Removal of lead from aqueous solutions using Ageratum conyzoides leaves powder with the emphasis on the affective factors

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Abstract: **The biosorptive potentials of *Ageratum conyzoides* leaves powder as biosorbents, were evaluated, for the first time for Pb(II) removal from aqueous solutions. The influence of biosorbent size (53-152 µm), agitation times (1-180min), pH from 2 to 8, initial concentrations of lead in aqueous solution with (50-200 mg/L), *Ageratum conyzoides* leaves powder dose (0.25-3.0g), temperatures (283-323 K), were investigated. The maximum sorption capacities of Pb(II) ions onto *Ageratum conyzoides* leaf powder was (89.1697 %).The kinetic data modeling resulted in good correlations with the pseudo-second (R^2= 0.9965) order.Thermodynamic parameters indicated the spontaneity and endothermic nature of lead biosorption on *Ageratum conyzoides* leaf powder biomass and the sorption capacities were in good agreement with the uptake capacity of Langmuir model.**

Keywords: Biosorption, Lead, Ageratum conyzoides leaves powder, SEM, Kinetics

Introduction

Pollution of aquatic ecosystems caused by heavy metals has been one of the major environmental threats over the last several decades and is of high ecological significance. These concerns arise from their non-biodegradability, high toxicity and huge discharge into the environment (Madiha Zaynab et al., 2022; Nuray Alizada et al., 2020). Heavy metals occur naturally in aquatic ecosystems, but with large variations in concentration. They also enter the environment from various man-made sources (Jessica Briffa et al., 2020). These metals are released into the aquatic environments through direct discharges into both freshwater and marine ecosystems or through indirect routes (Mohamed et al., 2014; Bashir et al., 2020). These hazardous pollutants tend to transfer through the food chains and potentially can cause adverse effects on the health of any organisms at any trophic level. Hence, the removal of heavy metal from contaminated waters has become one of the most imminent environmental problems (Cordes et al., 2016; Amelia et al., 2021; Yang et al., 2020).
Pb(II) is classified as a non-essential prevalent toxic metal ions. Lead in the form of Pb(II) ions is one of the most stable and toxic in aquatic ecosystems and shows considerable tendency to accumulate in various organs of aquatic organism(Jaishankar et al., 2014). Its widespread use has resulted in extensive environmental contamination, human exposure and significant public health problems in many parts of the world (Tchounwou et al., 2012; Wani et al., 2015; Yang et al., 2020).
Important sources of environmental contamination include mining, smelting, manufacturing and recycling activities, and, in some countries, the continued use of leaded paint and leaded aviation fuel (Karrari et al., 2012; Wani et al., 2015). More than three quarters of global lead consumption is for the manufacture of lead-acid batteries for motor vehicles. Lead is, however, also used in many other products, for example pigments, paints, solder, stained glass, lead crystal glassware, ammunition, ceramic glazes, jewellery, toys and some cosmetics and traditional medicines(Debnath et al., 2019; Obeng-Gyasi et al., 2018).
Much of the lead in global commerce is now obtained from recycling. Young children are particularly vulnerable to the toxic effects of lead and can suffer profound and permanent adverse health impacts, particularly on the development of the brain and nervous system (Wang et al., 2006; Roy et al., 2009). Lead also causes long-term harm in adults, including increased risk of high blood pressure and kidney damage. Exposure of pregnant women to high levels of lead can cause miscarriage, stillbirth, premature birth and low birth weight (Saeed et al., 2017; habani et al., 2020)
There are some widely used methods for removal of Pb(II) ions and other heavy metal ions from wastewater, such as membrane filtration, electrolytic recovery, precipitation, ion exchange, adsorption and so on; however, these conventional methods can cause some important problems such as management of generated wastes, production of toxic sludge that require safe disposal and high cost (Qasem et al., 2021; Nguyen et al.,2022; Kumar et al., 2022).In the past three decades, there has been a growing interest in developing low cost and environment friendly materials for removal of heavy metals from wastewater and natural environment(Tripathi et al., 2015 Dixit et al., 2015) Adsorption is a highly effective and economic separation and purification method that is increasingly being utilized for the removal of heavy metals ions from industrial effluents (Khulbe et al., 2018; Soliman et al., 2020).

This method is fast, selective, and with elevated efficiency and it can be also applicable against various types of pollutants, low cost and ease of operation, as well as the reusability potential of the adsorbents, make it beneficial (Adie et al., 2012; Yang et al., 2019). Nowadays, more green materials, raw or modified, are explored instead of conventional adsorbents, within the concept of 'Green Chemistry' (Anastopoulos et al., 2019). Leaf-based biosorbents like activated guava (*Psidium guajava*) leaves (Kumar et al., 2021), aloe vera leaves (Somayeh Abedi et al., 2016), powdered leaves of castor tree (*Ricinus communis* L.)(Shaban et al., 2008), *Azadirachta indica* (Neem) leaf powder (Krishna & Arunima Sharma, 2004) in raw or modified forms are used to sequestrate heavy metals from waters and wastewaters.

