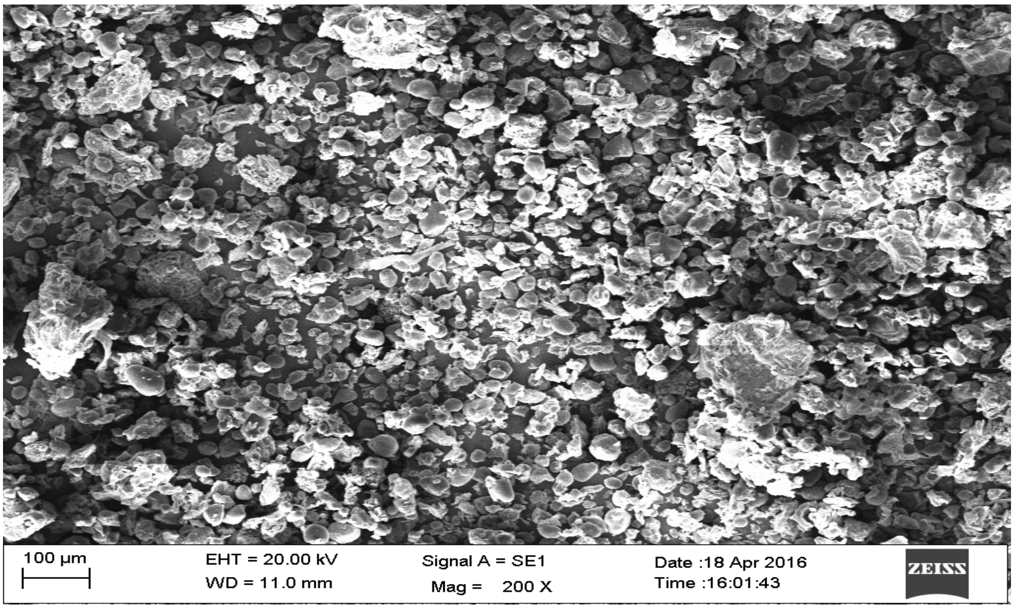

Fig:2(a) SEM image of powdered potato peel at Mag=200X

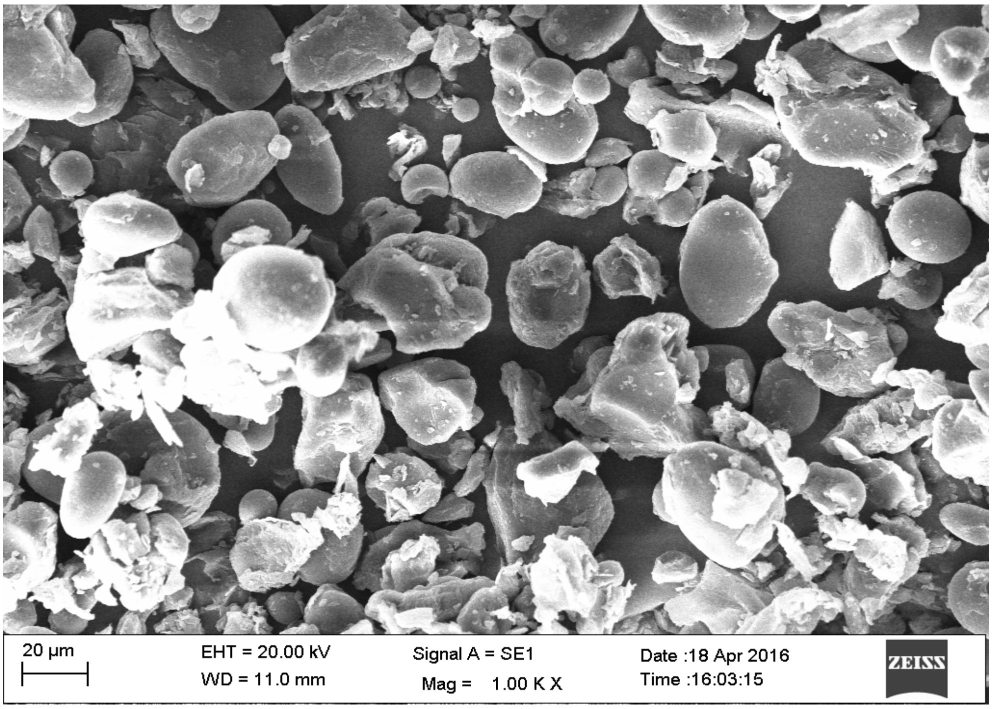

Fig: 2(b): SEM image of powdered potato peel at Mag=1.00 K X

PSA analysis

The particle size analysis (Fig. 3) of potato peel powder was done with the help of Shimadzu SALAD-2300 particle size analysis. Particle size analysis showed that particle size in diameter ranged from ≤ 1.733µm (10 %) to ≤ 70.174 µm(99.99%). The sample contains heterogeneous particle size distribution with majority of the particle size diameter ≤29.456 µm as indicated by 90th percentile. The mean particle diameter and standard deviation were recorded 6.81 µm and 0.56 respectively during PSA study. Results were showed in Table 1.

Table:1 Value of particle diameter of Potato peel (in µm)

99.999%D (µm)	90.000%D (µm)	50.000%D (µm)	10.000%D (µm)	0.001%D (µm)	0.000%D (µm)	0.000%D (µm)	0.000%D (µm)	0.000%D (µm)
70.174	29.456	9.622	1.773	0.388	0.000	0.000	0.000	0.000

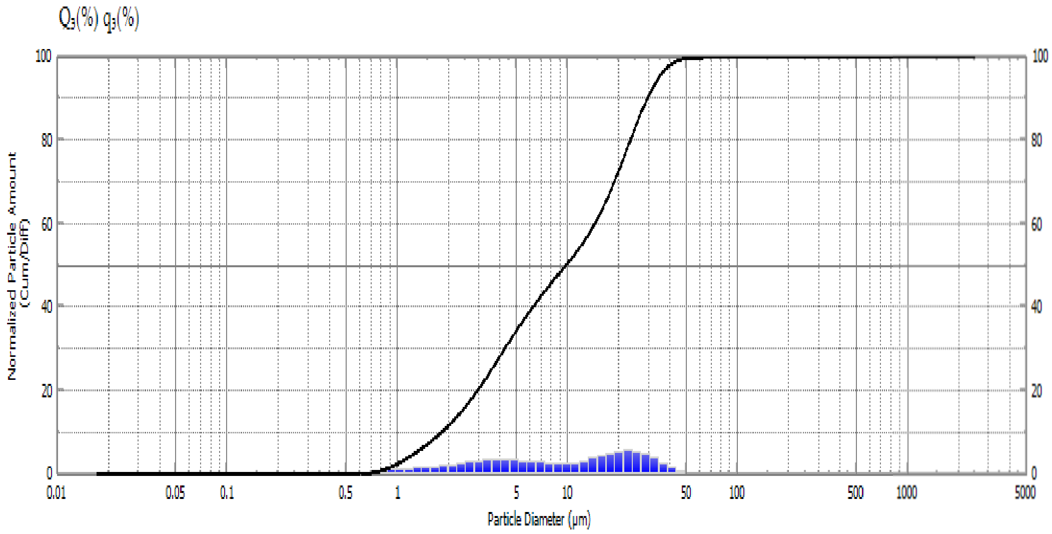

Fig: 3 Graph of Particle Diameter (in μm) of Potato peel.

RESULTS AND DISCUSSION

The ability of different adsorbents to remove heavy metals from aqueous solution by using the potato peel as an adsorbent and varying the different parameters has been studied. The parameters which have been optimized include pH, contact time, metal ion concentration and adsorbent dosage. All the parameters have been varied in order evaluate the effect of these varied parameters on the process of adsorption of Zn(II) and Pb(II).

Effect of Contact time:

The experiment has been carried out in order to evaluate the effect of contact time needed by the system to reach the equilibrium. Experiments have been conducted at different contact time and taking the other parameters constant. The effect of contact time was studied at a room temperature of 30°C. From the result obtained, it is evident that the removal of metal ions increased as contact time increases. The result shows that the removal rate for Pb(II) and Zn(II) was rapid within the first 30 min and starts increasing for another 90 min (Fig.4) and the maximum percent removal was obtained at the contact time of 90 min. that was 88 % for Zn(II) and 89% for Pb(II). The initial faster rate is attributed due to the availability of the large number of uncovered surface area of the adsorbents, since the adsorption kinetics depends on the surface area of the adsorbents. On the other hand, percentage removal for zinc and lead increased gradually with increasing contact time. The adsorption takes place at free and the more reactive sites as observed in case of Zn(II) and Pb(II). The filling of absorption sites made the sorption process difficult by further increase in contact time and becomes unfavorable subsequently.

