



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

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Abstract

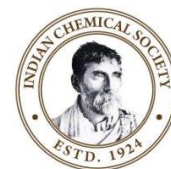
The present study aims to investigate adsorption of chromium ions from affected groundwater of Ukhrul district in Manipur. Hydroxyl and amines functionalized bio-adsorbent, Ash gourd (*Benincasahispida*) [AGP] peel was employed as adsorbent in batch mode. For effective adsorption of chromium ions, the 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 were 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 ± 5 °C, agitation speed 250rpm) after a reaction time of 180 minutes. The results showed that adsorption of chromium by AGP reached to equilibrium at 120 minutes thereafter, a minimal or no change of Cr (VI) removal was observed. The decreased 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 correlation coefficient greater than 0.95.

Keywords: Adsorption, Bio – adsorbent (*Benincasahispida*), 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 ground waters. Cr (VI) is considered very toxic, due to the association of chromium with oxygen as chromate ions (CrO_4^{2-}) 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 properties¹, due to which exposure to it harms our liver, kidney, lungs, skin and even our digestive systems². Inhalation of Cr (VI) causes acute toxicity and asthma³.

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 ores⁴. In Manipur, Chromite is mainly found at places of Phangrei, Lunghar, Sirohi and Chatrik in Ukhrul district⁵. 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)⁶. 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%⁷. But its disposal cost is high due to the production of secondary waste such as metal hydroxide sludge and gypsum⁸. 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 highly expensive. Ion exchange method has a demerit for loss of exchange capacity in presence of oxygen⁹ and in the membrane treatment method the membrane needs to be cleaned frequently also leading to high capital cost¹⁰. Various bio adsorbents like porous activated carbon¹¹, peanut husk powder¹², orange peel¹³ 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, perlite, coir pith and vermiculite were used for aqueous Cr (VI) removal¹⁴. 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 (*Benincasahispidia*) is cultivated all throughout the year. The peel constitutes 15% of the whole of Ash Gourd has a high waste index¹⁵. 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 physio chemical properties, batch equilibrium studies and isotherms exploring Ash gourd as a novel bio adsorption. 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 were 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 (*Benincasahispidia*) 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 0.01M 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 (0.1N) after which, 0.15g of each samples were immersed in the flasks. After 24 hours 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 minutes) were studied¹⁶. 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:

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

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

m = mass of used solution of Cr (VI).

Adsorption isotherms

Langmuir Isotherm

The Langmuir isotherm presumes that interaction amongst the adsorbed molecules is nil¹⁷. 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 Fruendlich isotherm model assumes the interaction between the adsorbed molecules¹⁸. The Fruendlich isotherm can be expressed as:

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

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 and

q_{max} = maximum bio-adsorption capacity,

K_f = Fruendlich capacity factor and

n = Fruendlich'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 0.1N HCl. The pH_{pzc}



was found to be 7.4 suggesting that the surface of AGP is positive below pH of 7.4 and negative above 7.4. This also suggests that AGP can be used for the adsorption of both the cationic and anionic contaminants.

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 NH_3^+ group which is responsible for Cr(VI) adsorption. Another reason for the improved removal 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 Ca^{2+} , Mg^{2+} , Na^+ , K^+ and 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 grams). The results showed the increase in Cr (VI) removal with the increase in adsorbent dose from 0.5 to 3 grams because of the availability of exchangeable sites for the ions but remains unsaturated adsorption sites at higher dosage¹⁹ as shown in Fig. 5. Hence, optimum dose was obtained at 3 grams 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, Ukhru District.

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 minutes as shown graphically in Figure 6. It was found that the adsorption had a rapid increase and then gradually approaches towards equilibrium. The optimum contact time was obtained past 120 minutes. The

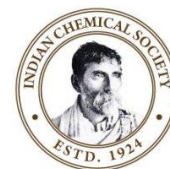
rapid increase of adsorption is due to the interaction of Cr (VI) ions and AGP surfaces onto which the ions are adsorbed²⁰.

