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Research paper

Simultaneous adsorption of phenol and nickel from wastewater using tea fiber waste

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Abstract

The present work explores the potential of tea fibre waste as an adsorbent to remove phenol and nickel from wastewater in both single and binary component mode. The properties of the tea fibre such as surface area, pore volume and particle size were improved by treating with hydrochloric acid. The isotherm models were verified for single component system to find the adsorption mechanism. The equilibrium data were obeying Freundlich model. The simultaneous adsorption of two pollutants were carried out in order to evaluate the interaction mechanism such as synergic, antagonistic or non-interaction effect. It was observed that overall the system was exhibiting synergistic type of behavior.

Keywords: *Phenol; Nickel; Interaction; Synergistic; Isotherm.*

1. Introduction

Because of the rapid growth of industries and the release of various chemicals from the wastewater, the ecosystems are degraded and the water pollution has become a major environmental concern [1]. The industrial wastewater contains different pollutants like heavy metals, organic compounds, nuclear waste and dyes and is a multi-component mixture. Phenol and nickel are considered as major toxic pollutants present in wastewater. Phenol causes adverse effects on the human beings and the water bodies. The metabolism of aquatic animals is retarded in the water polluted with phenol. In human beings it leads to health problems like diarrhea, mouth sores, vomitting and effects nervous system, urinary system and cardiovascular system [2-3]. It is also considered as toxic even when it is present at very low concentration [4]. As per the environmental protection agencies, the permissible concentration of phenol in sewage water is 1 mg/L and in drinking water should be lower than 0.001 mg/L [5-6].

Nickel which is one of the heavy metal existing in wastewater and causes harmful effects like kidney and lung disorder, cancer, tissue damage, skin dermatitis and other problems [7-8]. It is recognized as potential carcinogen to humans [9]. As per World health organization the nickel concentration should not be more than 0.02 mg/L before released into the groundwater [7]. The US Environmental protection agency defines the nickel concentration to be lower than 0.5 mg/L in drinking water [8]. Therefore it is required to treat these pollutants before it is released into the environment. The pollutants are present in wastewater of industries like petroleum, plastic, fertilizer, rubber, pharmaceutical, coal and steel industries [2], [10]. Different methods are used for reducing the pollutant concentration such as chemical oxidation, coagulation, membrane separation, pervaporation, extraction, electrodialysis, adsorption and ion exchange [9-11]. Adsorption is a well-chosen technique because of the reasons that low cost of the process, environmentally effective and the efficient to remove the pollutant [12]. The activated carbon is generally used for treating the pollutant from wastewater. Since the activated carbon is expensive in nature, the adsorbent can be produced from agricultural materials [13]. From available literature, it was investigated that majority of the research work conducted with wastewater are with respect to adsorption of the single pollutant from the wastewater. The multicomponent adsorption explains how the individual component occupies the adsorbent sites on the solid surface, the way in which the component is attracted towards the adsorbent and the possible interaction with the adsorbent [10]. Therefore there is a need to study on the simultaneous adsorption of the pollutants from multicomponent mixture.

Thus in the present study tea waste fibres are used as potential adsorbent for the treatment of phenol and nickel from wastewater. The isotherm models were verified to investigate the mechanism of adsorption. The simultaneous adsorption of the pollutants were conducted to determine the interaction mechanism between the pollutants in binary solution.

2. Interaction effects between the pollutants in the solution

The interaction between the adsorbent and the pollutants in a binary solution happens in mainly three types. The basic principle used to study the interaction mechanism is by comparing the adsorption capacity of the component (i) in the binary solution $(q_{i,m})$ and the adsorption capacity of the same component in the solution containing only one component$(q_{i,s})$. The various interactions are as follows.

(a) Synergistic interaction effect: The adsorption capacity of a component is increased by the presence of another component in the solution $(q_{i,m} > q_{i,s})$.

(b) Antagonistic interaction: The adsorption capacity of a component is decreased by the other pollutant in the solution $(q_{i,m} < q_{i,s})$.