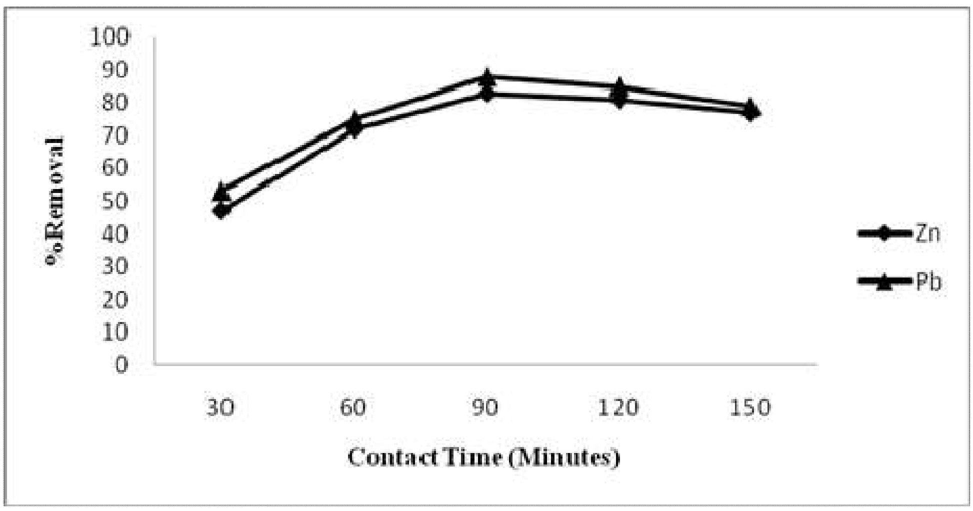

Fig: 4 Percentage removal of Zn(II) and Pb(II) by potato peel at different contact time.

Effect of metal concentration:

To study the effect of metal ion concentration on the process of adsorption all the experiment were carried out by the procedure mentioned in the methodology. The experiment was performed by varying the concentration of metal from 5ppm to 100pp and taking the other parameters constant. It was observed that the percentage removal of lead and zinc increased with the increase in the metal ion concentration from 5 to 10 ppm. The maximum removal was observed at the metal concentration of 10ppm for both the metals and the removal percentage were 82% and 86% for Zn(II) and Pb(II) respectively, (Fig 5). During the course of study it was observed that the maximum removal was observed at low metal concentration and by increasing the concentration removal percentage also increases to some extent but by further increasing the concentration the removal of metal decreases. During the initial stage the number of binding sites are more hence more metal ions are adsorbed and by increasing the metal ion concentration the binding sites get saturated and results in low adsorption at higher concentration.