Adsorption isotherm studies

Isotherm studies were conducted at various Cr (VI) concentrations. To get the equilibrium data, initial Cr (VI) concentrations were varied along with the adsorbent mass and an equilibrium time of 240 minutes was used for adsorption experiments on the actual sample. The isotherm data were analysed with 3 different forms of linearized Langmuir models (Eq. 4,5 and 6) and Freundlich isotherm models (Eq. 8). The plot of the Langmuir equation and Freundlich equation are shown in Fig. 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 equation 1 suggest the well fitting 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 equation (2) with λ^2 of 0.062 only. The q_{max} value which signify maximum adsorption capacity however were negative in synthetic sample. Therefore, the adsorption isotherm can be explained by Freundlich's isotherm. For the case of Ground water sample from Ukhru, λ^2 were below unity only in case of Langmuir's Equation (1 and 2). The q_{max} was obtained as 0.821 mg/g from Langmuir's equation 3. These findings suggest that the study of adsorption fitting 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 ground water and synthetic solution. The optimum



dose were 3 g/L with removal (%) of 82.37% and 76.58% for synthetic and actual ground water 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 ground water sample from

Ukhrul with maximum adsorption capacity of 0.821 mg/g.

Conflict of interest

The authors hereby declared there is no conflict of interest for this manuscript.

References

1. P. Waranusantigula, P. Pokethitiyook, M. Kruatrachue and E. S. Upatham, *Environ. Pollution*, 2003, **125**, 385-392;
2. D. Mohan and C. U. Pittman, *J. Hazard. Mater. B.*, 2006, **137**, 762-811;
3. E. Pehliva and H. Kahraman, *Fuel Proc. Tech.*, 2011, **92**, 65-70;
4. [http://www.pmfias.com/copper-nickel-chromite-distribution/\(2016\)](http://www.pmfias.com/copper-nickel-chromite-distribution/(2016))
5. F. Varah, Chromite mining in Manipur 49, 2014, **25**;
6. WHO, 2nd ed., World Health Organization, 2016;
7. Matlock, M. M. Howerton, B. S. Henke and D. A. Atwood, *Water research*, 2002, **36**, 4757-4764;
8. C. L. Shen, T. X. Nguyen and N. P. Hankins, *Sep. and pur. Tech.*, 2015, **152**, 101-107;
9. A. T. Le, Pung, S. Y. Sreekantan, Matsuda and D. P. Huynh, *Chem. Engg. Research and Design* 90, 2019, **9**, 1397-1406;
10. K. Sunil, G. Karuna Karan, S. Yadav, M. Padaki, V. Zadorozhnyy and K. R. Pai, *Chem. Engg. Jr.*, 2018, **348**, 678-684;
11. S. Yao, W. Liancheng, L. Baoliang, G. Chang, W. Jiao and Youzhi Liu, *Environ. Sci. and Poll. Research*, 2019, **27**, 7015-7024;
12. I. Abdelfattah, A. A. Ismail, Fathy Al Sayed, A. Ali and K. M. Aboelghait, *Environ. Nanotech., Monitoring and Manage.*, 2016, **6**, 176-183;
13. G. Lopez-Tellez, C. E. Barrera-Diaz, P. Balderas-Hernandez, G. Roa-Morales and B. Bilyeu, *Chem. Engg. Journal*, 2016, **173**, 480-485;
14. K. M. S. Sumathi and R. M. Naidu, *Bioresources Tech.*, 2005, **96**, 309-316;
15. K. M. Sreenivas, M. B. Inarkar, S. V. Gokhale and S. S. Lele, *Jr. of Environ. Chem. Engg.*, 2014, **2**, 455-462;
16. M. Nigam, S. Rajoriya, R. S. Singh and P. Kumar, *Environ. Chem. Engg.*, 2019, **7**, 103-188;
17. A. P. Kumar, M. Ray and S. Chakraborty, *Jr.l of Hazd. Mat*, 2008, **143**, 24-32;
18. S. Elabbas, L. Mandi, F. Berrekhis, M. N. Pons, J. P. Leclerc and N. Ouazzani, *Jr. of Environ. Manage.*, 2016, **166**, 589-595;
19. E. Pehlivan and H. Kahraman, *Fuel Process Tech.*, 2011, **92**, 65-70;
20. S. Elabbas, N. Ouazzani and L. d'Antonio, *Jr.l of Environ. Manage.*, 2013, **117**, 1-6;

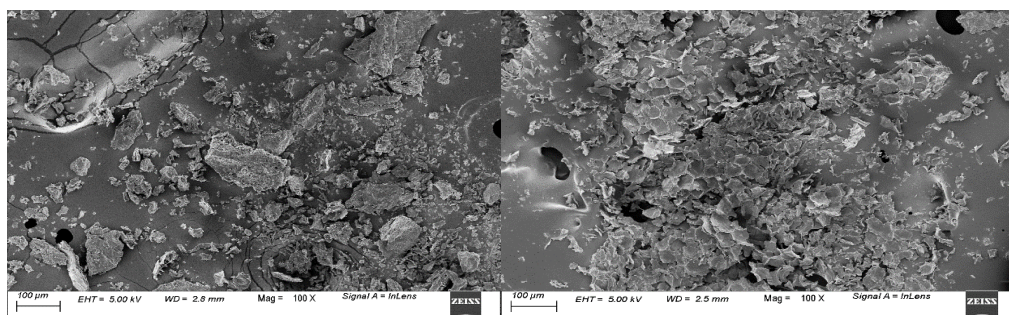


Fig. 1. SEM images of AGP (a) before and (b) after adsorption of Cr (VI).