The main objective of this study is to evaluate the potential of *Ageratum conyzoides* leaves powder as biomass to remove lead ions from synthetic aqueous solution. The surface of the sorbent was studied by high resolution microscopy. The influence of various parameters, related isotherm and kinetic models, and thermodynamic parameters were investigated for a better understanding of the biosorption process.To our best knowledge, this type of experiments used to test the biosorption affinity of *Ageratum conyzoides* leaves powder biomass has not been reported so far.

Materials and methods

Preparation of *Ageratum conyzoides* leaf powder: *Ageratum conyzoides* leaves were collected from ICFAI campus, Dehradun. *Ageratum conyzoides* leaves were washed thoroughly with water, and then with distilled water and completely dried in sunlight. The dry mass was grinded and the resulting powder was separated into different sizes (53, 75, 105, 125 and 152 µm) using BSS sieves. These size fractions were stored in air tight packing for further use as biosorbent.

Scanning electron Microscope (SEM) studies

The pretreated biosorbent samples were examined in Scanning Electron Microscope and electron probe micro analyzer. The samples were coated with ultra thin film of gold by an ion sputter JFC-1100 and exposed under SEM.The working height was 15 mm with a voltage ranging from 10 to 15 kV.The compositional image analyses of untreated and treated samples as shown in the Fig.1 (a, b) were taken using equipment (JEOL Ltd., Tokyo, Japan) at 15 kV and 40-100 nA beam current.

Metal solution preparation

The Pb stock solution was prepared by dissolving 1.615 g of 99% lead (II) nitrate (Merck, Germany) in 100 mL of ultrapure water, diluted with deionized water up to 1000 mL. The working solutions (20, 50, 100, 150 and 200 mg/L) were prepared by diluting the stock solution with double distilled water. The pH of the solutions was adjusted by the addition of 0.1 M HCl or NaOH. All chemicals used in the present study were of analytical grade

Batch Studies on Biosorption

The experimental tests were conducted in batch mode by varying parameters like biosorbent size (53-152 µm), agitation times (1-180min), pH from 2 to 8, initial concentrations of lead in aqueous solution with (50-200 mg/L), *Ageratum conyzoides* leaves powder dose (0.25-3.0g),temperatures (283-323 K), For each experiment, an accurate quantity of *Ageratum conyzoides* leaves powder was added to 50 mL of aqueous solution containing 20 mg/L concentration in conical flasks (250mL), shaken in a thermostatic shaker (180rpm). The suspensions were filtered with Whatman 41 filter paper. The lead (II) nitrate quantities before and after equilibrium were analyzed by atomic adsorption spectrometry (PerkinElmer 3030), and the adsorbed amount (qe) was calculated from the formula.

$$qe = V/m * (C0 - Ce) \qquad (1)$$

Where $C0$ and Ce are the initial and equilibrium concentrations (mg/L), m the amount of adsorbent (g), and V the volume of solution (L).The percentage removal efficiency (E%) of lead is calculated as

$$(E\%) = (C_0\text{-}C_t)\ x100/C_0 \qquad (2)$$

Equilibrium data obtained was analyzed using isotherm models (Langmuir, Freundlich, and Temkin).

Kinetic models:

Kinetics investigation provides information on the rapidity of the biosorption. In this study, pseudo-first-order, pseudo-second-order kinetic models in linearized form have been used to determine the rate-controlling steps in Pb(II) biosorption on *Ageratum conyzoides* leaf powder (Table1).

Thermodynamic parameters

The free energy change of sorption can be calculated by Eq. $\Delta G^0 = -RT \ln K$ (3).

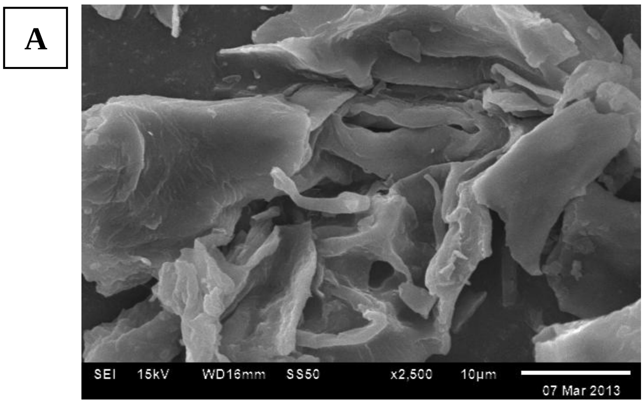
Where ΔG^0 is standard free energy change, R is the universal gas constant (8.314 J/mol/K), T is the absolute temperature and K is equilibrium constant. The apparent equilibrium constant of the biosorption, K'_c is obtained from Eq. $K'_c = C\ (\text{biosorbent})\ eq/C\ (\text{solution})$ (4).

Where C (biosorbent) eq and C (solution) eq are the metal ion concentrations on the biosorbent and in the solution at equilibrium.

Results and discussion

SEM analysis for untreated and treated *Ageratum conyzoides* leaf powder

The SEM pictures of untreated and lead treated *Ageratum conyzoides* leaf powder are shown in Fig.1 (a,b). It demonstrates that the surface morphology of powder is porous and uneven. The surface area analysis after lead loading confirms the increased surface area and porosity. The surface has a greater potential to biosorb metal.



