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Assessment of Surface Properties of *Benincasa Hispidia* and *Cucurbita* peels for Chromium Uptake

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Abstract

This study investigates the chromium adsorption feasibility by agricultural waste based activated ash gourd (AGP) and activated pumpkin peels (APP) by employing Kinetic models (Intra – particle diffusion, Elovich, First order and Second order models) and non – linear isotherms (Langmuir and Freudlich) models. The surface morphology and pore size distribution of AGP and APP were measured using Scanning Electron Microscope (SEM), Energy Dispersive X-ray Measurements (EDAX), and Brunauer Emmett Teller (BET). The adsorption data reveals fixing on Elovich equation with correlation coefficient (R^2) of 0.97 and 0.94 respectively for AGP and APP as compared to 0.89 and 0.91 for diffusion model. These finding suggest the predominantly physical adsorption behaviour of total chromium by both the adsorbents. Freundlich's isotherm model showed a better fit than Langmuir's equation for AGP and APP with lesser Chi square (χ^2) error of 0.31 and 1.11 respectively against that of Langmuir with 8.11 and 11.14 indicates the heterogeneous surface of these agricultural based adsorbents.

Keywords: Bioadsorbents, Elovich, Intra-particle diffusion and Non-linear Regressions

Introduction

Heavy metals are known toxic environmental pollutants. Some of the most toxic heavy metals includes chromium, arsenic, cadmium, mercury, lead, nickel, and zinc [1]. Various natural and anthropogenic sources of heavy metals include soil erosion, natural weathering, mining, industrial effluents and many others [2].The most commonly occurring forms of Chromium are Cr^{3+} and Cr^{6+}. Toxic Chromium are generated from welding on stainless steel, metal structures coated with chromate paints, sewage and fertilizers [3], electroplating (chrome plating), leather tanning, textile dyes, pigments in paints, inks and plastics etc. [4] leading to an adverse effects on both ecological and biological species. Ingestion of chromium causes cancer, haemorrhaging, irritation in the nose, lungs and throat and ulcers. Due to ample abundance of oxygen in the environment, lesser toxic Cr (III) gets reduced to highly toxic and soluble Cr (VI). Thus, becoming major concerns for its removal.

Many conventional and non - conventional methods were employed by several researchers for the removal and reduction of chromium ions from aqueous solutions. Some of the methods are chemical precipitation, reverse osmosis, ion exchange, electro - dialysis, adsorption and bio – sorption [4]. Among these methods, bio – adsorption is most commonly used in the past decade due to its cost effectiveness, technical feasibility, eco - friendly, easy handling and abundant availability of low cost bio – adsorbents.

In this study, activated carbon derived from Ash Gourd (AGP) and Pumpkin peels (APP) used for chromium removal were analysed by intra - particle diffusion model. Batch experiments were conducted at different pH, concentration and contact time. The parameters were analysed using different non – linear kinetic models and Isotherms.

Materials and Methods

A. Preparation and Characterization

Ash Gourd and Pumpkin used as adsorbents were procured from local market. They were peeled, washed and oven dried at 80 ^{0}C for 12 hours. The Ash gourd and pumpkin peels were crushed into fine powders and were further impregnated with H_3PO_4 acid and activated in the muffle furnace at 300 ^{0}C and 250 ^{0}C respectively. The activated carbons were washed thoroughly and oven dried at 100 ^{0}C and allowed to pass through 125 mesh size screen. The dried and activated carbon were then stored in the desiccator for further use.

To understand the surface morphologies and textures of the activated carbons, Scanning Electron Microscopy (SEM) (Sigma 300) was operated at 5.00 kV, magnification 100.00 KX coupled with Energy dispersive X-ay analysis (EDAX) (Zeiss Gemini) to give the confirmation for total chromium removal after the adsorption processes. Brunauer-Emmett-Teller (BET) analyser was also used to determine the size distribution and mean particle sizes of both the adsorbents [5].

