



## Efficacy of bio-carbon mediated chromium absorption from contaminated groundwater: A kinetic approach

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The present study aims to investigate adsorption of chromium ions from affected groundwater of Ukhrul district in Manipur. Hydroxyl and amines functionalized bio-adsorbent, Ash gourd (*Benincasa hispida*) [AGP] peel was employed as adsorbent in batch mode. For effective adsorption of chromium ions, the chemical modification of AGP was functionalized through treatment with phosphoric acid ( $H_3PO_4$ ), in order to induce more number of -OH groups onto the adsorbent surface. The physico-chemical properties of the prepared bio-carbon was characterized by their adsorptive nature towards zero point charge to estimate their surface charge density. SEM and EDAX analysis were done for determining the characteristics of the material. The AGP removed Cr(VI) from the aqueous synthetic solution and actual groundwater with maximum removal efficiency of 82.37% and 76.58% respectively from the conducted batch adsorption at optimized parameters (pH = 2, adsorbent dose = 3 g/L, temperature  $25\pm 5^\circ C$ , agitation speed 250 rpm) after a reaction time of 180 min. The results showed that adsorption of chromium by AGP reached to equilibrium at 120 min thereafter, a minimal or no change of Cr(VI) removal was observed. The decreased in removal efficiency of the actual groundwater sample suggests the interference of co-ions present in the sample. The conducted adsorption studies explained that the data fitted well with Langmuir and Freundlich isotherms for both the synthetic as well as actual groundwater with a co-relation coefficient greater than 0.95.

Keywords: Adsorption, bio-adsorbent (*Benincasa hispida*), Cr(VI) removal, groundwater, isotherms.

### Introduction

Heavy metals are considered as prime pollutants and must be eliminated or reduced from the water bodies. Chromium is listed as one of the 14 most noxious heavy metals by the Environmental Protection Agency (EPA). Discharge of chromium metal affects the surface and groundwaters. Cr(VI) is considered very toxic, due to the association of chromium with oxygen as chromate ions ( $CrO_4$ )<sup>2-</sup> which is known to be an agent that oxidises strongly. Cr(VI) has high mobility, which makes it capable to contaminate groundwater. Cr(VI) is highly reactive and possesses carcinogenic properties<sup>1</sup>, due to which on exposure harms liver, kidney, lungs, skin and even our digestive systems<sup>2</sup>. Inhalation of Cr(VI) causes acute toxicity and asthma<sup>3</sup>.

Chromite is a major source of chromium, which is a lustrous and brittle metallic element. It is anti-corrosive and polishable being tarnish resistant. In India, Odisha is the sole producer of chromite ore, Karnataka is the second largest

producer and Krishna district of Andhra Pradesh, Ukhrul and Tamenglong districts of Manipur are other producers of chromite ores<sup>4</sup>. In Manipur, chromite is mainly found at places of Phangrei, Lunghar, Sirohi and Chatrik in Ukhrul district<sup>5</sup>. They are also known for receiving heavy rainfall throughout the year, making the areas vulnerable to contamination by chromite run-offs. As per World Health Organization (WHO), maximum permissible limit of chromium concentration is 0.0001 g/L in drinking water and 0.0005 g/L in wastewater for Cr(VI)<sup>6</sup>. Hence, it has become a must to eliminate or reduce chromium deposits from the water bodies. Numerous conventional techniques were employed for the separation of Cr(VI). Lime is used as a precipitant for the removal of Cr(VI) from wastewater, reporting an efficiency of 99.37%<sup>7</sup>. But its disposal cost is high due to the production of secondary waste such as metal hydroxide sludge and gypsum<sup>8</sup>. Coagulation and flocculation for the removal of chromium using polyethylene amine gives maximum removal of 99% but has a high dependency on raw water quality and is highly expensive.

