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Adsorptive removal of water poisons from contaminated water by adsorbents

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Abstract

Adsorptive removal of water poisons such as Pb(II), Cu(II), Mn(II), Hg(II), CN⁻, microbes, nerve and blister agents (concentration range from 100 to 1000 mg/L) were studied by using adsorbents such as active carbon, impregnated carbon and bentonite loaded fabric strip. Removal of water poisons (99.5%) could be achieved with an optimum stirring time of 5–15 min and weight of adsorbent of 0.8-8.0 g/100 mL contaminated water, respectively. However, 85% bentonite loading was found to be most effective for Pb(II) removal. Effect of contaminants concentration was also studied.

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1. Introduction

Adsorptive removal of water poisons from contaminated water is one of the prime necessities on this planet for survival of living being. The water and air are being polluted and are undrinkable and unbreathable, respectively, due to release of effluents from the industrial plants, vehicular emissions, and exhaust gases from the industries. As if, it is not enough, there are other dimensions, that make the environment contaminated, which include the possibility of sabotage of water supply by terrorists using water poisons such as heavy metal ions, CN⁻, microbial contaminants, nerve and blister agents, etc. The same situation may hold good between two warring nations. World Health Organization (WHO) has very stringent standards for drinking water and Table 1 describes the health-based guideline values of contaminants.

Heavy metal elements and other water poisons including chemical warfare agents in water will cause physiological disorder, if contaminated water is used for drinking. Besides that, microbes can cause gastro-intestinal disorder and are the serious threat for mankind. In order to avoid this threat and to make water

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potable, several methods and technologies have been adopted for the water purification. Main water purification methods are complexation [1,2], ion exchange [3,4], membrane based method [5], chemisorption [6–8], adsorption [9–17], etc. Ion exchange ability and physical adsorption properties of different adsorbents have been exploited for the removal of contaminants found in water. Chlorination, ozonization, filtration, aeration, etc. are the other popular water purification processes.

On the other hand, we have developed water poison detection kit (WPDK) in Fig. 1 for the detection of various poisons such as Hg(II), Mn(II), Cu(II), Pb(II), CN⁻, As(III), microbes, nerve and blister agents.

The kit is highly useful for checking the potability of water in a very short period of time (30 min). However, the detection of microbes takes 18 h. The kit in the present form can only indicate the quality of water but not useful to make water potable. Therefore, it was necessary to incorporate a water purification bottle for this purpose. Table 2 describes the detectable concentration ranges of contaminants by WPDK.

In the present case, adsorptive removal capacity of various adsorbents such as active carbon, impregnated carbon, bentonite loaded fabric strips was considered of paramount importance and the adsorptive removal has been studied for the heavy metals, microbes (*E. coli*), cyanide, nerve and blister agents from their aqueous solution in concentration range from 100 to 1000 mg/L.

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 Table 1

 Safe level of contaminants as per WHO standards

Serial number	Contaminant	Safe level (mg/L)		
1	Copper	2.0		
2	Cyanide	0.07		
3	Arsenic	0.01		
4	Lead	0.01		
5	Manganese	0.5		
6	Mercury	0.001		
7	Microbes	0/100 mL		
8	Nerve agents	0.01 ^a		
9	Sulfur mustard	2.0 ^a		

^a As per defence standard.



Fig. 1. Water poison detection kit (WPDK).

2. Experimental

2.1. Material

Active carbon, grade 80 CTC of coconut shell origin, $1250 \text{ m}^2/\text{g}$ surface area, $12 \times 30 \text{ BSS}$ particle size and hardness more than 90%, moisture content less than 5%, ash content 3%, pH 10 (approximately) was obtained from M/s. Active Carbon India Ltd., Hyderabad and was used for the adsorption studies. Active carbon was heated for 2 h at 105 °C to make it free from moisture and then used as adsorbent. Copper sulphate (CDH), bentonite (Aldrich), ethyl cellulose (Aldrich), manganese sulphate (Sigma), sodium arsenate (S. D. Fine Chem. Ltd.) and

 Table 2

 Details on detectable concentration ranges of contaminants by WPDK

Serial number	Contaminant	Detectable concentration (mg/L)		
1	Copper	≥1.5		
2	Cyanide	≥ 0.05		
3	Arsenic	≥0.2		
4	Lead	≥0.001		
5	Manganese	≥ 0.2		
6	Mercury	≥0.5		
7	Microbes	\geq 1–3 coliform/100 mL		
8	Nerve agent	≥ 0.01		
9	Sulfur mustard	≥2.0		

potassium cyanide (BDH), lead nitrate (Aldrich), mercuric chloride (Aldrich), nerve and blister agents (in-house) were used for adsorption studies.