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(c) Non interaction effect: The adsorption capacity of a component is not influenced by the presence of the other component($q_{i,m} = q_{i,s}$). [14-17]

3. Materials and methods

3.1. Chemicals used

Phenol was obtained from Merck India Limited and used for preparing stock solution of concentration 1000 mg/L. The chemicals nickel chloride hexahydrate (Merck India Limited) was used for nickel solution preparation. The other chemicals hydrochloric acid (Merck India Limited) and sodium hydroxide pellets (Fischer Scientific Limited) were used for the experiments.

3.2. Preparation of the adsorbent

The tea waste fibres were collected from tea plantation from Sivasagar, Assam for adsorbent preparation. The material was cleaned with distilled water so that all earthy matter is removed and subjected to drying inside oven at 110ºC for 1 hr to remove the moisture content [18-19]. 50 g of the dried powder and 50 ml of 0.1 M HCl solution are mixed in 1:1 ratio in 1000 ml beaker. The acid was made to react with the material for 15-20 min and then heated inside the muffle furnace at 450ºC for 1.5 hr to improve the properties of the adsorbent. Later the slurry was washed continuously with water to remove excess chemicals [20]. The washing was continued till the pH value comes to 6.5-7.5 [21]. Then it was once again dried oven for a day and ground to fine size particles lower than 0.075 mm. Finally the prepared powder was stored and used for the experiments.

3.3. The characterization of the adsorbent

By using the standard procedure the proximate analysis of the chemically treated adsorbent was carried out and the parameters volatile matter, ash content, fixed carbon and moisture were determined [22]. The surface area and pore volume were measured with the help of BET apparatus (Smart Instruments, India). The average particle size was determined by particle size analyzer (CILAS 1064, France). The different functional groups and chemical bonds existing on the adsorbent surface were found using Fourier transform infrared spectroscopy (FTIR) instrument, Shimadzu, Japan.

3.4. Adsorption experiments

The adsorption experiments were conducted in 250 mL flask having 250 mL of phenol solution of concentration 10, 25, 50, 75 and 100 mg/L or 250 mL of nickel solution in the concentration range 5, 10, 15, 25 and 40 mg/L in the single solution mode. The studies in two-component solution mode were performed by 125 mL of phenol solution and 125 mL of nickel solution of different concentrations as shown in table3. The influence of experimental parameters were studied by varying pH value from 4-8 and dosage from 0.25-2 g. The optimum value of adsorbent dosage and pH were found to 1.5 g and 4 respectively from the preliminary experiments. The equilibrium time was obtained as 8 hours for both the pollutants. Then the isotherm experiments were conducted by mixing the solutions with 1.5 g of the adsorbent at pH 4 and were shaken in an agitator at 120-rpm speed at a temperature of 303K for 8 hours. After the equilibrium time, the residual concentration of phenol was determined using UV spectrophotometer (Shimadzu, Japan) at 270 nm. The final concentration of nickel was found using atomic absorption spectrophotometer (Thermo Scientific, Australia) at 232.1 nm.

4. Results and discussion

4.1. Characterization of the adsorbent

The average particle size was obtained as 60.12 µm which signifies that improvement of surface area takes place and thus efficiency of adsorbent increases. The surface area and pore volume of the adsorbent were found to be 14.73 m^2/g and 0.0184 cm^3/g respectively proving that adsorbent is capable of removing the pollutant effectively [23-24]. The proximate analysis of the chemically treated adsorbent was carried out to find the moisture, volatile matter, ash and fixed carbon content and is given in table1. From the value of fixed carbon content it can be found that the adsorbent is having better adsorption capability to remove the pollutant from wastewater [25].