Ion exchange method has a demerit for loss of exchange capacity in presence of oxygen<sup>9</sup> and in the membrane treatment method the membrane needs to be cleaned frequently also leading to high capital cost<sup>10</sup>. Various bio-adsorbents like porous activated carbon<sup>11</sup>, peanut husk powder<sup>12</sup>, orange peel<sup>13</sup> etc. were also employed for the removal of chromium ions at an optimum adsorbent dosages which were well fitted to various adsorption isotherm models. So among these, bio-adsorption can be considered as the most suitable alternative for purification of Cr(vi) contaminated water due to its operating comfort, effectiveness and economical feasibility. Various bio-adsorbents such as husk of raw rice, pertite, coir pith and vermiculite were used for aqueous Cr(vi) removal<sup>14</sup>. So, an attempt has been made using Ash gourd peel to remove Cr(vi) from adulterant ground waters of Ukhrul district, Manipur.

In India, Ash gourd (*Benincasa hispida*) is cultivated all throughout the year. The peel constitutes 15% of the whole of Ash gourd and has a high waste index<sup>15</sup>. This work focuses on effective utilization of Ash gourd peel powder for the removal of Cr(vi) ions from the water bodies of Phangrei, Ukhrul District of Manipur, including physico-chemical properties, batch equilibrium studies and isotherms exploring Ash gourd as a novel bio-adsorbent. Effects related to pH of the solution, dosage of adsorbent, exposure time and inactive concentrations of chromium were also investigated. Energy Dispersive X-ray Analyser (EDAX) was employed to provide elemental identification and quantitative compositional information and Scanning Electron Microscopy (SEM) for the possible adsorption mechanism.

## Experimental

### *Chemicals and instruments:*

The chemicals used were of analytical grade and deionized water was used to prepare the aqueous solution. Moreover, the stock solution (1 g/L) of Cr(vi) was prepared by dissolving  $K_2Cr_2O_7$  salt in deionized distilled water. The solution pH were adjusted using 0.1 N NaOH or 1 N  $H_2SO_4$  solution using pH meter (PCS Testr 35). In the presence of 1,5-diphenylcarbazide reagent the chromium content in both the standard and treated solutions were determined using UV Visible spectrophotometer (Evolution 201) at a wavelength of 540 nm. And to determine the adsorbent characteristics

before and after the adsorption process, SEM (Scanning Electron Microscope) (Sigma-300) and EDAX (Energy Dispersive X-ray Analysis) (Zeiss Gemini) were used.

### *Adsorbent preparation:*

Ash gourd (*Benincasa hispida*) was purchased from a local market, it was then peeled, washed and dried at 80°C. The dried peels were crushed into fine powders and allowed to pass through 125 mesh size screen and labelled as AGP. The AGP was further treated using 10%  $H_3PO_4$  and kept in the dessicator for use at later stage.

### *Characterization:*

Scanning electron microscopy (SEM) was used to study the surface morphology of the activated carbon. SEM was operated at 5.00 kV, magnification 100X coupled with Electron dispersive X-ray analysis (EDAX) to give the confirmation for the presence of Cr(vi) after the adsorption process.

### *Determination of $pH_{pzc}$ :*

$pH_{pzc}$  is described as the pH at which the net charge of adsorbent's surface is equal to zero. The solid addition method was used for the calculation of  $pH_{pzc}$  of the samples. Herein, in 100 ml conical flasks NaCl solution of 0.01 M were prepared and boiled to get rid of  $CO_2$ . The pH ranges from 2.0 – 10.0 and were adjusted using HCl and NaOH (0.1 N) after which, 0.15 g of each samples were immersed in the flasks. After 24 h the final pH of suspensions were determined and plotted against the initial pH. The  $pH_{pzc}$  was finally evaluated as the value which cuts the X-axis.

### *Adsorption experiments:*

The batch adsorption experiments were conducted by the addition of appropriate amount of adsorbent to a series of 500 ml jars at various initial Cr(vi) concentration into the Phipps and Bird Jar Test Apparatus (PB – 600). It was then operated in the shaker at 250 rpm. The effects of the main parameters such as Cr(vi) concentrations (5–20 mg/L), pH (2 to 10), adsorbent dose (0.5–5 g/L) and contact time (5, 15, 30, 60, 120, 180 min) were studied<sup>16</sup>. Finally, the particles were filtered using Whatman No. 47 filter paper and thus separated from the suspension.