2.2. Impregnation of carbon

Active carbon was impregnated with the aqueous solution of Cu(II) (6–13.5%, w/w) by using incipient wetness technique. Obtained copper impregnated carbon was also impregnated with Ag(I) (w/w) to observe the effect of Ag(I) on adsorption of poisons from aqueous solution. The impregnated carbon was dried at 105 °C for 2 h and dried impregnated carbon was stored in an airtight container. Polyester fabric was coated with bentonite with the help of ethyl cellulose polymer and was used for adsorptive removal of poisons. E. coli was cultured in both broth and nutrient agar for removal study by using carbon. Atomic absorption spectrophotometer (Model-AA6) of Varian Techtron, Australia make was used for quantitative determination of the concentration of contaminants before and after treatment. Water poison detection kit, which was developed in-house, was used for checking the potability of water after the adsorptive removal of poisons from their aqueous solutions. Adsorptive removal of nerve and blister agents was estimated by gas chromatography. Chemito GC model no. 8610 equipped with flame ionization detector (FID) and BP–5, a capillary column ($30 \text{ m} \times 0.3 \text{ mm}$ I.D.) was used. Mechanical stirrer of M/s. Toshniwal, India was used for stirring during adsorption.

2.3. Batch process for adsorptive removal

Hundred milliliter of contaminated water in concentration range from 100 to 1000 mg/L was taken in a 250 mL conical flask, stirred with adsorbents such as active carbon, impregnated carbon, bentonite loaded fabric strips. Stirring time was varied while the adsorbent quantity and contaminant concentration were kept constant, which enabled the optimization of stirring time. However, in order to optimize the adsorbent quantity, experiments were conducted by varying the adsorbent quantity while keeping the stirring time and contaminants concentration constant.

Figs. 2 and 3 indicate the optimization of adsorbent quantity and stirring time for lead removal, where the details for other contaminants including Pb(II) are described in Table 3. The concentration of the contaminants before and after adsorptive removal was measured using AAS, titrimetric analysis [18] and GC techniques. Oven, injector port and detector were maintained at 70 °C, 220 °C, and 280 °C, respectively, for quantitative estimation of sarin. The GC conditions for quantitative estimation of sulfur mustard, however, were the same except that oven temperature was kept 140 °C. Nerve and blister agents were extracted in dichloromethane and chloroform for their estimation in water before and after adsorptive removal. Calibration curves were made using standard solution of nerve and blister agents in dichloromethane and chloroform, respectively.

Treated water was tested with WPDK for checking the potability. For microbial contaminant removal on carbon, water was contaminated with *Escherichia coli* (10⁶ *E. coli*/100 mL) and



Fig. 2. Adsorptive removal of Pb(II) on carbon: (a) effect of adsorbent quantity and (b) effect of stirring time.



Fig. 3. Adsorptive removal of Pb(II) on bentonite loaded polyester fabric: (a) effect of bentonite loading on polyester strip and (b) effect of stirring time.

treated the contaminated water with carbon under batch process. Extent of *E. coli* removal was based on the detection of *E. coli* using pour and plate method.

3. Results and discussion

In order to develop suitable method for treating the contaminated water and to make it potable, adsorptive removal of heavy metals, CN⁻, microbes, nerve and blister agents on adsorbents such as active carbon, impregnated carbon, bentonite loaded fabric strips was studied. The details are described in Figs. 2–4 and Table 3. Figs. 2 and 3 indicate the optimization of stirring time, adsorbent quantity and bentonite loading on polyester strip. In order to determine the optimum stirring time, adsorbent quantity and bentonite loading, isotherms (Figs. 2 and 3) of Pb(II) adsorption from aqueous solution on bentonite loaded polyester strip were used and the data are presented in Table 3. Fig. 3 also indicated that minimum 85% bentonite loading is required on polyester for effective adsorption. This study (Table 3) also indicated that bentonite is promising adsorbent for Pb(II) removal. However, it is required to be immobilized on polyester. Carbon does not require any modification and removes Pb(II) with

 Table 3

 Details on the removal of contaminants from their aqueous solution

Serial number	Contaminants	Contaminants concentration (mg/L)	Adsorbents	Optimum adsorbents weight (g)	Optimum stirring time (min)	Extent of contaminants removal (%)	Equilibrium pH
1	Lead	100	Carbon	1.4	10	99.5	5.58
2	Lead	100	Bentonite loaded fabric strips	0.581 ^a	5	99.6	6.4
3	Copper	100	Carbon	0.8	14	99.45	6.04
4	Copper	1000	Carbon	8.8	14	99.36	_
5	Manganese	100	Carbon	6.0	6	95.45	7.45
6	Cyanide	500	Cu(II) impregnated carbon	3.0	12	99.56	10.5
7	Mercury	1000	Carbon	8.0	15	99.06	7.6
8	Nerve agent (GB)	1000	Carbon	4.0	15	100	7.5
9	Blister agent (SM)	1000	Carbon	3.0	15	100	7.5
10	Microbes (E. coli)	10 ⁶ /100	Carbon	4.0	15	100 ^b	9.0

^a 85% Bentonite loaded fabric.