B. Batch Experiments

The stock solution (1000 mg/L) was prepared by dissolving required amount of $K_2Cr_2O_7$ in double distilled water. A series of sample solution were further diluted from the stock solution and appropriate amounts of both the adsorbents were added onto the series of 500 mL Tarson beakers at various initial chromium concentrations. The solution were operated in the orbital shaker at 250 rpm (Phipps and Bird Jar Test Apparatus, (PB-600) for 150 min. All the experiment tests were conducted in triplicates and if the average value has more than a standard deviation of 5, the values are discarded and the experiments are repeated again to avoid any experimental errors. The samples were then diluted and filtered using Whatman No. 47 filter paper. Finally, the filtered solution were determined by Atomic Absorption Spectroscopy (AAS, Perkin Elmer, USA) and UV Visible Spectrometer (Evolution 201, Thermo Fischer Scientific) at a wavelength of 540nm. Cr (III) reduced is calculated from the difference between the total chromium and Cr (VI) adsorbed. The adsorption capacity is given by:

$$q = \frac{C_o - C_t}{m} V \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where, q is the amount of adsorbed in mg/g, C_o and C_t are the initial and final concentrations, m is the mass of the adsorbent used and V is volume of the solution in litres.

C. Kinetics, Isotherms and Error analysis

In order to stimulate the adsorption kinetics, intra – particle diffusion model (IDP), Elovich model, Pseudo 1st order and 2nd order equations were applied for chromium – AGP and APP interactions. After the attainment of equilibrium conditions, Langmuir and Freundlich Isotherm models were applied to better understand the monolayer adsorption by identical sites and/or surface heterogeneity of the adsorbents respectively [5]. The non – linear regression involves the error distributions between the calculated and predicted values based on the convergence data and were used for analysing the adsorption processes. Lower values of χ^2 indicated the similarities of the data experimented.

$$X^2 = \sum_{i=1}^{n} \frac{(q_{e,cal.} - q_{e,pred.})^2}{q_{e,pred.}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Results and Discussions

A. Characterization

The SEM analysis of AGP and APP before and after total chromium adsorption indicates the presence of large sizes pores on their surfaces, which were responsible for the enhancement of the adsorption of chromium ions. The SEM images are shown in Fig 1. The hollow and porous portions available on the surfaces binds the adsorbate with the adsorbents [6]. The chemical nature of the adsorbents before and after the adsorption were obtained from the EDAX analysis. It focuses on the different areas and the peaks are shown in Fig 2 (1B and 2B), confirming the presence of chromium after the adsorption processes. The specific surface area, pore sizes and volume distributions were studied using BET method. The particulate properties are listed in Table 1.