The percentage of Cr(vi) was calculated as:

$$\text{Removal efficiency (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

where,

$C_0$  = initial concentration and

$C_e$  = equilibrium concentrations of Cr(vi) in mg/L

And the equilibrium adsorption capacity was calculated as:

$$q_e = \frac{C_0 - C_e}{m} V \quad (2)$$

where,  $q_e$  = capacity of adsorption at equilibrium in mg/L,

$V$  = volume of used solution of Cr(vi) solution and

$m$  = mass of used solution of Cr(vi).

*Adsorption isotherms:*

*Langmuir isotherm:*

The Langmuir isotherm presumes that interaction amongst the adsorbed molecules is nil<sup>17</sup>. Langmuir isotherm equation is given by:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (3)$$

where,

$q_e$  = amount of Cr(vi) adsorbed in mg/g,

$q_{\max}$  = maximum adsorption capacity in mg/g,

$b$  = Langmuir's constant and

$C_e$  = equilibrium concentration of Cr(vi) solution.

The Langmuir isotherm equation can be linearized into 3 different types:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{b q_{\max}} \quad (4)$$

$$\frac{1}{q_e} = \frac{1}{b q_{\max} C_e} + \frac{1}{q_{\max}} \quad (5)$$

$$\frac{q_e}{C_e} = q_{\max} b - b q_e \quad (6)$$

The linear plot of  $1/q_e$  vs  $1/C_e$ ,  $C_e/q_e$  vs  $C_e$  and  $q_e/C_e$  vs  $q_e$  agreed well with the Langmuir isotherm over the chromium concentration range.

*Fruendlich isotherm:*

The Freundlich isotherm model assumes the interaction

between the adsorbed molecules<sup>18</sup>. The Freundlich isotherm can be expressed as:

$$q_e = K_f C_e^{\frac{1}{n}} \quad (7)$$

where,  $q_e$  = amount of Cr(vi) adsorbed (mg/g).

The adsorption isotherm models were employed to study the equilibrium correlation between adsorbed ions ( $q_e$ ) and the aqueous concentration ( $C_e$ ). The isotherm data were then validated with both the adsorption isotherms.

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{b q_{\max} C_e} \quad (8)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (9)$$

where,

$C_e$  = equilibrium concentration in mg/L,

$q_e$  = amount of ion adsorbed in mg/g,

$b$  = adsorption capacity constant,

$q_{\max}$  = maximum bio-adsorption capacity,

$K_f$  = Freundlich capacity factor and

$n$  = Freundlich's intensity factor.

## Results and discussion

*SEM and EDAX analysis:*

SEM analysis was performed to understand the surface morphology of the adsorbent. The AGP before adsorption have a smooth and uniform micro porous structures whereas after adsorption most of the available pores are occupied by Cr(vi) adsorption leading to the saturation of the adsorbent sites. The peak on the EDAX image confirms the adsorption of Cr(vi) onto the AGP which was in the range of 0.52 – 0.65 keV in the EDAX spectra.

*Point of zero charge ( $pH_{pzc}$ ):*

$pH_{pzc}$  determines the degree of ionization on the adsorbent surface and its interaction with the adsorbate. Fig. 3 shows the  $pH_{pzc}$  values determined in a solution of 0.1 N HCl. The  $pH_{pzc}$  was found to be 7.4 suggesting that that the surface of AGP is positive below pH of 7.4 and negative above 7.4. This also suggest that AGP can be used for the adsorption of both the cationic and anionic contaminants.