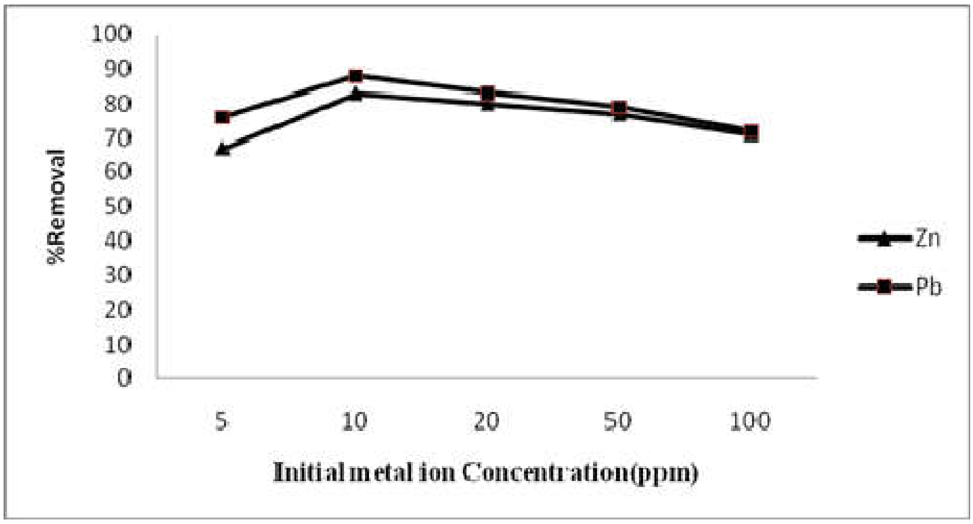

Fig: 5 Percentage removal of Zn(II) and Pb(II) by potato peel at different metal ion concentration.

Effect of adsorbent dosage

The amount of adsorbent dose in the adsorption of metal from aqueous solution is an important parameter as it presents available surface to adsorbate for adsorption process. The effect of adsorbent dosage on the removal of Zn(II) and Pb(II) ion at 10mg/L were investigated at optimum parameters and were shown in Fig (6) The adsorbent dosages were varied from 0.5, 1.0, 1.5, 2.0 and 2.5 g/100mL. The maximum removal observed were 83% and 86% for Zn(II) and Pb(II), respectively at the adsorbent dose of 1.0 g. As adsorbent dosage was increased keeping all other parameters constant, removal efficiency first increases, reaches maximum and then decreases. From the results it was observed that the rate of removal of Zn(II) and Pb(II) was higher at the initial stage due to the availability of more active sites and removal rate becomes slower at later stages due to decreased or lesser number of active sites available. With increase in the dose of absorbent aggregation of particles take place that result in the decrease of efficiency and metal up take. The linear trend was observed as the dosage increased from 0.5 to 1 g.

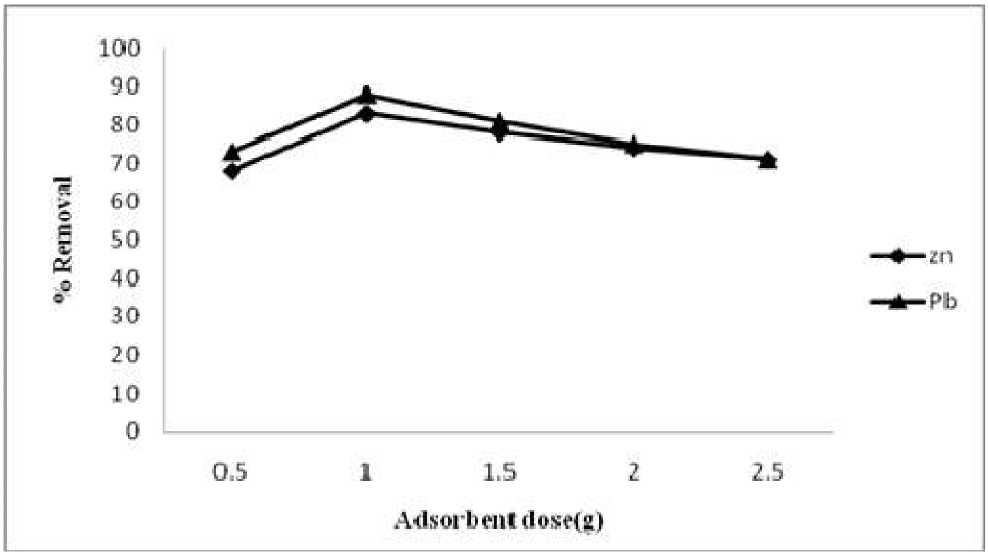

Fig: 6 Percentage removal of Zn(II) and Pb(II) by potato peel at different adsorbent dose.

Effect of pH

The pH plays an important role in the adsorption process by affecting the surface charge of adsorbent, the degree of ionization and species of the adsorbent. The effect of pH on the removal efficiency of zinc and lead was studied at different pH values ranging from 3.0 to 8.0 under the optimized condition. The removal of zinc and lead was found to increase by increasing the pH from 3 to 5 and the maximum removal was observed at the pH value of 5. By further changing pH and by maintaining the alkaline pH does not favour the adsorption and removal start decreasing. Observation have shown that the maximum uptake of Zn(II) was at pH 5, (almost 85% removal) similarly the adsorption of Pb(II) was 87% , at pH 5 (Fig 7). As pH increases the surface becomes more negatively charged that causes repulsion between metal particles and potato peel surface particles that may decrease the removal efficiency at high pH.The lower removal efficiency at low pH was apparently due to the presence of higher concentration of H^+ in the solution which competes with the metal ions for the adsorption sites of the potato peel. With the increase in pH, the H^+ concentration decreases leading to increased zinc and lead uptake.