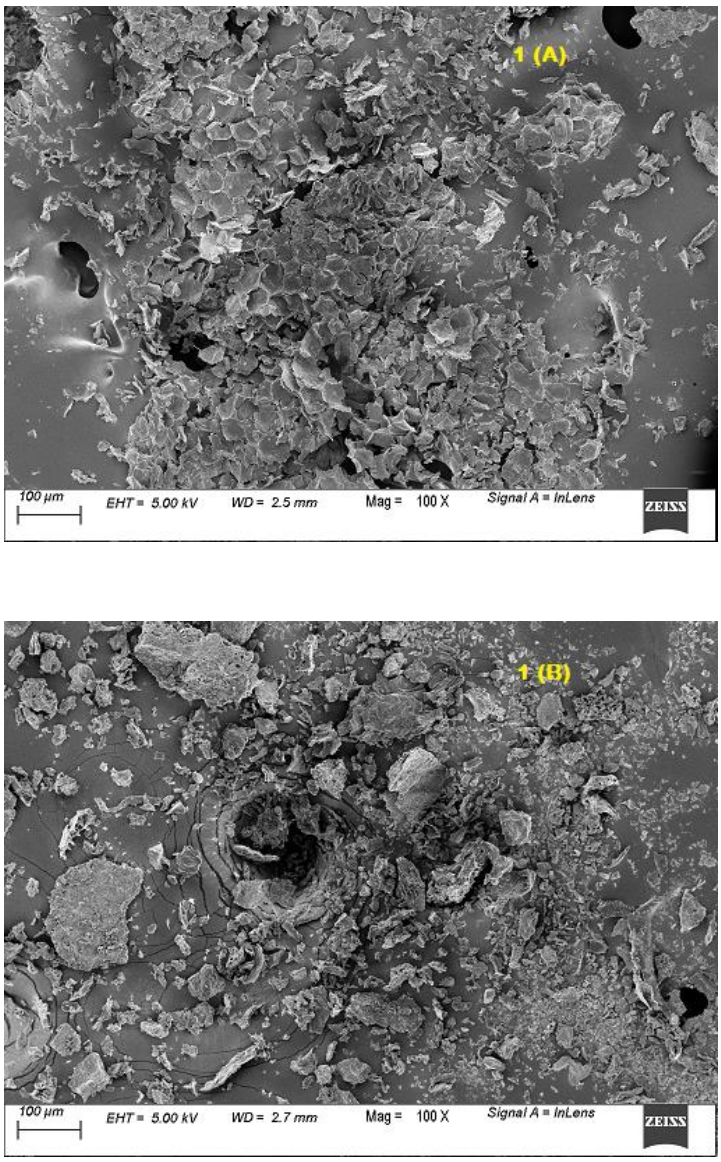


Fig. 1: SEM images (A) before and (B) after adsorption of total chromium by AGP

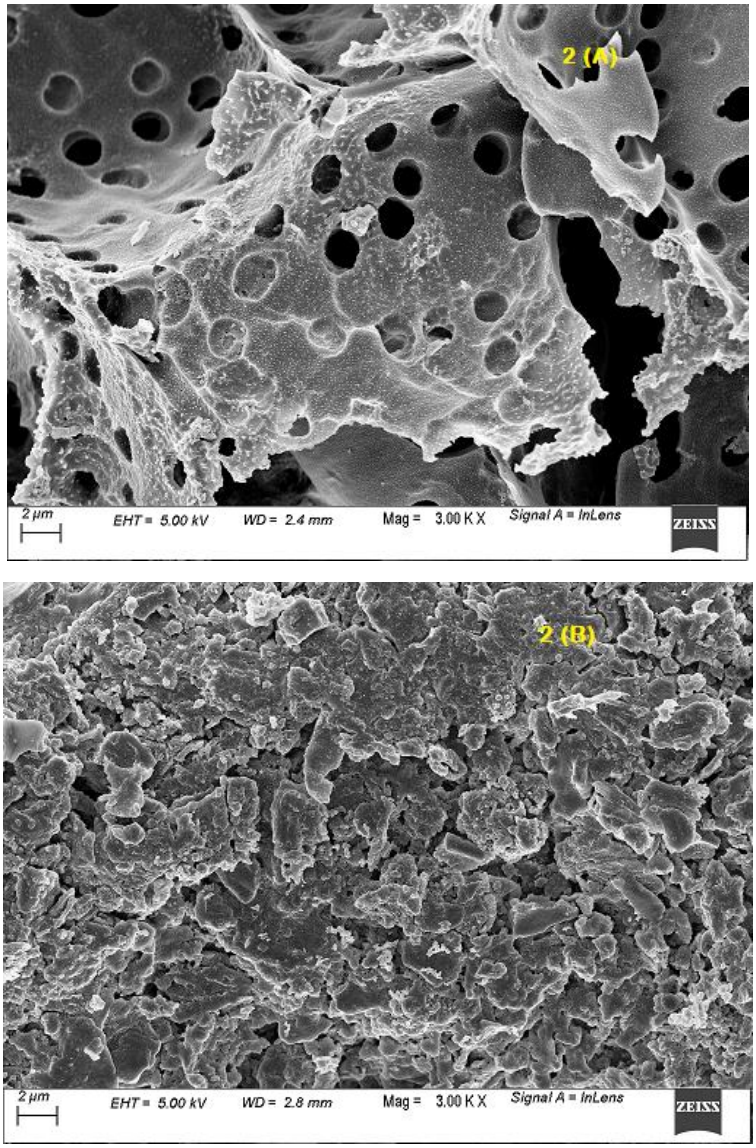
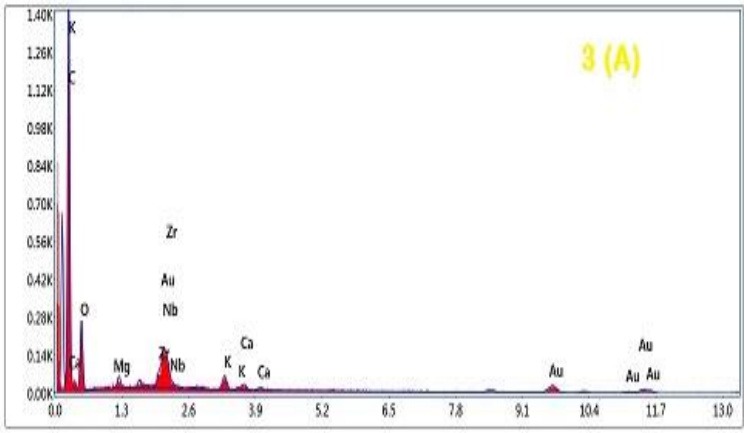