^b No colony was detected in treated water.



Fig. 4. Effect of initial concentration on adsorptive removal of (a) Pb(II); (b) CN⁻; (c) Mn(II); and (d) Cu(II) from contaminated water.

same efficiency. This makes the carbon, a better adsorbent than bentonite. In addition to Pb(II), the adsorptive removal of other contaminants indicated the rate of adsorption was very high, initially as indicated by the data presented in Table 3. This is due to the abundance of active sites on adsorbent in the initial stage. Effect of initial concentration was also studied for the adsorptive removal of contaminants. Fig. 4 indicates the effect of initial concentration on the removal of Pb(II), CN⁻, Mn(II), and Cu(II). It can be inferred from the study that rate and extent of adsorption decrease with the increase in the initial concentration. It is probably because of the reduced movement of adsorbate in the concentrated solution, as the number of collisions of metal ions in high concentration metal solution will be more than the low concentration solution and the time taken by metal ions in highly concentrated solution will be more to reach to adsorption sites [19].

Table 3 indicates that the contaminated water with equilibrium pH values ranging from 5.5 to 9.0 should be stirred for minimum time of 5, 14 12, 6, 15, 15, 15, 15 min for removal of Pb(II), Cu(II), CN⁻, Mn(II), Hg(II), microbes, nerve and blister agents, respectively. Table 3 also indicates that extent of removal was more than 99.55% for all the studied contaminants through physical adsorption and water became potable. However, active charcoal could not remove CN⁻. Therefore, chemisorbent carbon {Cu(II) impregnated} was used for the removal of CN⁻. The extent of removal was found to be more than 99.5%.

It can be observed from Table 3 that lead can be removed through physical adsorption on carbon and bentonite. However, bentonite being a powder makes turbidity in solution when added to contaminated water therefore, it was necessary to immobilize it on some support. Polyester fabric was used as a support and 85% bentonite loading (Fig. 3a) was found to be optimum for 99.6% removal of lead from contaminated water in an optimum stirring time of 5 min. It can be inferred from the results

$$\begin{array}{rcl} CuO & + & 2HCN & \rightarrow & Cu(CN)_2 & + & H_2O \\ 2Cu(CN)_2 & & \rightarrow & Cu_2(CN)_2 & + & (CN)_2 \\ CuO & + & (CN)_2 & & \rightarrow & Cu(CN) & (OCN) \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$$

(Table 3), that Cu(II) impregnated carbon can be used for the water purification bottle development as carbon will remove all the contaminants except CN^- which will be removed due to chemisorption of CN^- with Cu(II) present as an impregnant over the carbon. CN^- will react with Cu(II) to make Cu₂(CN)₂ (Scheme 1) which will be retained by carbon [20], thus, making the water free from CN^- . The catalytic effect of silver was also studied for removal of CN^- by adding silver in carbon along with Cu(II). No additional efficiency was observed due to silver in carbon, hence it can be interpreted that Cu(II) (7%, w/w) impregnated carbon is the suitable adsorbent for the effective removal of CN^- from contaminated water. The possible reactions schemes are given in the following as Scheme 1.

Moreover, it is also necessary to remove microbes from contaminated water as these are causative agents for various diseases. The adsorptive removal of *E. coli* was studied using activated carbon. $10^{6}/100 \text{ mL } E. coli$ could be removed with 4.0 g activated carbon. There was no bacterial colony observed on nutrient agar plates after the treatment, indicating 100% removal of bacteria. Similar findings were observed by Ujang et al. [21] and Naka et al. [22] and reported complete adsorption of *E. coli* from contaminated water.

4. Conclusion

The study of adsorptive removal of water poisons such as heavy metal ions, chemical warfare agents (nerve and blister agents), CN^- , microbes indicated that copper impregnated

carbon is a suitable adsorbent, as it can remove the contaminants based on physical and chemical adsorption. The study of effect of concentration has indicated the initial enhancement of adsorptive removal, with the increased concentration of the contaminants. Optimum removal time was found to be 5-15 min for the water purification in a batch of 100 mL with 0.8–8.0 g of adsorbent.

It can be inferred from the study that a water purification bottle (1.0 L capacity) can be developed with copper impregnated carbon and two sachets, each of 50 g adsorbent can be useful for water purification upto five cycles minimum for the removal of contaminants in concentration range of 100–1000 mg/L.

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