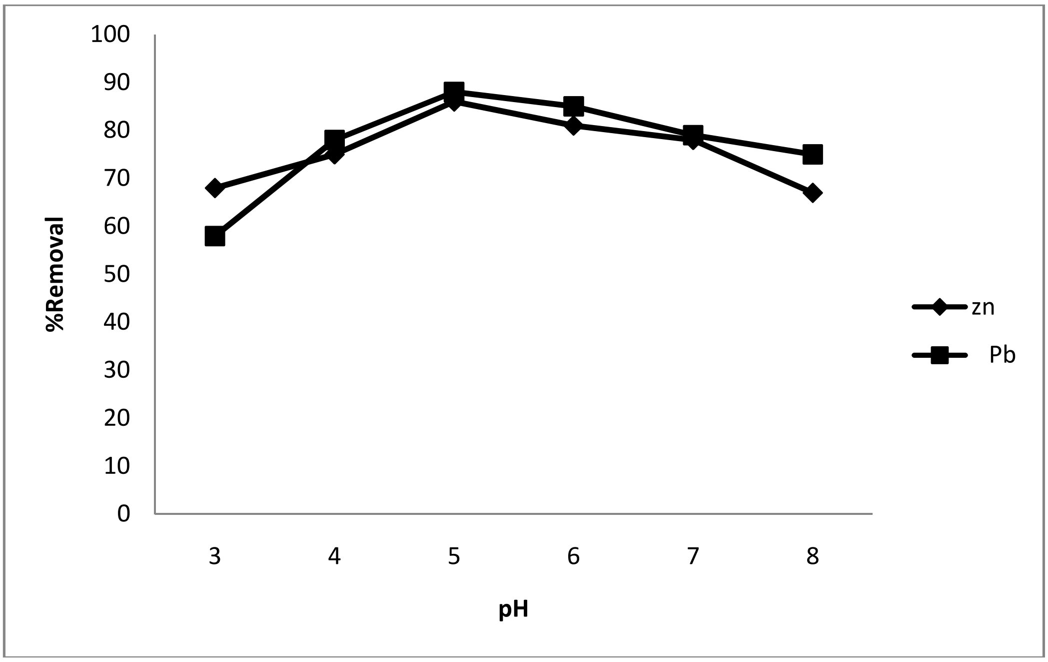

Fig: 7Percentage removal of Zn(II) and Pb(II) by potato peel at different adsorbent dose.

Adsorption Isotherm

The adsorption isotherm for lead and zinc was studied by using initial metal concentrations of 10 ppm, pH = 5, temperature at 30°C and amount of adsorbent dosage (1g/100 ml). The data obtained were fitted to the Langmuir and Freundlich isotherms. These models were tested to determine the maximum capacity of lead and zinc removal using potato peel. The experimental data was fitted to the Langmuir equation.

$$\frac{Ce}{Qe} = \frac{1}{bqmax} + \frac{Ce}{qmax}$$

where C_e is the equilibrium concentration of adsorbate (mg/L), Q_e is the amount of adsorbate adsorbed at equilibrium , q_{max} is the maximum adsorption capacity (mg/g), and b is the adsorption equilibrium constant (mg/L).

For the Freundlich equation, the linear form was used as:

$$\log q_e = \log K + \frac{1}{n}\log Ce$$

where K and n are the constants characteristics of the system.

The best estimated values of all the equation parameters are summarized in Table 2. Langmuir model was found with correlation coefficient (R^2=0.99) and (R^2= 0.99) for lead and zinc, respectively and similarly the Freundlich model was found to fit better with correlation coefficient (R^2=0.95) and (R^2= 0.96) for lead and zinc respectively. The adsorption isotherm data were well fitted with the linearized Langmuir equations and the data obtained from the equations for zinc and lead are shown in Figures 8 (a,b) and Fig 9 (a, b). The value of R^2 was found higher for Freundlich isotherm than the Langmuir isotherm; that means Freundlich equation represented the adsorption process well. Values of K_f, n, Q_0 and b are given in Table 2.