Fig. 2: SEM images (A) before and (B) after adsorption of total chromium by APP



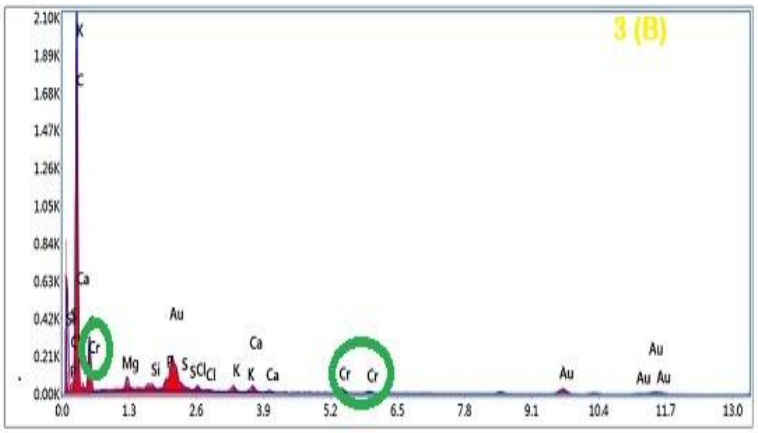


Fig. 3: EDAX images (A) before and (B) after adsorption of AGP

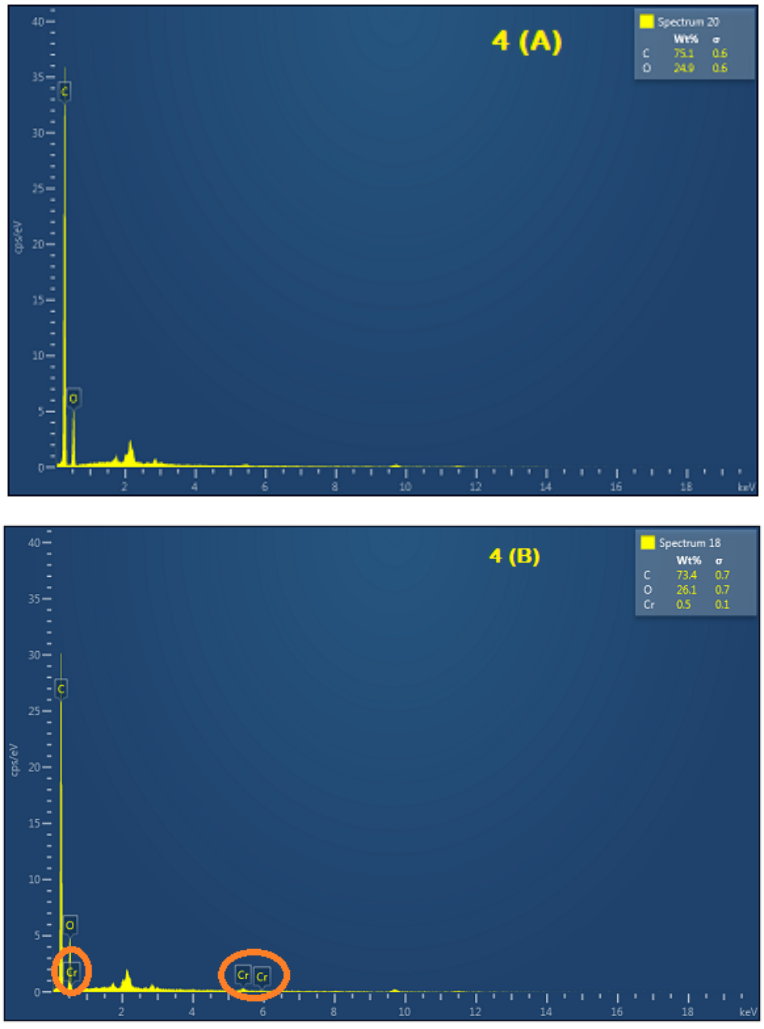


Fig. 4: EDAX images (A) before and (B) after adsorption of total chromium by APP

Table 1: BET analysis data for AGP and APP adsorbents

Adsorbents	Surface Area (m^2/g)	Average pore diameter (nm)	Pore volume (cm^3/g)
AGP	36.036	7.612	0.153
APP	33.979	4.102	0.175

B. Adsorption kinetics

For any adsorption system design, prediction of kinetic models is most important [7]. The initial adsorption was analysed by Intra – particle Diffusion model. It is a 3 step process, external diffusion, diffusion inside the pores and diffusion on the surface phase. This step determines the rate of the reaction. It is given by:

$$q_t = K_{IPD} t^{1/2} + C \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where, q_t is the adsorption capacity in mg/g, K_{IPD} is the rate constant in mg/g $min^{1/2}$ and C is the boundary thickness in mg/g.

