



Research Journal of
**Environmental
Sciences**

ISSN 1819-3412



Academic
Journals Inc.

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Research Article

Nutrient Deportation Efficiency of Selected Natural and Synthetic Adsorbents from Municipal Wastewater for Environmental and Economic Benefits

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Abstract

Background and Objective: In view of scarcity of water resources due to huge amount of wastewater generated from population increase and industrialization, it has become a challenge to protect and conserve these water resources through proper treatment driven reuse. The present study was aimed at assessing the effectiveness of some natural and synthetic-adsorbent for eutrophication control by phosphate-P and nitrate-N removal from wastewater so that the resulting water can be safely reused for various economic-driven-activities. **Materials and Methods:** Phosphate-P and nitrate-N removal potentials from municipal-wastewater of some natural (fly-ash, coarse-sand and cattle-dung-cake-ash and their mixture-combination) and synthetic (Ferosorp, ferric-hydroxide, activated-alumina and their mixture-combination) adsorbents were tested in batch-experiment for 10 days at room temperature (30°C). Ten gram of each adsorbent was added to 500 mL of wastewater in battery jar. Different parameters (pH, phosphate-P, nitrate-N and available-P) were monitored using the standard protocol. Desorption of saturated Ferosorp was also examined using different extractants. The fertilizer value of spent adsorbent (Ferosorp) was tested for the growth of Bengal gram (*Cicer arietinum*) in pot. **Results:** Synthetic-adsorbents (activated-alumina, Ferosorp and ferric-hydroxide) removed 92-93% phosphate-P, whereas both synthetic and natural (fly-ash, coarse-sand and cattle-dung-cake-ash) removed 100% NO₃-N from wastewater within 10 days of contact time. The nutrient removal capacity of the test adsorbents was correlated with their porosity and surface area. Cattle-dung-cake-ash and fly-ash were also good adsorbents for removal of NO₃-N. Though the amount of phosphate-P adsorbed by water with saturated Ferosorp was relatively less (47.58%) than other extractants (75.50%), the spent Ferosorp with soil revealed a pronounced effect on growth of *Cicer arietinum*. **Conclusion:** It is reasonable to conclude that Ferosorp would be a low-cost and environmentally-sound sorbent for the treatment of phosphorous contaminated effluents and generated spent Ferosorp could be used as potential fertilizer for enhancing crop-production.

Key words: Cattle-dung-cake-ash, ferrosorp, economic-driven-activities, removal efficiency, crop production, potential fertilizer

Citation: Ankita Bhattacharjee, Bana Behari Jana, Sushil Kumar Mandal, Jatindranath Bhakta, Debarati Ghosh and Susmita Lahiri, 2018. Nutrient deportation efficiency of selected natural and synthetic adsorbents from municipal wastewater for environmental and economic benefits. Res. J. Environ. Sci., 12: 234-246.

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

It has become a worldwide challenge to protect and conserve surface and groundwater-resources through proper and effective management practices. Urbanization and industrialization are largely responsible for more than 38524 million liters of sewage generation (98 liters/capita/day) in India¹. If not properly managed for its safe reuse, this would act as a threat to surface and ground-water-resources. So the approach should aim not only water-conservation but on nutrient recovery and environmental-remediation as well. Wastewater is considered as an immense nutrient-resource with about 90 t of nitrogen, 32 t of phosphorus and 55 t of potassium that could be recovered daily from domestic-sewage in India². Lack of efforts to recover nutrients through proper wastewater-treatment for reuse may lead to undesired nutrient load causing eutrophication of water-bodies. This nutrient loss is a huge economy loss to the country as well as unintended ground-water-pollution. Therefore, it is urgent to address the sustainable issues of municipal-wastewater management for safe reuse and water conservation.

Excess nitrogen-N and phosphate-P of municipal-wastewater can be controlled by physical, chemical³ and microbial activities under aerobic and anaerobic-conditions through trickling-filter⁴ and activated-sludge-processes⁵ which can remove upto 97% of the total-phosphorus⁶. Struvite-technology has emerged as sustainable method to remove 80-90% of phosphate-P from municipal-wastewater through chemical precipitation⁷ and is temperature and composition dependent⁸.

Conventional wastewater-treatment technologies in economically poor countries are suffering from lack of infrastructure and maintenance costs. On the other hand, some eco-friendly potential-adsorbents are gaining much importance due to operation ease, simplicity, low-maintenance-costs and green-driven sustainable approach.