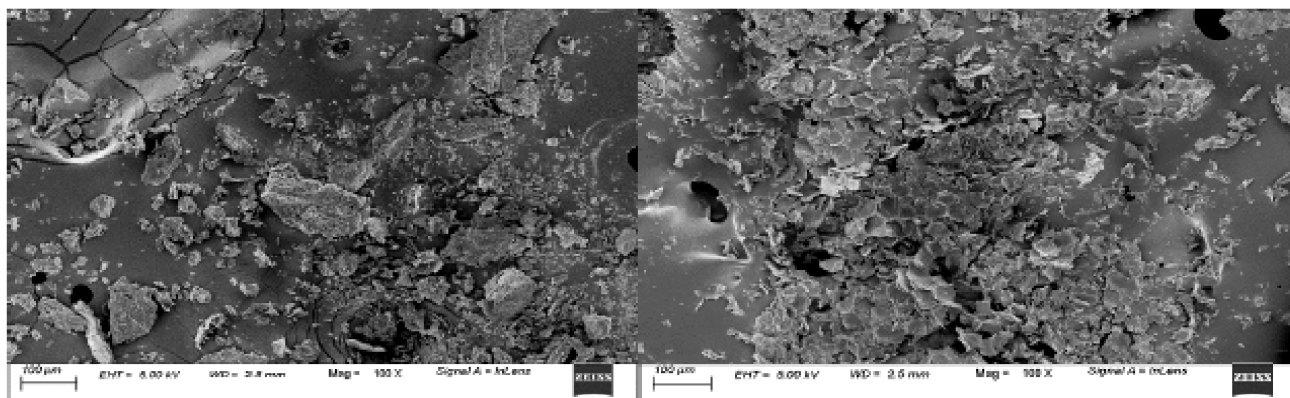


Fig. 1. SEM images of AGP: (a) before and (b) after adsorption of Cr(vi).

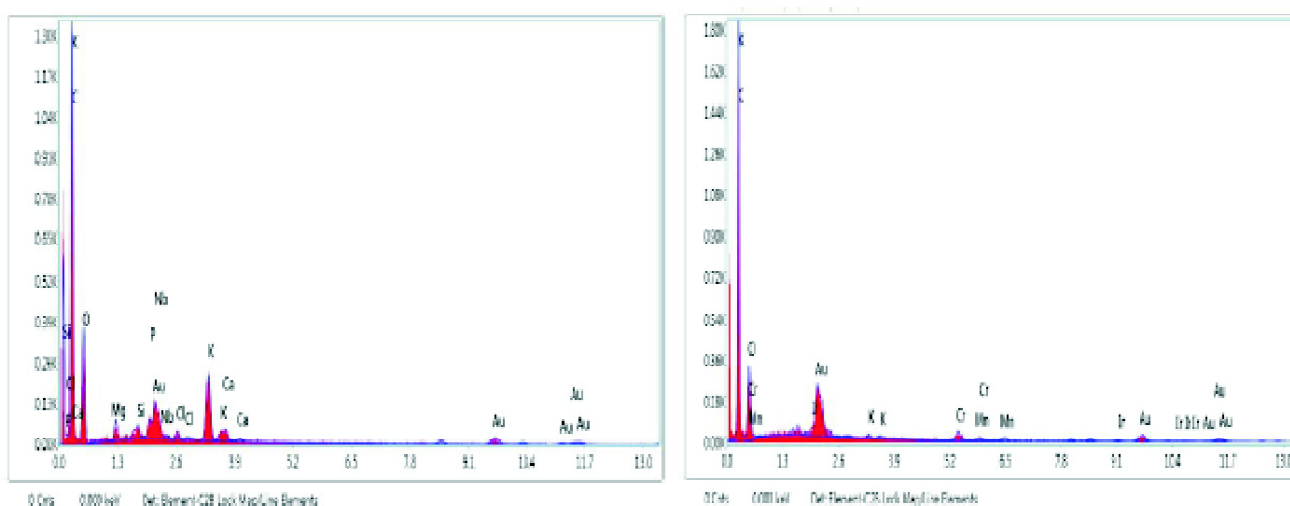


Fig. 2. EDAX spectra of AGP: (a) before and (b) after adsorption of Cr(vi).

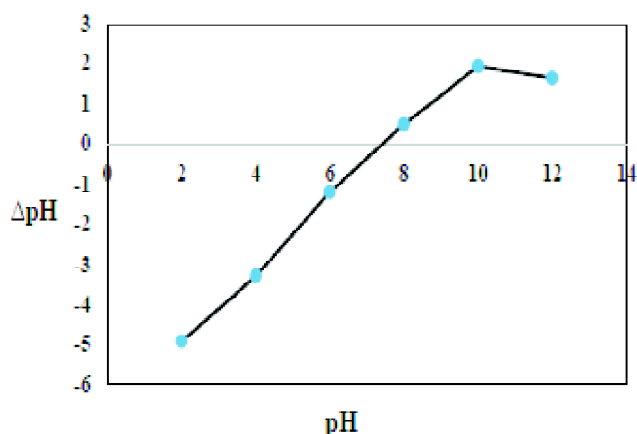


Fig. 3. Determination for point of zero charge (pH<sub>pzc</sub>).