The intra – particle diffusion model fit and data for chromium adsorption onto the adsorbents AGP and APP is shown in the Fig. 5 and Table 2. The first phase ranges from 5 to 20 min of contact time with rapid removal from 26% to 72% and the second phase from 20 to 120 min with removal from 72% to 86%. The initial stage indicates rapid fast adsorption, where rates (K_{IPD}) and boundary thickness (C) increases with the increase in concentration. But the second stage indicates slower rates.

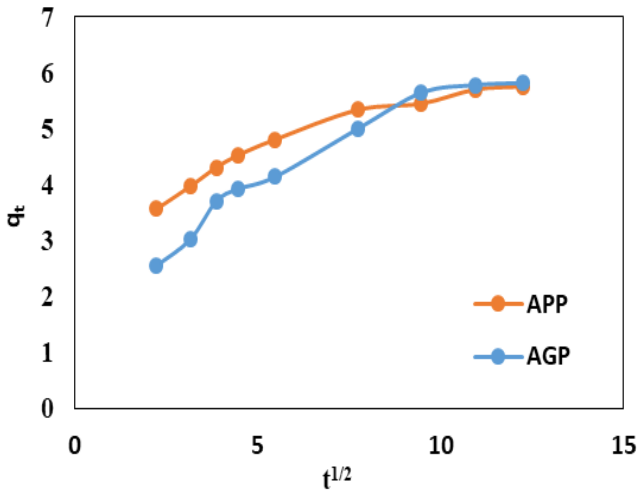


Fig. 5: Intra – particle diffusion model plot for chromium adsorption by AGP

The Non – linear kinetic models of Elovich, first order and second order kinetic equations are given by:

$$q_t = \frac{1}{\beta}\ln(1 + \alpha\beta t) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$$q_t = q_e - e^{-K_1 t} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where, q_t is the adsorption capacity in mg/g, α and β are Elovich constants in mg/g min and g/mg respectively, t is the time in min, q_e is the amount adsorbed at equilibrium in mg/g, $K_1$and K_2 are the first order and second order constants in /min and mg/gm min respectively.