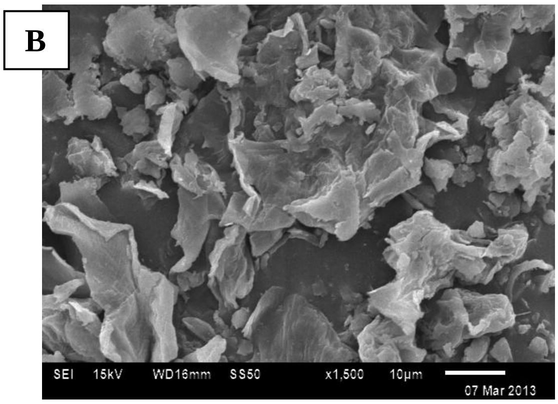


Fig.1 (a, b) Electron micrographs of untreated and lead treated *Ageratum conyzoides* leaf powder

Effect of biosorbent size

The variations in % biosorption of lead from the aqueous solution with biosorbent size are obtained. The results are drawn in fig. 2 with percentage biosorption of lead as a function of biosorbent size.

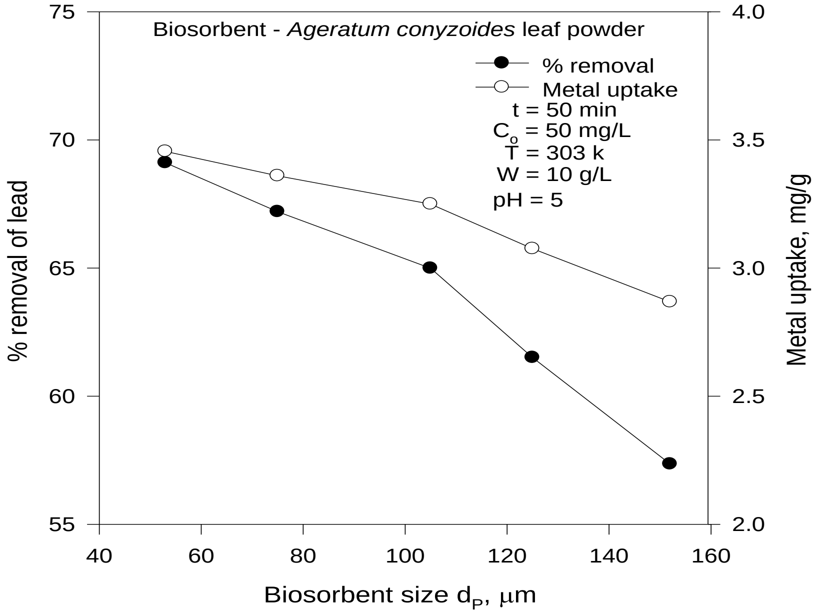


Fig.2 Percentage biosorption of lead as a function of biosorbent size

The percentage biosorption is increased from 57.35 % to 69.10 % as the biosorbent size decreases from 152 to 53 μm. This phenomenon is expected, as the size of the particle decreases, surface area of the biosorbent increases; thereby the number of active sites on the biosorbent also increases (Irina Morosanu et al., 2017; Waseem Mahyoob et al., 2022).

Effect of agitation time

Duration of equilibrium biosorption is defined as the time required for heavy metal concentration to reach a constant value during biosorption.The equilibrium agitation time is determined by plotting the % biosorption of lead against agitation time as shown fig.3 for the interaction time intervals between 1 to 180 min. For 53 μm size of 10 g/L biosorbent dosage, 53.952 % (2.6976 mg/g) of lead is biosorbed in the first 5 min. The % biosorption is increased briskly up to 50 min reaching 69.336 % (3.4668 mg/g).Beyond 50 min, the % biosorption is constant indicating the attainment of equilibrium conditions