Table 2: Estimated values of all the equation parameters.

Metal ions	Langmuir Constants			Freundlich constants		
	Q^0_e (mg g^{-1})	b (L mg^{-1})	R^2	K_F	N	R^2
Pb(II)	1.98	0.482	0.95	0.2.63	1.086	0.99
Zn(II)	2.35	0.609	0.96	1.05	1.05	0.99

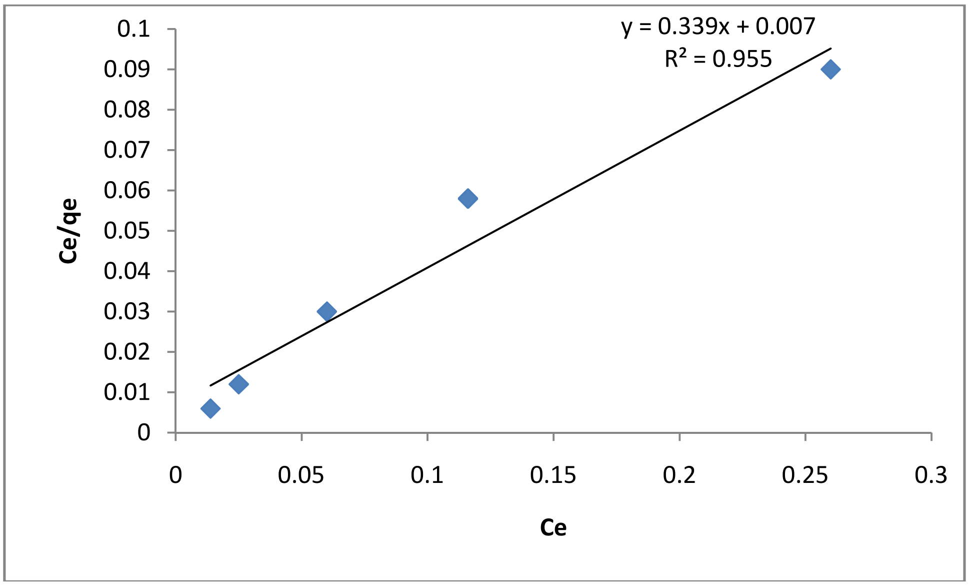

Fig: 8(a) Langmuir isotherms plot for adsorption of Pb(II) onto adsorbent potato peel

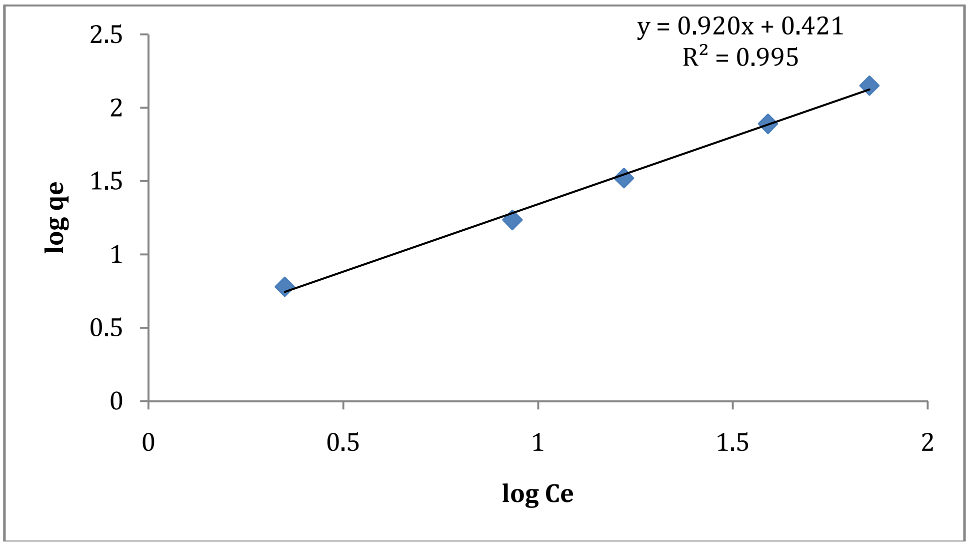

Fig: 8(b) Freundlich isotherms plot for adsorption of Pb(II) onto adsorbent potato peel.