Table 1: Proximate Analysis of the Treated Adsorbent

Sl.No	Parameter	Percentage	Sl.No	Parameter	Percentage
1	Moisture	6.25	2	Ash content	27
3	Volatile matter	23.67	4	Fixed carbon content	43.08

The FTIR spectrum of the chemically treated adsorbent before and after adsorption are shown in figure 1 and 2. It can be observed that the peak formed at 3614.60 and 3641.60 cm^{-1} was due to the O-H bonding of the phenol group [26], the peak found at 3387.00 and 3361.93 cm^{-1} was because of the O-H bonding of hydrogen bonded alcohols [26]. The peak observed at 1610.56 and 1624.06 cm-1 was contributed due to stretching of C-C bond [27], the peak exhibiting at 1656.85 cm^{-1} was because of C=C stretching of alkenes [28]. The peak obtained at 2858.51 cm^{-1} was because of aliphatic C-H stretching [29]. These bonds were significant and were responsible for the adsorption of the pollutant onto the adsorbent.

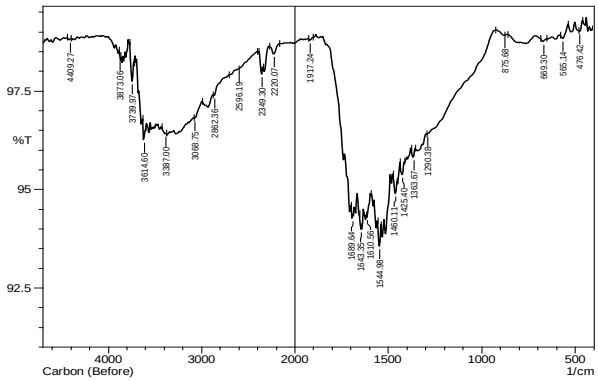


Fig. 1: The FTIR Analysis of the Sample before Adsorption.

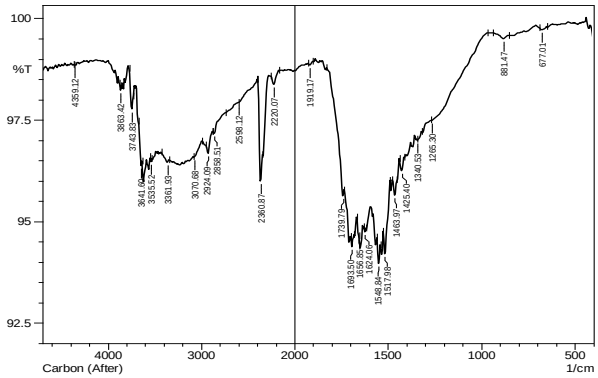


Fig. 2: The FTIR Analysis of the Sample after Adsorption.

4.2. Single adsorption isotherm

The concept of adsorption equilibrium is very important in analyzing and designing adsorption process for separating the components. The relation between the concentration of the solute in the liquid solution and that in the adsorbent can be formed at a constant temperature at the conditions of equilibrium. Thus the relationship

is known as adsorption isotherm [30]. It is also important in understanding the interaction of the solute with the adsorbent and also for investigating the adsorption mechanism [31]. Various isotherm models are available from the literature. The isotherm models such as Langmuir, Freundlich, Temkin, Dubinin-Radushkevich (D-R), Brunauer–Emmer–Teller (BET) model and Flory–Huggins isotherm models were investigated in order to determine the adsorption mechanism.

Langmuir model is derived by assuming that adsorption happens on specific sites on the surface. It describes that once the particular site is occupied, no more solute molecule will adsorb on that site and it leads to monolayer adsorption. It also explains that energy of adsorption is uniform at all the adsorbent sites and the adsorbed molecules have no interaction with the surrounding molecules [2], [23], 32]. The model can be represented in the simplified form as

$$\frac{C_{eq}}{q_{eq}} = \frac{C_{eq}}{q_{mx}} + \frac{1}{k_{lg}q_{mx}} \quad (1)$$

q_{mx}(mg/g) the maximum adsorption capacity and k_{lg} (L/mg) the affinity of the solute to the adsorbent and q_{eq} (mg/g) and C_{eq} (mg/L) are the adsorption capacity and solute concentration at equilibrium. The values of model parameters are obtained from the plot of $1/q_{eq}$ against $1/C_{eq}$.