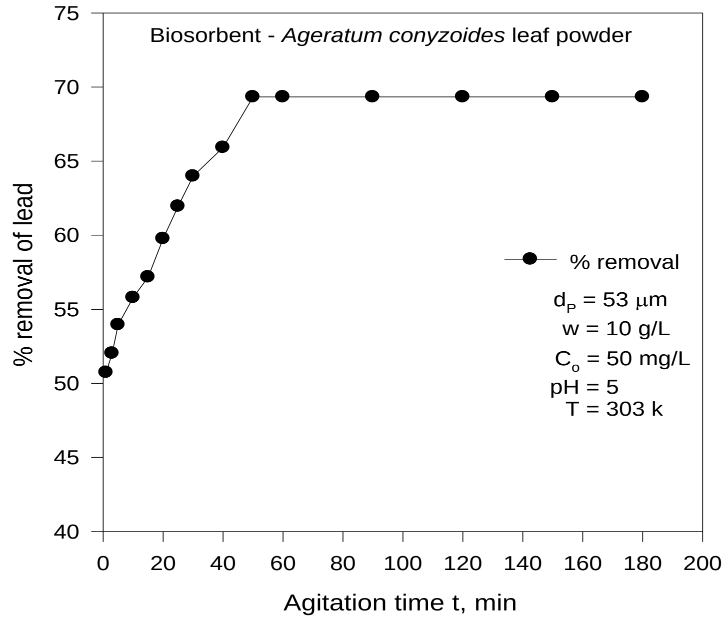


Fig.3 Effect of agitation time on % biosorption of lead

The maximum biosorption of 69.33 % is attained for 50 min of agitation time with 10 g/L of 53 μm size biosorbent mixed in 50 mL of aqueous solution (C_0 = 50 mg/L). The rate of biosorption is fast in the initial stages because adequate surface area of the biosorbent is available for the biosorption of lead. As time increases, more amount of lead gets biosorbed onto the surface of the biosorbent due to vanderwaal forces of attraction and resulted in decrease of available surface area. The biosorbate, normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers the surface, the biosorbent capacity is exhausted. The maximum percentage of biosorption is attained at 50 minutes. The percentage biosorption of lead becomes constant after 50 min. Therefore, all other experiments are conducted at this agitation time (Mahmood et al., 2017; El-Naggar et al., 2018).

Effect of pH

pH controls biosorption by influencing the surface change of the biosorbent, the degree of ionization and the species of biosorbate. In the present investigation, lead biosorption data are obtained in the pH range of 2 to 8 of the aqueous solution (C_0 = 50 mg/L) using 10 g/L of 53 μm size biosorbent.

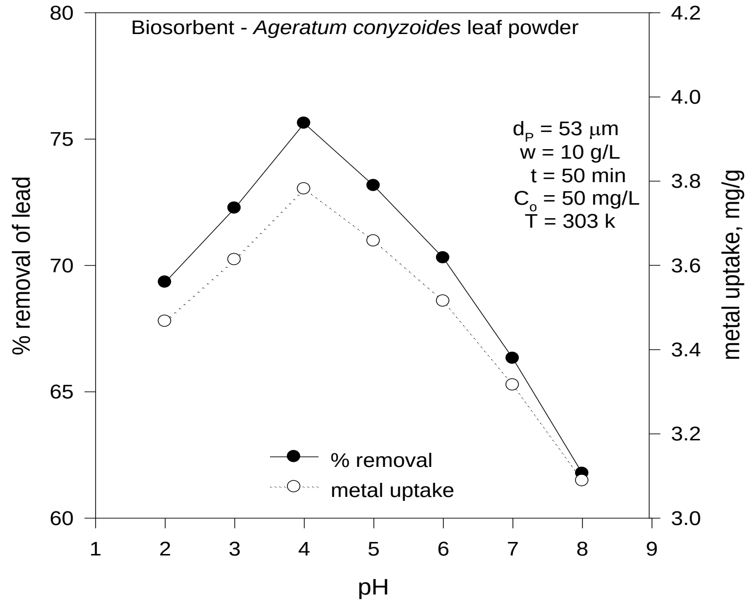


Fig.4 Observation of pH along with % biosorption of lead

The effect of pH of aqueous solution on % biosorption of lead is shown in fig.4. The % biosorption of lead is increased from 69.33 % to 75.62% as pH is increased from 2 to 4 and decreased beyond the pH value of 4.0. The percentage biosorption is decreased from pH 4 to 8 reaching 61.76 % from 75.62 %. Low pH depresses biosorption due to competition with H^+ ions for appropriate sites on the biosorbent surface. However, with increasing pH, this competition weakens and Lead ions replace H^+ ions bound to the biosorbent (Al-Qahtani et al., 2021; Khajavian et al., 2019)

Effect of initial concentration of lead

The effect of initial concentration of lead in the aqueous solution on the percentage biosorption of lead is shown in fig.5. The percentage biosorption of lead is decreased from 75.89 % to 60.007 % with an increase in C_0 from 20 mg/L to 200 mg/L. Such behavior can be attributed to the increase in the amount of biosorbate to the unchanging number of available active sites on the biosorbent(Chintalpudi et al., 2022; Coelho et al., 2022)

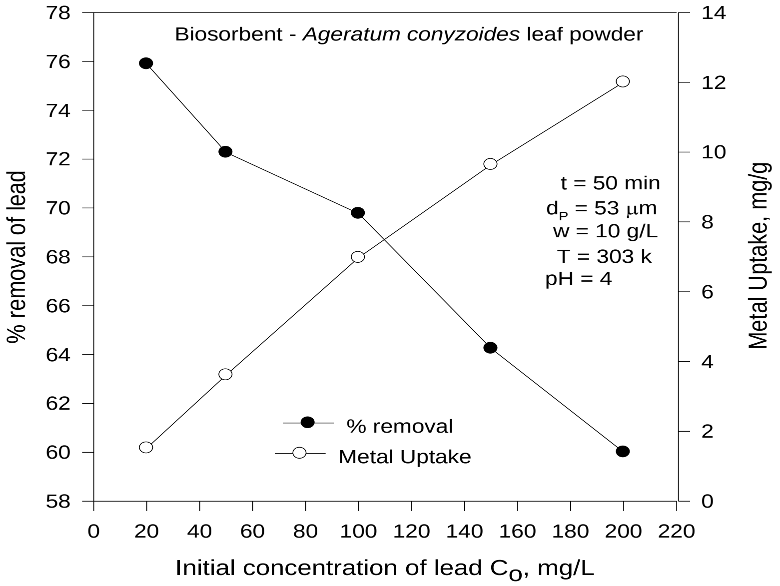


Fig. 5 Variation of initial concentration with % biosorption of lead

Effect of biosorbent dosage

The percentage biosorption of lead is drawn against biosorbent dosage for 53 µm size biosorbent in fig.6. The biosorption of lead increased from 63.67 % to 80.07 % with an increase in biosorbent dosage from 10 to 25 g/L. Such behavior is obvious because with an increase in biosorbent dosage, the number of active sites available for lead biosorption would be more. The change in percentage biosorption of lead is marginal from 80.07 % to 84.46 % when 'w' is increased from 25 to 50 g/L. Hence all other experiments are conducted at 25 g/L dosage (Guiyin Wang et al., 2018).