The plots for all the three models (Elovich, First order and Second order) are shown in Fig. 6 and 7 for both the adsorbents AGP and APP. The Elovich coefficients (α and β), rate constants (K_1 and K_2), adsorption capacities (q_e), correlation coefficients (R^2) and χ^2 for both the adsorbents for all kinetic models are given in Table 2. The evaluated data of R^2clearly indicates that Elovich model have performed better for both the adsorbents. The first and second order kinetics are discarded due to higher χ^2 values (5.33 and 1.74) and lesser R^2 (0.84 and 0.66) values. Considering all the evaluated values, the kinetics of adsorbents (AGP and APP) adsorption can be described in the order of fitting: Elovich, Pseudo second order and Pseudo first order equations.

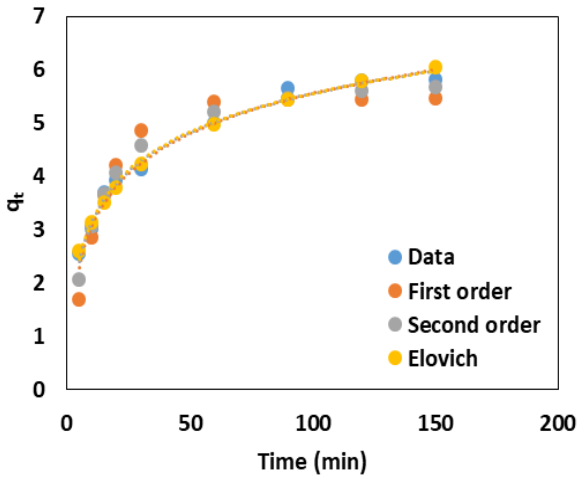


Fig. 6: Non – linear fit of kinetic models for chromium adsorption by AGP

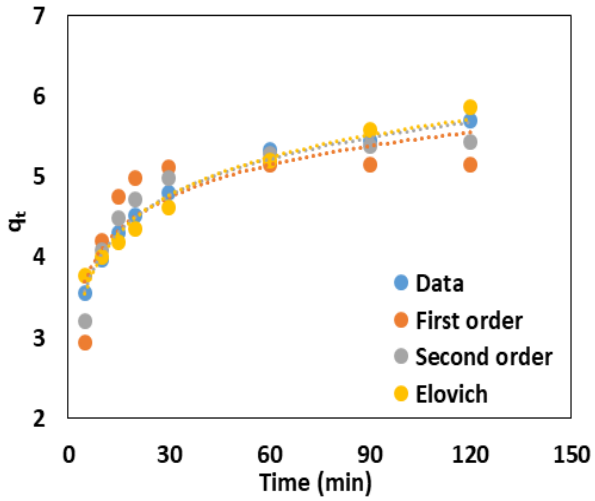


Fig. 7: Non – linear fit of kinetic models for chromium adsorption by APP

Table 2: Parameters of different Kinetic models

Kinetics							
Intra – particle diffusion model					*Pseudo first order*		
	K_{IPD} (mg/g $min^{1/2}$)	C	R^2	χ^2	K_1	R^2	χ^2
AGP	1.86	0.24	0.89	2.56	5.45	0.84	5.33
APP	2.89	0.14	0.91	1.562	5.15	0.66	1.74
Elovich model					*Pseudo second order*		
	α (mg/g min)	β (g/mg)	R^2	χ^2	K_2	R^2	χ^2
AGP	1.20	3.62	0.97	0.132	0.62	0.93	6.13
APP	1.19	1.95	0.94	1.254	1.51	0.91	3.21

C. Adsorption Isotherm

The adsorption isotherm indicates the molecular distribution phenomena of adsorbate adsorbent interaction phase on reaching the equilibrium [7]. Langmuir and Freundlich isotherm models are analysed for the theoretical evaluation and interpretation of all the predicted data for equilibrium adsorption capacity of chromium on both the adsorbents (AGP and APP). The equations are given by:

$$q_e = \frac{K_L C_o}{1 + a_L C_o} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (7)$$

$$q_e = K_F C_e^{1/n} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (8)$$

Where, q_e is the amount adsorbed at equilibrium in mg/g, K_L and K_F is the Langmuir and Freundlich constant in L/g, C_o and C_e are the initial and equilibrium concentrations in mg/L.