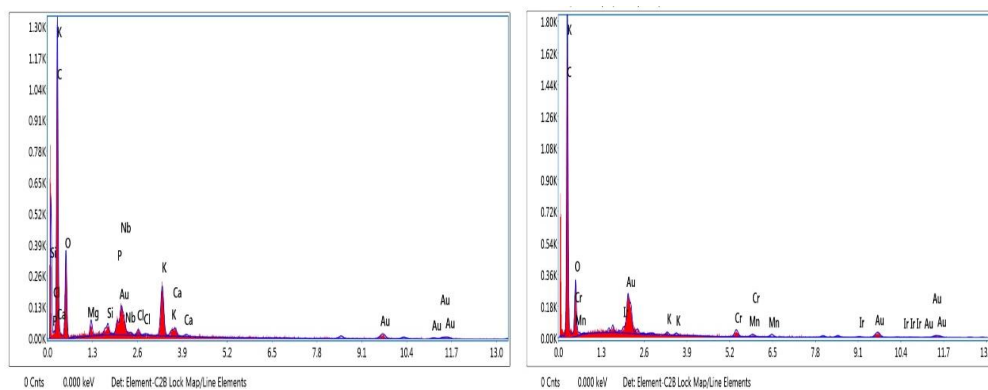


Fig. 2. EDAX spectra of AGP (a) before and (b) after adsorption of Cr (VI).

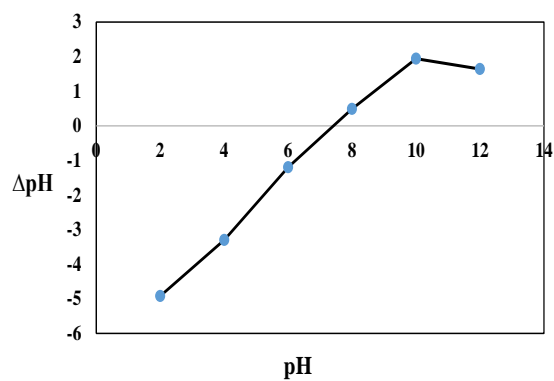


Fig. 3. Determination for point of zero charge (pH_{PZC}).

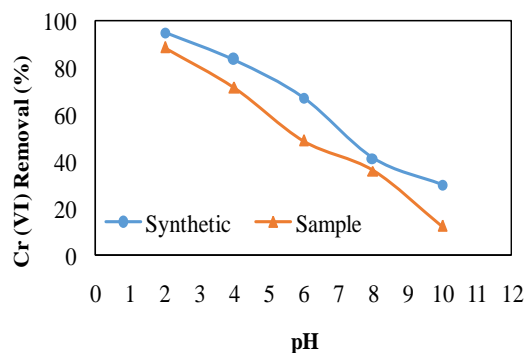


Fig. 4. Effect of solution pH on the removal efficiency of Cr (VI).

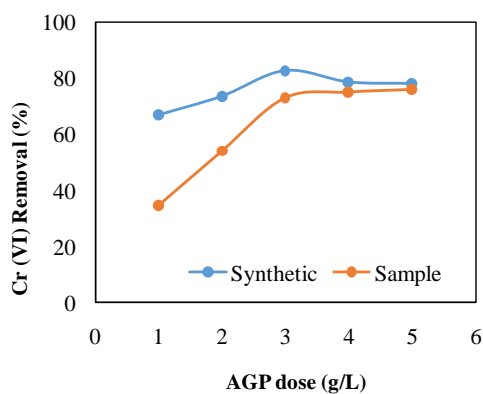


Fig. 5. Effect of adsorbent dosage on the removal efficiency and adsorption capacity of Cr (VI).