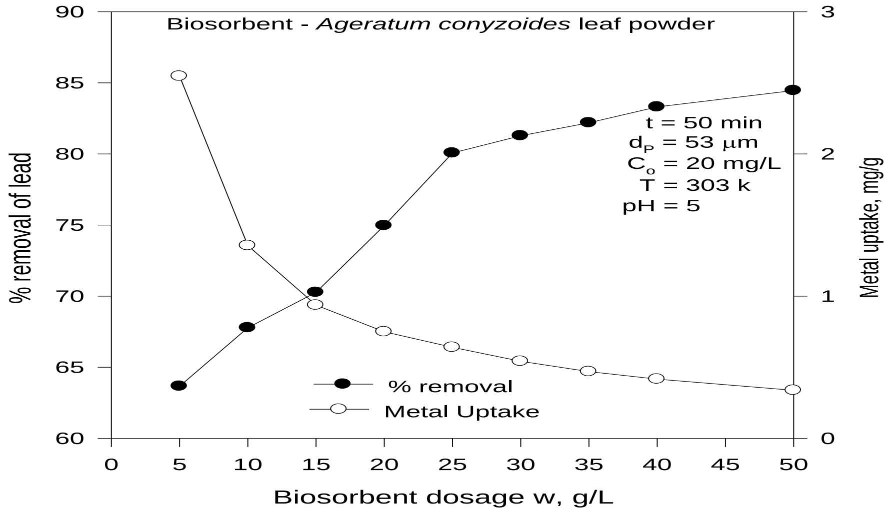


Fig.6 Dependency of % biosorption of lead on biosorbent dosage

Effect of Temperature

The effect of temperature on the equilibrium metal uptake was significant. The effect of changes in the temperature on the lead uptake is shown in fig.7. When temperature was lower than 303 K, lead uptake increased with increasing temperature. This response suggested a different interaction between the ligands on the cell wall and the metal. Below 303 K, chemical biosorption mechanisms played a dominant role in the whole biosorption process, biosorption was expected to increase by increase in the temperature, while at higher temperature, the plant powder were in a nonliving state, and physical biosorption became the main process. Biosorption for the present study has increased as the process is endothermic and a slight increase in % biosorption is found with further increase in temperature above 303 K (Smoczyński et al., 2020;García-Rosales et al., 2012).

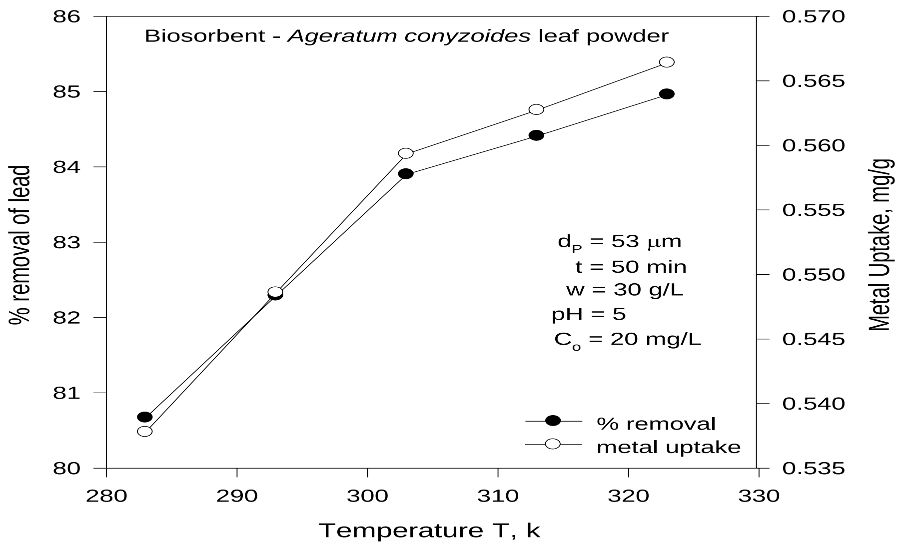


Fig.7 Effect of temperature on % biosorption of lead

Langmuir isotherm

Langmuir isotherm (Langmuir,1918) is drawn for the present data and shown in fig.8. The equation obtained 'n' $C_e/q_e = 0.04554\ C_e + 3.05236$ with a good linearity (correlation coefficient, R^2~0.9939) indicating strong binding of lead ions to the surface of *Ageratum conyzoides* leaf powder.