The parameters of both the Langmuir and Freundlich equations were evaluated by using non – linear regression analysis and are summarized in Table 3. The experimental data and plots for both the adsorbents are shown in Fig. 8 and 9 for both the adsorbents AGP and APP. The values of χ^2 and R^2 suggest that Freundlich isotherm is the better fit isotherm for both the adsorbents (AGP and APP). The Freundlich isotherm exponents indicates the surface heterogeneity and formation multiple layer physisorptions. The maximum adsorption capacity obtained were 8.429 mg/g and 6.214 mg/g for the adsorbents AGP and APP respectively.

Table 3: Parameters of Langmuir and Freundlich Isotherm non – linear models

Langmuir Isotherm						**Freundlich Isotherm**				
Adsorbents	**K_L**	**a_L**	**R^2**	**SD**	**$\sum\chi^2$**	**K_f**	**b_F**	**R^2**	**SD**	**$\sum\chi^2$**
AGP	1.11	0.48	0.91	0.03	8.114	1.09	1.93	0.99	0.08	0.31
APP	0.62	-0.3	0.90	0.32	11.241	9.86	1.14	0.96	0.4	1.115

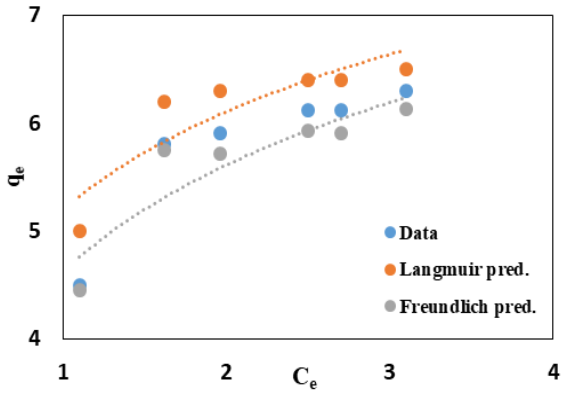


Fig. 8: Langmuir and Freundlich isotherm for total chromium adsorption by AGP

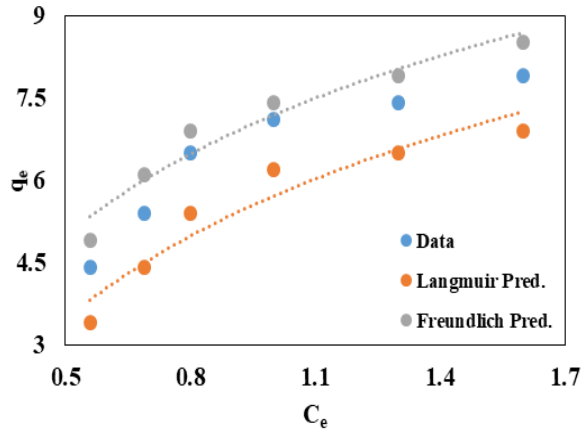


Fig. 9: Langmuir and Freundlich isotherm for total chromium adsorption by APP

Conclusion

The experimental data were tested against the different models. The data evaluated in the previous findings for the linear regression fitted better with pseudo second order kinetics with a correlation coefficient R^2 of 0.99 and $\chi 2$ of 0.012 [8]. But for the non – linear regression, the adsorption process follows Elovich kinetic model with R^2 of 0.97 and 0.94 for AGP and APP respectively. The adsorption follows Freundlich isotherm model with a maximum adsorption capacity of 8.429 mg/g and 6.214 mg/g and R^2 value of 0.99 and 0.96 for AGP and APP respectively. This study proves that both the bio – adsorbents AGP and APP are suitable for the removal of total chromium from aqueous solutions containing chromium ions.

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