Freundlich model is applicable to adsorption on heterogeneous surfaces where energy distribution is non-uniform. The solute molecules gets adsorbed on the solid surface in the form of multilayers. It also describes that the energy of adsorption decreases exponentially with the coverage on the active sites. The linear form of the model is given by

$$log q_{eq} = log k_{fr} + (1/n)\, log C_{eq} \quad (2)$$

k_{fr} The adsorption coefficient and n signifies the adsorption intensity [33], [32], [34].

Temkin isotherm explains the interaction between the adsorbate molecules which occupies the sites on the solid surface. It also describes that the adsorption energy of all the molecules on the adsorbent surface decreases linearly with respect to adsorption of the pollutants [35-36]. It is given in the simplified form as

$$q_{eq} = B ln A + B ln C_{eq} \quad (3)$$

A the model constant and B the constant related to heat of sorption. The constants are evaluated by plotting q_{eq} v/s $ln C_{eq}$.

The Dubinin–Radushkevich (D-R) model is used to evaluate the apparent free energy of adsorption and is given in the form [37-38]

$$q_{eq} = q_{mr} e^{\beta \varepsilon^2} \quad (4)$$

(4) β The sorption energy constant, q_{mr} the D–R capacity (mg/g) and by plotting $ln q_{eq}$ v/s ϵ^2 the model constants β and q_{mr} are obtained. ϵ the Polanyi potential which is calculated using

$$\epsilon = RT\, ln\left(1 + \frac{1}{C_{eq}}\right) \quad (5)$$

The Flory –Huggins (FH) model is used for investigating the degree of suface coverage characteristics of the solute on the adsorbent [30, 31]. It is written in the simplified form as

$$log(\theta/C_o) = log k_{fh} + n_{fh} log(1-\theta) \quad (6)$$

k_{fh} equilibrium constant, n_{fh} model constant. θ the surface coverage value is obtained by

$$\theta = 1 - \frac{C_{eq}}{C_o} \quad (7)$$

The isotherm studies are carried out by varying the initial concentration of phenol in the range 10, 25, 50, 75 and 100 mg/L and nickel concentration 5, 10, 15, 25 and 40 mg/L. The isotherm models were verified with respect to the single component equilibrium data. The values of model constants with the regression coefficient for both the components are shown in table2. From the values of regression coefficient, it can be observed that isotherm data was fitting better with the Freundlich model showing that physical adsorption takes place and the solute is adsorbed onto the adsorbent in multilayers. The higher the k_{lg} value, the higher the affinity of the solute to the adsorbent. Therefore it shows that nickel ions have more attraction towards the adsorbent [39]. The adsorption intensity n is used to assess the type of process. The value of n lower than one shows that the process is chemical in nature. The obtained values of n higher than one signifies that the process is physical. Thus the obtained values of n indicates that the adsorption process is physical in nature [34]. The higher value of k_{fr} signifies the higher uptake of phenol onto the adsorbent when compared to nickel [40].

Table 2: The Values of Isotherm Parameters from Different Models For Individual Components.

	Langmuir isotherm			Freundlich isotherm		
Solute	q_{mx}(mg g^{-1})	k_{lg}	R^2	k_{fr}	n	R^2
Phenol	11.23	0.2219	0.8835	1.329	1.618	0.9307
Nickel	6.11	0.2838	0.7778	1.0115	1.3824	0.9289
	D-R model			Temkin model		
	q_{mr}(mg g^{-1})	β	R^2	A(L/g)	B(J/mol)	R^2
Phenol	2.0341	0.0202	0.6434	1.071	2.8121	0.908
Nickel	1.1516	0.00495	0.7104	1.070	2.2849	0.898
	F-H isotherm					
	k_{fh}	n_{fh}	R^2			
Phenol	0.4528	1.6743	0.5971			
Nickel	0.8713	1.5695	0.6167			