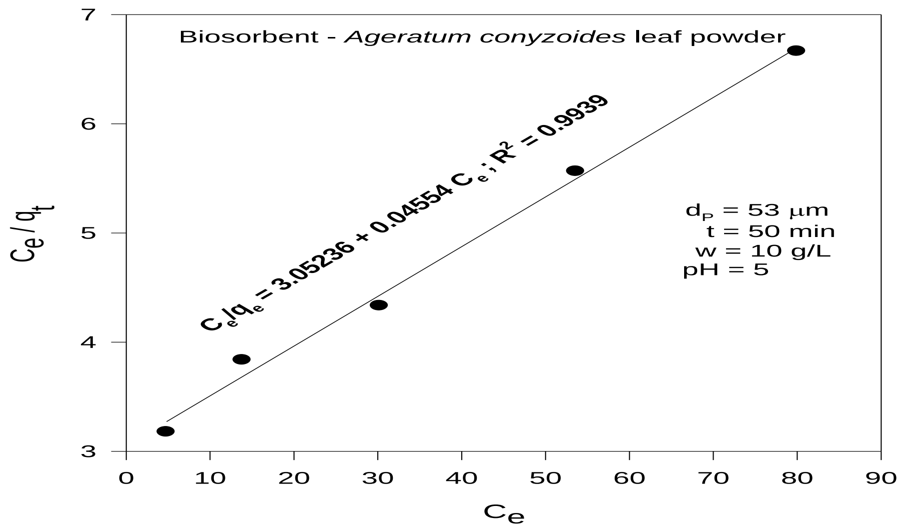


Fig.8 Langmuir isotherm for % biosorption of lead

Freundlich isotherm

Freundlich isotherm (Khayyun et al., 2019) is drawn between ln C_e and ln q_e in fig.9 for the present data. The resulting equation has a correlation coefficient of 0.9926; ln q_e = 0.7452 ln C_e - 0.7020; The 'n' value in the above equations satisfies the condition of $0 < n < 1$ indicating favorable biosorption.

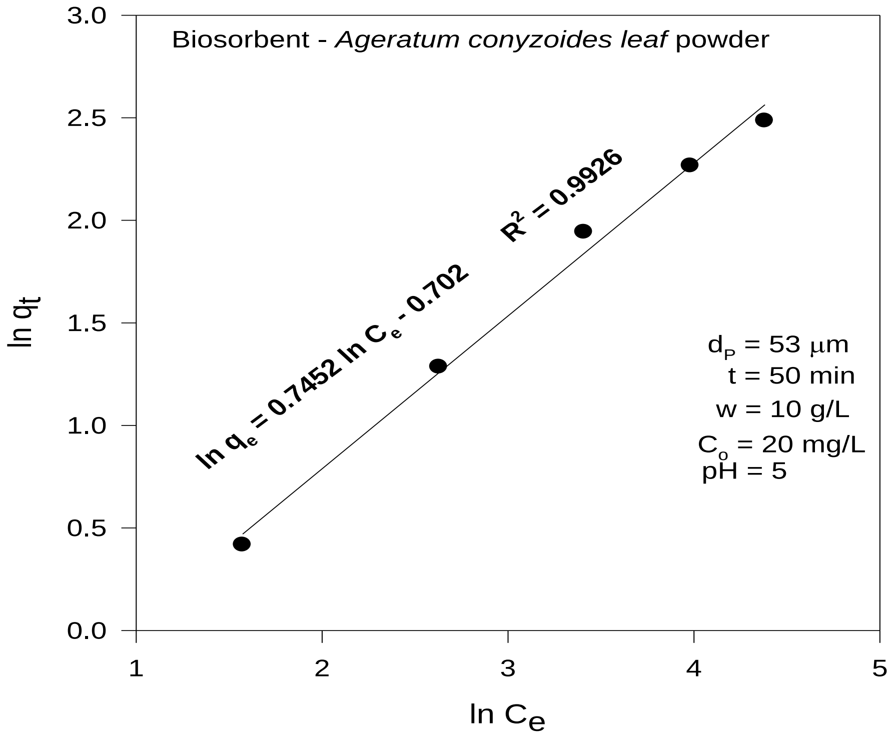


Fig.9 Freundlich isotherm for % biosorption lead

Temkin isotherm

The present data are analyzed according to the linear form of Temkin isotherm (Temkin & Pyzhev 1940) and the linear plot is shown in fig.10. The equation obtained for lead biosorption is: $q_e = 3.7447 \ln C_e - 5.2151$ with a correlation coefficient 0.9627. The best fit model is determined based on the linear regression correlation coefficient (R). From the Fig. 8, 9, 10 it is found that biosorption data are well represented by Langmuir isotherm with higher correlation coefficient of 0.9939, followed by Freundlich and Temkin isotherms with correlation coefficients of 0.9926 and 0.9827 respectively.