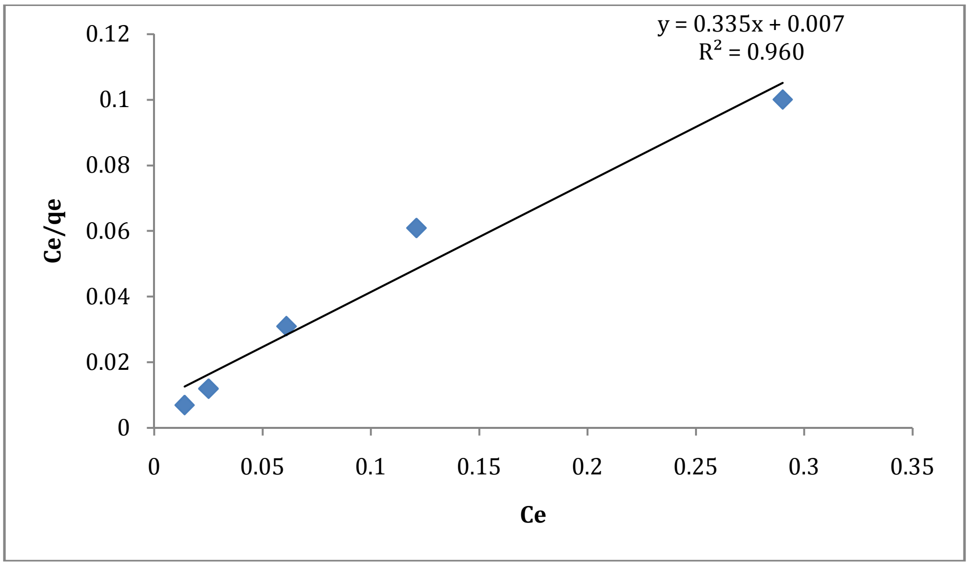

Fig: 9(a) Langmuir isotherms plot for adsorption of Zn(II) onto adsorbent potato peel.

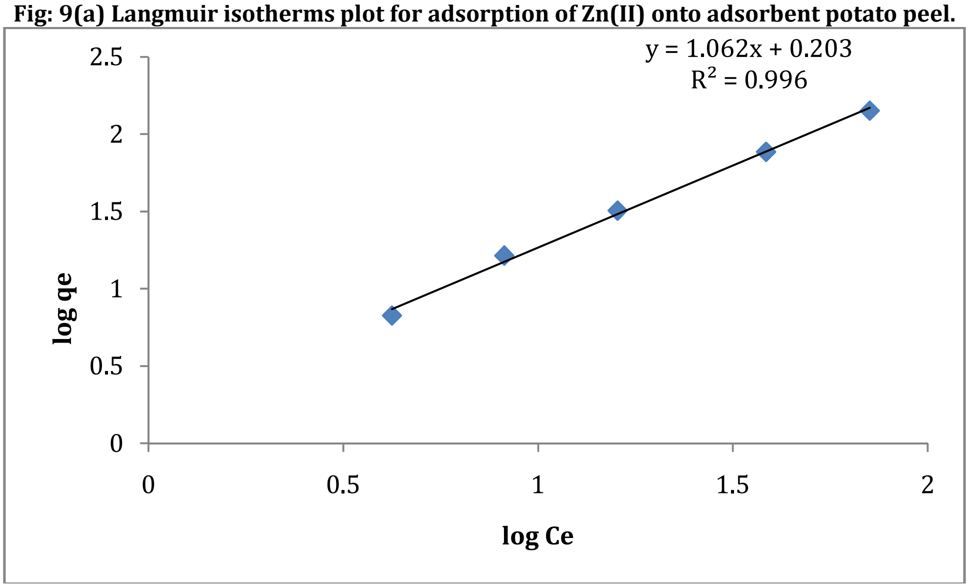

Fig 9(b): Freundlich isotherms plot for adsorption of Zn(II) onto adsorbent potato peel.

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