4.3. The interaction effect of the pollutants in the solution (Single and binary adsorption of the components)

The various isotherm experiments conducted for different concentrations of phenol and nickel and the combination of two pollutants, adsorption capacity and the percent removal in the single and binary solution mode are shown in Table3. Additive rule was used to determine the interaction effect. The total adsorption capacity of all the components in binary solution mode and single solution mode were compared. The total adsorption capacity of all the components in the single solution mode ($\sum_{j=1}^{2} q_{j,s}$) and binary solution mode ($\sum_{j=1}^{2} q_{j,m}$) are calculated using

$$\sum_{j=1}^{2} q_{j,s} = q_{i,s} + q_{j,s} \quad (8)$$

$$\sum_{j=1}^{2} q_{j,m} = q_{i,m} + q_{j,m} \quad (9)$$

If the value of $(\sum_{j=1}^{2} q_{j,m}) > (\sum_{j=1}^{2} q_{j,s})$ then synergistic action exists in the system. If the value of $(\sum_{j=1}^{2} q_{j,m}) < (\sum_{j=1}^{2} q_{j,s})$ antagonistic effect plays a significant role [39-41].

Table 3: The Total Adsorption Capacity and Percent Removal for the Combined and Individual Systems.

C_o, phenol (mg/l)	C_o, nickel (mg/l)	C_{eq} phenol (mg/l)	C_{eq}, nickel (mg/l)	q_{eq} phenol (mg/g)	q_{eq} nickel (mg/g)	$(\sum_{j=1}^{2} q_{j,m})$ (mg/g)	$(\sum_{j=1}^{2} q_{j,s})$ (mg/g)	$\%\ rem$, phenol	$\%\ rem$, nickel	$\%tot\ rem$, com	$\%tot\ rem$, ind
0	0	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	
10	0	2.17	0.00	1.30	0.00	1.30		78.29	0.00	78.29	
25	0	2.86	0.00	3.69	0.00	3.69		88.55	0.00	88.55	
50	0	11.58	0.00	6.40	0.00	6.40		76.84	0.00	76.84	
75	0	21.18	0.00	8.97	0.00	8.97		71.75	0.00	71.75	
100	0	37.04	0.00	10.49	0.00	10.49		62.96	0.00	62.96	
0	5	0.00	1.37	0.00	0.61	0.61		0.00	72.66	72.66	
10	5	0.46	0.55	1.59	0.74	2.33	1.91	95.39	88.95	93.25	76.41
25	5	0.46	0.51	4.09	0.75	4.84	4.30	98.16	89.89	96.78	85.90
50	5	1.81	0.36	8.03	0.77	8.81	7.01	96.38	92.89	96.06	76.46
75	5	3.22	0.29	11.96	0.79	12.75	9.57	95.70	94.24	95.61	71.81
100	5	7.40	0.31	15.43	0.78	16.22	11.10	92.60	93.83	92.66	63.42
0	10	0.00	1.41	0.00	1.43	1.43		0.00	85.86	85.86	
10	10	2.99	0.87	1.17	1.52	2.69	2.74	70.07	91.26	80.66	82.07
25	10	1.58	0.98	3.90	1.50	5.41	5.12	93.68	90.16	92.68	87.78
50	10	2.40	1.05	7.93	1.49	9.43	7.83	95.20	89.52	94.25	78.34
75	10	4.11	1.03	11.81	1.50	13.31	10.40	94.52	89.74	93.95	73.41
100	10	18.45	1.04	13.59	1.49	15.08	11.92	81.55	89.59	82.28	65.04
0	15	0.00	3.60	0.00	1.90	1.90		0.00	76.00	76.00	
10	15	4.21	2.30	0.96	2.12	3.08	3.20	57.89	84.67	73.96	76.91
25	15	5.33	2.19	3.28	2.13	5.41	5.59	78.68	85.39	81.20	83.84
50	15	6.05	2.12	7.32	2.15	9.47	8.30	87.89	85.86	87.42	76.65
75	15	10.86	1.93	10.69	2.18	12.87	10.87	85.53	87.11	85.79	72.46
100	15	16.32	1.89	13.95	2.19	16.13	12.39	83.68	87.40	84.17	64.66
0	25	0.00	4.35	0.00	3.44	3.44		0.00	82.59	82.59	
10	25	6.28	3.08	0.62	3.65	4.27	4.75	37.17	87.68	73.25	81.36
25	25	6.22	2.77	3.13	3.71	6.84	7.13	75.13	88.93	82.03	85.57
50	25	8.19	2.92	6.97	3.68	10.65	9.84	83.62	88.32	85.19	78.76
75	25	15.10	3.13	9.98	3.65	13.63	12.41	79.87	87.49	81.77	74.46
100	25	16.09	2.58	13.99	3.74	17.72	13.93	83.91	89.67	85.07	66.89
0	40	0.00	8.95	0.00	5.17	5.17		0.00	77.62	77.62	
10	40	9.34	6.40	0.11	5.60	5.71	6.48	6.58	84.00	68.51	77.76
25	40	7.24	5.73	2.96	5.71	8.67	8.86	71.05	85.68	80.05	81.83
50	40	7.34	5.73	7.11	5.71	12.82	11.58	85.33	85.66	85.48	77.19
75	40	12.86	5.31	10.36	5.78	16.14	14.14	82.85	86.74	84.20	73.80
100	40	20.53	5.48	13.25	5.75	19.00	15.67	79.47	86.29	81.42	67.15