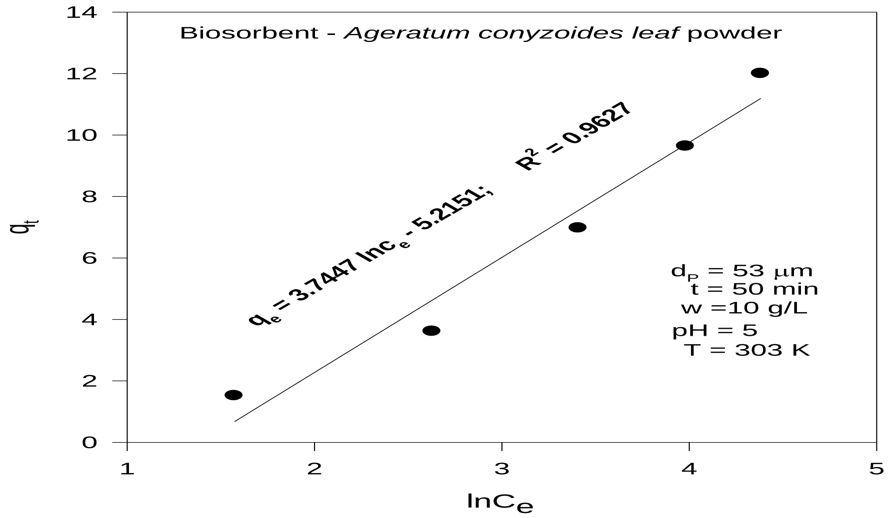


Fig. 10Temkin isotherm for % biosorption of lead

The resulting calculated constants are shown in Table1.

Table.1

Isotherms constants

Langmuir	Freundlich	Temkin
q_m = 21.958	K_f = 0.4955	A_T = 0.2484
K_L = 0.0149	n = 0.7452	b_T = 672.7219
R^2 =0.9939	R^2 =0.9926	R^2 =0.9627

Kinetics of biosorption

In the present study, the kinetics are investigated with 50 mL of aqueous solution (C_0= 50 mg/L) at 303 K with the interaction time intervals of 1 min to 180 min. Lagragen plots of log (q_e-q_t) versus agitation time (t) for biosorption of lead the biosorbent size (53 µm) of *Ageratum conyzoides leaf powder* in the interaction time intervals of 1 to 180 min are drawn in Fig.11&12.

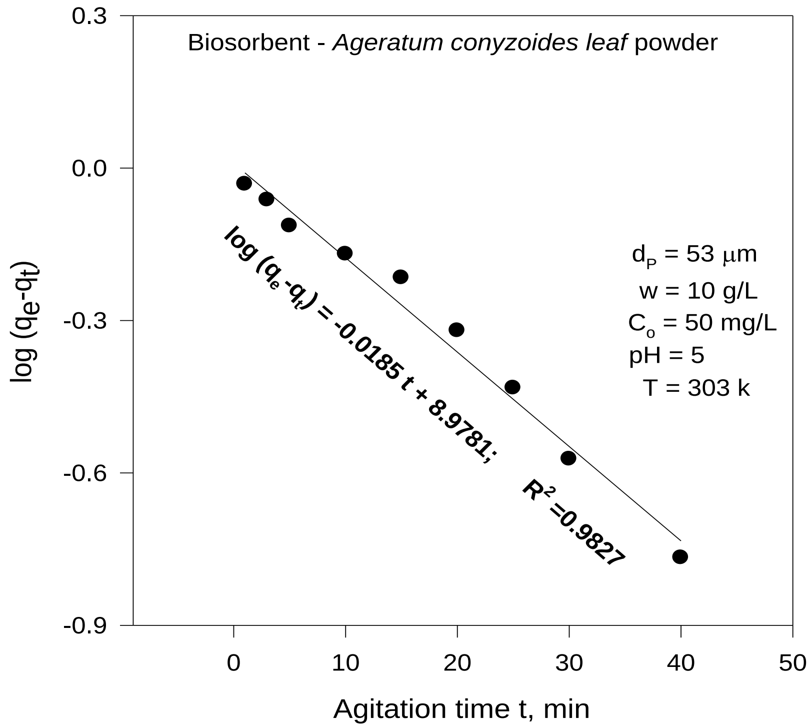


Fig.11 first order kinetics for % biosorption of lead

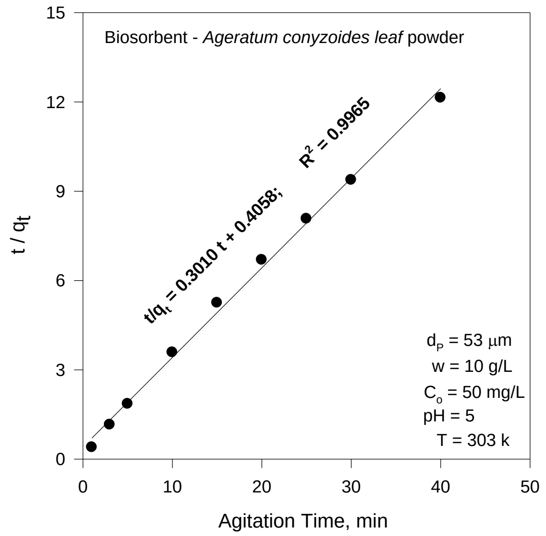


Fig. 12 Second order kinetics for % biosorption of lead

The resulting equations and constants are shown in table 2.