#### Effect of pH:

The effect of pH was evaluated at a pH ranging from 2–10 as shown in Fig. 4. It was seen that the maximum removal and Cr(vi) adsorption were found at pH of 2. Almost 97.32% and 82.275% removals of Cr(vi) were obtained at a solution pH of 2 for synthetic water and the actual sample water respectively. The removal efficiency decreases from 97.32% to 38.38% and 82.275% to 19.35% for the synthetic and sample water respectively as the initial pH varies from 2 to 10. At acidic pH, the amine group on AGP is protonated leading to the formation of  $\text{NH}_3^+$  group which is responsible for Cr(vi) adsorption. Another reason for the improved removal

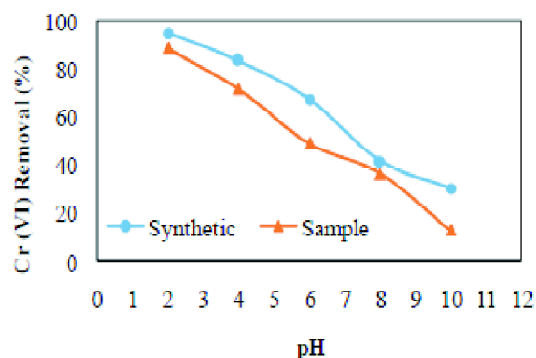


Fig. 4. Effect of solution pH on the removal efficiency of Cr(VI).

of Cr(VI) at low pH is due to reduction of Cr(VI) to Cr(III) ions by around 10%. Also, the decrease in removal efficiency of the actual groundwater is due to the interference of co-ions like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cl}^-$  in the water sample.

*Effect of concentration:*

The Cr(VI) adsorption onto the activated carbon from AGP powder was investigated at different adsorbent dosage (0.5, 1, 2, 3, 4, 5 g). The results showed the increased in Cr(VI) removal with the increase in adsorbent dose from 0.5 to 3 g because of the availability of exchangeable sites for the ions but remains unsaturated adsorption sites at higher dosage<sup>19</sup> as shown in Fig. 5. Hence, optimum dose was obtained at 3 g of the adsorbent dose with removal efficiency of 82.37% for the synthetic water and 76.58% for that of actual sample water collected from Phangrei, Ukhrul district.

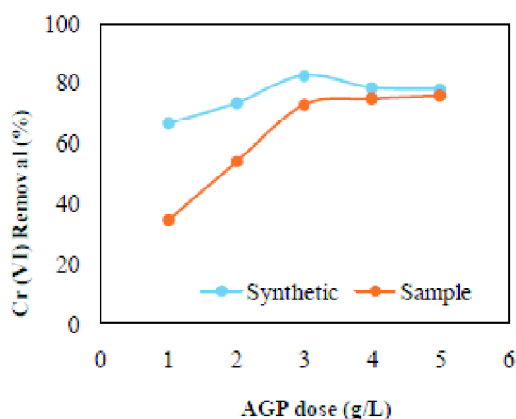


Fig. 5. Effect of adsorbent dosage on the removal efficiency and adsorption capacity of Cr(VI).

*Effect of contact time:*

The effect of contact time was analysed at pH of 2 and a mass loading of 3 g/L with different time intervals varying from 5–180 min as shown graphically in Fig. 6. Initially, adsorption was rapid but towards equilibrium the rate of adsorption decreases gradually approaches towards equilibrium. The optimum contact time was obtained past 120 min. The rapid increase of adsorption is due to the interaction of Cr(VI) ions and AGP surfaces onto which the ions are adsorbed<sup>20</sup>.