The total percent removal ($\%tot\ rem$) for the combined and individual system was obtained using

$$\%tot\ rem = \frac{\left((C_{oi}-C_{ei})+(C_{oj}-C_{ej})\right)}{(C_{oi}+C_{oj})} \quad (10)$$

Where $\boldsymbol{C_{oi}}$ and $\boldsymbol{C_{ei}}$ are the initial and equilibrium concentrations for the components.

It was observed from the table that by increasing the phenol concentration from 0 to 100 mg/L, the adsorption capacities for nickel concentration (5, 10, 15, 25, 40 mg/L) were increasing and phenol is having synergistic effect on the nickel. It can be explained that with the increase in concentration the interface between the solute and the adsorbent increases and the driving force for the mass transfer improves and the adsorption capacity [42].

It was investigated from the studies that with the increase in nickel concentration from zero to 40 mg/L, the adsorption capacities for phenol concentration (10, 25, 50, 75, 100 mg/L) decreased. The nickel molecules might have adsorbed initially on the adsorbent surface. Therefore the nickel molecules will block the surface sites for the phenol molecules to adsorb. It is also due to the fact that nickel was competing more for the active sites on the adsorbent [43-44]. Therefore, it can be observed that by increasing the nickel concentration the phenol capacity was decreasing and nickel was showing antagonistic effect on the phenol.

It can be studied from the table that the total adsorption capacity $(\sum_{j=1}^{2} q_{j,m})$for the combined system was more than the total adsorption capacity$(\sum_{j=1}^{2} q_{j,s})$ for the individual components signifying that the process was showing synergistic effect. This can be due to the properties of the solutes like ionic size, reduction potential, molecular polarity, molecular weight, and the properties of the adsorbent such as surface properties, structure and functional groups [16], [45], and [46]. The same trend was observed with respect to total percent removal of the combined system and the total percent removal of the individual system.

5. Conclusions

From the studies, it can be proved that tea fibre waste was used efficiently to remove phenol and nickel from wastewater. The chemically treated adsorbent was showing improved properties because of which the overall adsorption capacity increases. The isotherm data followed Freundlich isotherm signifying the process is physical adsorption. From the simultaneous adsorption studies, it was investigated that phenol was having synergistic effect on nickel, while nickel was having antagonistic effect on phenol adsorption capacity. But the total adsorption capacity of the combined system was higher than the total adsorption capacity of the individual components inferring that the overall system followed synergism.

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