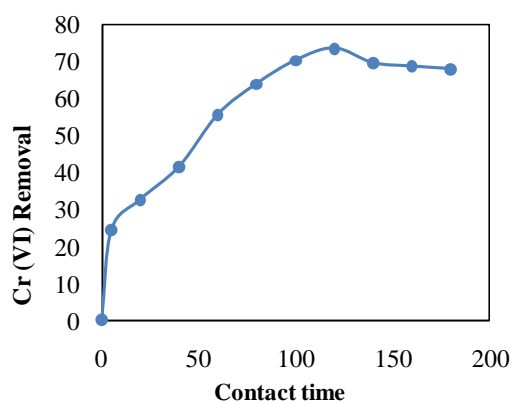


Fig. 6. Effect of contact time on the removal efficiency of Cr (VI).

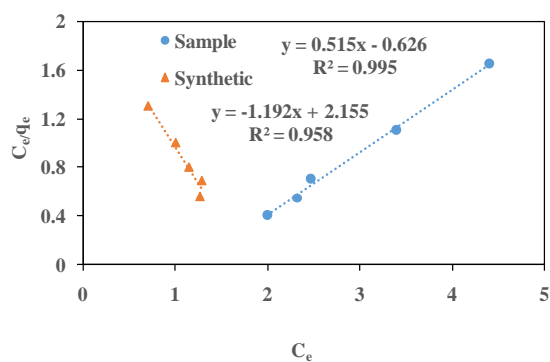


Fig. 7. Langmuir isotherm plot (C_e vs C_e/q_e).

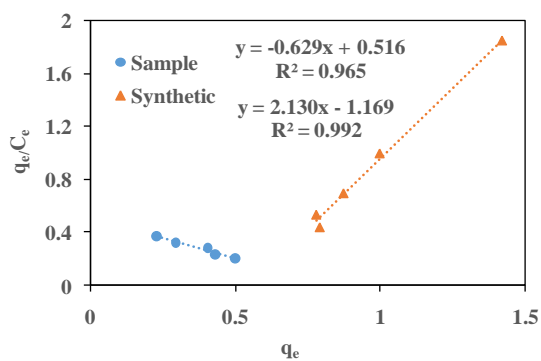


Fig. 8. Langmuir isotherm plot (q_e vs q_e/C_e).

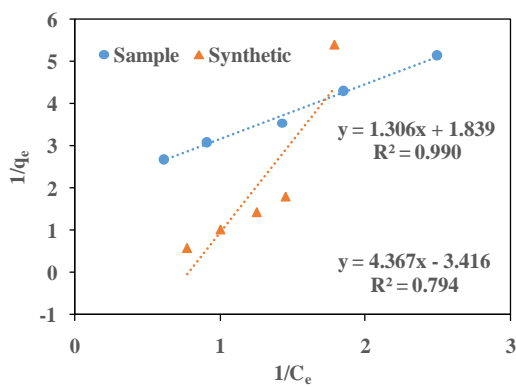


Fig. 9. Langmuir isotherm plot ($1/C_e$ vs $1/q_e$).

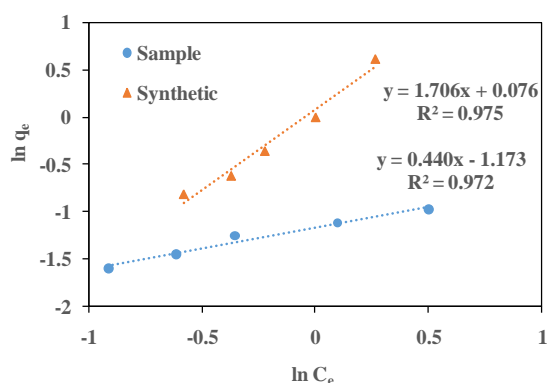


Fig. 10. Freundlich isotherm plot ($\ln q_e$ vs $\ln C_e$).

Table 1. Regression data of Langmuir and Freundlich isotherm models

Isotherms	Equation	Eq. no	Synthetic				Sample			
			q_{\max}	b	R^2	λ^2	q_{\max}	b	R^2	λ^2
Langmuir isotherm equations	$1/q_e = 1/bq_{\max}C_e + 1/q_{\max}$	1	-0.292	-0.782	0.795	201.6	0.543	1.408	0.99	0.001
	$C_e/q_e = 1/q_{\max}C_e + 1/bq_m$	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	$\ln C_e$ vs $\ln q_e$	1	K_f	$1/n$	R^2	λ^2	K_f	$1/n$	R^2	λ^2
			0.309	0.44	0.972	2.184	1.079	1.706	0.975	15.68