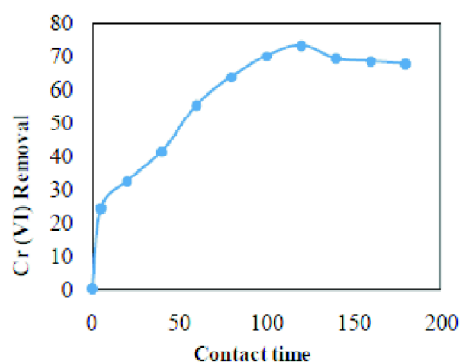


Fig. 6. Effect of contact time on the removal efficiency of Cr(VI).

*Adsorption isotherm studies:*

Isotherm studies were conducted at various Cr(VI) concentrations. To get the equilibrium data, initial Cr(VI) concentrations were varied alongwith the adsorbent mass and an equilibrium time of 240 min was used for adsorption experiments on the actual sample. The isotherm data were analysed with 3 different forms of linearized Langmuir models (eqs. (4), (5) and (6)) and Freundlich isotherm models (eq. (8)). The plot of the Langmuir equation and Freundlich equation are shown in Figs. 7, 8, 9 and 10. The regression coefficients ( $R^2$ ) for the isotherms, coefficients are evaluated and shown in Table 1. The correlation coefficient ( $R^2$ ) of higher than 0.95 for all equation except for Langmuir's eq. (1) suggest the well fixing of data on both the isotherms. However, the experimental and predicted value were compared using chi square and observed that for synthetic sample, the adsorption of Cr(VI) by AGP can be well explained by Langmuir's eq. (2) with  $\lambda^2$  of 0.062 only. The  $q_{\text{max}}$  value which signify maximum adsorption capacity however were negative in synthetic sample. Therefore, the adsorption isotherm can be ex-

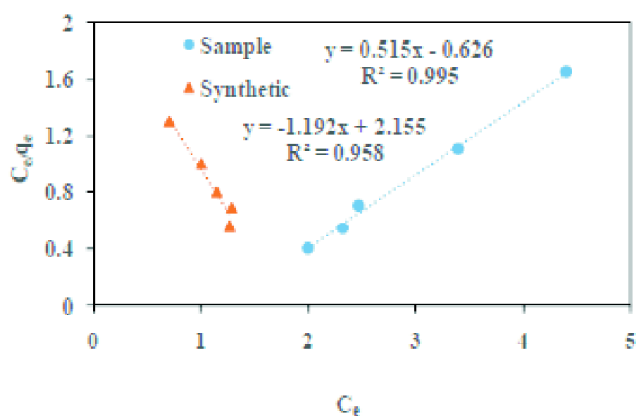


Fig. 7. Langmuir isotherm plot ( $C_e$  vs  $C_e/q_e$ ).

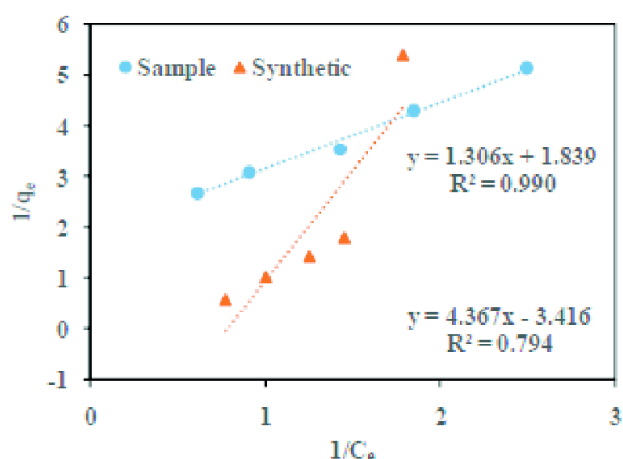


Fig. 9. Langmuir isotherm plot ( $1/C_e$  vs  $1/q_e$ ).