Table-2 Kinetics equations and coefficients

Order	Equation	Const	R^2
I^{st}	log (qe-qt) = -0.0185 t + 8.9781	K_1 = –0.0426 min^{-1}	0.9827
II^{nd}	t/qt = 0.3010 t + 0.4058	K_2 = 0.2232 g/(mg-min)	0.9965

As the correlation coefficient values for the pseudo second order kinetics (Gialamouidis et al., 2010) (R^2 = 0.9965), and lagergren first order kinetics (R^2 = 0.9827) are nearly same we can say that both the equations describes the mechanism of lead – *Ageratum conyzoides* leaf powder.

Thermodynamics of biosorption

Experiments are conducted to understand the biosorption behavior by varying the temperature from 283 to 323 K. The Van't hoff (Aksu et al., 2005) plot for the biosorption of lead is obtained and is shown in fig. 13.

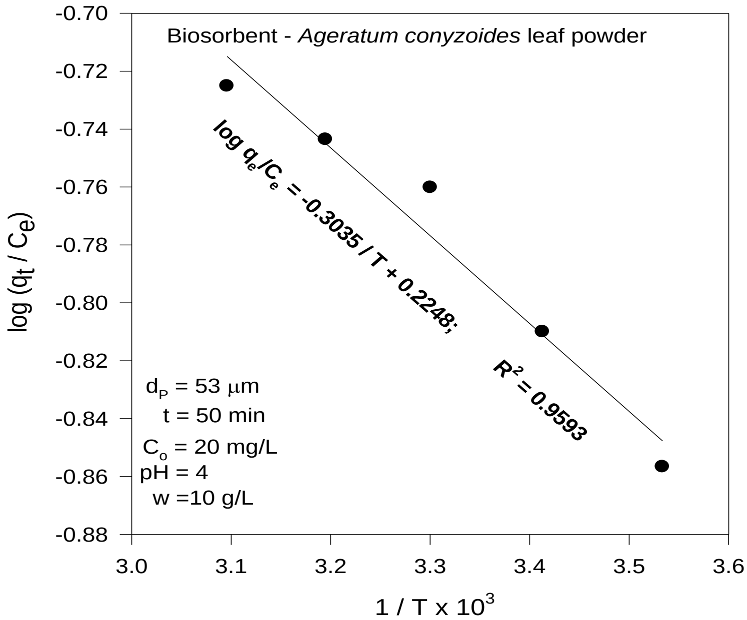


Fig.13 Van't hoff plot for % biosorption of Lead

The calculated values obtained are ΔG = –1298.3849, ΔH = 5.811157 and ΔS = 4.3042775 and signify that the entire process is endothermic, spontaneous and irreversible. The process of biosorption involves a solid phase (sorbent) and a liquid phase (solvent) contains a dissolved species to be sorbed. Due to high affinity of the sorbent for the metal ion species, the latter is attracted and bound by rather complex process affected by several mechanisms involving chemisorption, complexation, adsorption on surface and pores, ion exchange, chelation, adsorption by physical forces, entrapment in inter and intrafibrillar capillaries and spaces of the structural polysaccharides network as a result of the concentration gradient and diffusion through cell wall and membrane

Plants and marine seaweed as biosorbents

Plants, as agricultural waste materials and food industries discarded material have been used as biosorbents as shown in table 3, it is a form of reusing and recycling those waste materials thus no significant costs are associated with using plant materials. The potential of plant biosorbents are mainly due to the presence of carboxylic and phenolic functional groups in the cellulosic matrix or components associated with cellulose such as lignin and hemicelluloses (Bilal et al., 2018). Aloe vera wastes were used as biosorbent for the removal of lead from water; it was found that the carboxyl, carbonyl and hydroxyl groups facilitated metal binding (Qasem et al., 2021,).

Table 3

Lead uptake capacities for different biosorbents

Biosorbent	q_t, mg/g	Authors
Ageratum conyzoides leaf powder	21.958	Present investigation
rice husk ash	158	S.A. Abo-El-Enein *et al.*,2009
Pokeweed (untreated)	13.19	Wang *et al.*,2018
Sargassum	20.2	Vijayaraghavan *et al.*,2009
black carrot	5.003	Fuat Guzel *et al.*,2008
Spirogyra sp.	140.84	Gupta *et al.*,2008
Ponkan peel	112.1	Flavio *et al.*,2008
Lactarius scrobiculatus	56.2	Ruhan *et al.*,2009

Conclusion

The *Ageratum conyzoides* leaf powder was used as an effective low cost biosorbent for the removal of lead in aqueous solution. The equilibrium agitation time for lead biosorption was 50 minutes. The percentage removal of lead increased significantly with an increase in biosorbent dosage from 20 mg/L to 200 mg/L. In the range of variables optimized, percentage removal of lead increased to (89.1697 %) at pH 4. The maximum uptake capacity of biosorbent at 21.958 mg/g is obtained at 303 K. Langmuir equilibrium isotherm model (R^2=0.9939) proved to be good fit for the experimental data of lead biosorption on *Ageratum conyzoides* leaf powder. The kinetics of the biosorption of lead described by a pseudo-second-order kinetic model with (R^2=0.9965). The negative value of DG and the positive values for DH and DS indicated the spontaneity, endothermic nature and randomness of the process under study. *Ageratum conyzoides* leaf powder can be used in cleaning lead polluted water and it is eco-friendly, effective, affordable. Further research includes more investigations regarding the operating parameters of waste water containing lead.

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