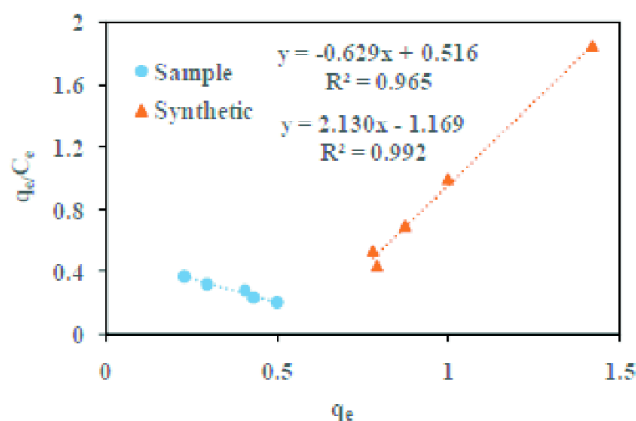


Fig. 8. Langmuir isotherm plot ( $q_e$  vs  $q_e/C_e$ ).

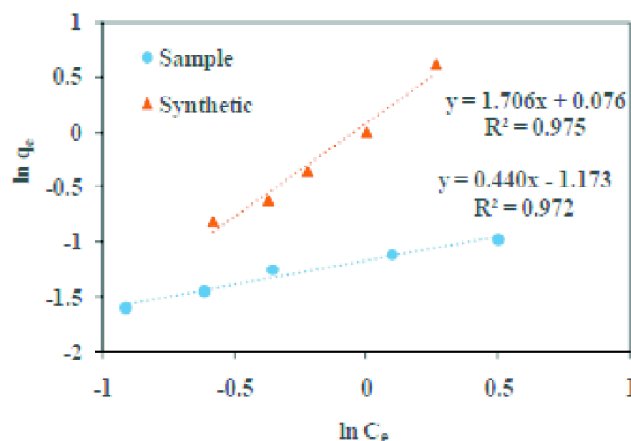


Fig. 10. Freundlich isotherm plot ( $\ln q_e$  vs  $\ln C_e$ ).

Table 1. Regression data of Langmuir and Freundlich isotherm models

Isotherms	Equation	Eq. no.	Synthetic				Sample			
			$q_{max}$	$b$	$R^2$	$\lambda^2$	$q_{max}$	$b$	$R^2$	$\lambda^2$
Langmuir	$1/q_e = 1/bq_{max}C_e + 1/q_{max}$	1	-0.292	-0.782	0.795	201.6	0.543	1.408	0.99	0.001
isotherm equations	$C_e/q_e = 1/q_{max}C_e + 1/bq_{max}$	2	-0.838	-0.553	0.958	0.062	1.939	-0.823	0.995	1334.1
	$q_e/C_e = q_{max}b - bq_e$	3	0.548	-2.13	0.99	133.9	0.821	0.629	0.965	0.017
Freundlich isotherm			$K_f$	$1/n$	$R^2$	$\lambda^2$	$K_f$	$1/n$	$R^2$	$\lambda^2$
	$\ln C_e$ vs $\ln q_e$	1	0.309	0.44	0.972	2.184	1.079	1.706	0.975	15.68

plained by Freundlich's isotherm. For the case of groundwater sample from Ukhru,  $\lambda^2$  were below unity only in case of Langmuir's eqs. (1) and (2). The  $q_{max}$  was obtained as

0.821 mg/g from Langmuir's eq. (3). These findings suggest that the study of adsorption fixing on isotherm can't be concluded by correlation coefficient ( $R^2$ ) only.

## Conclusions

In this current study, AGP was successfully used for Cr(VI) removal. The studies also indicated that AGP powder can be considered as an effective, inexpensive, eco-friendly, easily available natural adsorbent for the toxic Cr(VI) removal from the contaminated groundwaters. It indicates that the optimum pH for Cr(VI) adsorption on adsorbent synthesized from Ash gourd peel (AGP) was observed at acidic pH 2 for both Cr(VI) from groundwater and synthetic solution. The optimum dose were 3 g/L with removal (%) of 82.37% and 76.58% for synthetic and actual groundwater respectively. The decrease in removal efficiency of the actual groundwater sample suggests the interference of co-ions present in the sample. The equilibrium adsorption data fitted on Freundlich's isotherm for synthetic sample with correlation coefficient ( $R^2$ ) of 0.97 and Langmuir's isotherm with ( $R^2$ ) of 0.99 for groundwater sample from Ukhrlul with maximum adsorption capacity of 0.821 mg/g.

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