Adsorption is a surface-phenomenon creating a film of the adsorbate on the surface of the adsorbent or it is mass transfer-process that involves the accumulation of substances at the liquid-solid-interface^{9,10}. The adsorption process may be classified as physisorption, chemisorption and electrostatic-attraction. Many varieties of traditional and novel adsorbents including alternative inexpensive adsorbents¹¹ are used for pollutants removal from wastewater.

Adsorbents used for water treatment are either of natural origin with low adsorption capacities but cost-effective or of industrial production/activation process which are expensive

but with high adsorption capacities¹². The performances of several adsorbents such as powdered-activated-carbon (PAC), granular-activated-carbon¹³, granular-ferric-hydroxide¹⁴, activated-alumina¹⁵ have been examined.

Little or no systematic study has been done to address for a complete solution for eutrophication control in wastewater especially with respect to its safe reuse in various economic activities and environmental-remediation. The purpose of the present study was to assess the effectiveness of some natural and synthetic-adsorbent for eutrophication control by phosphate-P and nitrate-N removal from wastewater so that the resulting water can be safely reused for various economic-driven-activities.

MATERIALS AND METHODS

The experiment was performed in the research laboratory of the Department of Ecological Studies, University of Kalyani, West Bengal, India in order to examine the effectiveness of some low-cost, natural and synthetic adsorbents and residues of carbonaceous-materials for the phosphorus and inorganic-nitrogen removal from municipal-wastewater. The total study was completed within 3 months in 2017. Six adsorbents were grouped in to three-activated-alumina (synthetic), Ferrosorp and ferric-hydroxide (industrial by-product), fly-ash and cattle-dung-cake-ash (residues of carbonaceous-materials) for the experiment.

Characteristics of adsorbents: Ferrosorp and ferric-hydroxide were provided by Nacotec Co. Ltd., Bangkok, Thailand and activated-alumina (Sigma-Aldrich) was procured from the market containing the following details (Table 1). Cattle-dung-cake-ash, fly-ash and coarse-sand were procured from neighboring areas. Particle-density, bulk-density, porosity and specific-gravity of these adsorbents were determined following the standard protocols¹⁶.

Zeta-potential of adsorbents was measured by Malvern zetasizer (Nano-series) following the Maurya *et al.*¹⁷ method. Specific surface-area and pore-volume were analyzed by BET study¹⁸ using Micrometrics Gemini 2375 and Gemini V.

Characteristics of municipal wastewater: Wastewater (primary effluent) used in the study was procured from a sewage treatment system of Kalyani township (22°58/N latitude and 88°26-58/E longitude), West Bengal, India, with a total population of around 1,00,000. Physico-chemical and nutrient parameters of wastewater analyzed¹⁹ were: temperature (20.3-24.1°C), pH (6.7), dissolved-oxygen

Table 1: Details obtained from the procured adsorbents

Name of the adsorbent	Nature		Grain/particle size	Surface-area	Recommendations
	Physical	Chemical			
Ferrosorp	Granular	–	0-0.5 mm	–	Removal of phosphate-P, arsenic, heavy metals from water and wastewater
Ferric-hydroxide	Granular	–	0.5-2 mm	–	
Activated-alumina	Porous	Aluminum oxide (alumina, Al ₂ O ₃)	150 µm	150 m ² g ⁻¹	Filtration of fluoride, arsenic and selenium from drinking-water.
Coarse-sand	Granular	Mineral-particles and rocks	0.0625-2 mm	–	Used as water-filtering-media and for construction-work
Cattle-dung-cake-ash	Fine	Carbon, nitrogen, hydrogen, oxygen, phosphorus	1004 nm	–	Used as adsorbent for removal of pond-turbidity and to correct acidity of fish-ponds
Fly-ash	Fine and spherical	Silicon dioxide (SiO ₂) (both amorphous and crystalline), aluminum oxide (Al ₂ O ₃) and calcium oxide (CaO)	0.5-300 µm	–	Used for waste-stabilization, solidification as distemper and in manufacturing cement

(1.34 mg L⁻¹), total-organic-carbon (219 mg L⁻¹), phosphate-P (2.462 mg L⁻¹), ammonia-N (19.112 mg L⁻¹), nitrite-N (0.13 mg L⁻¹), nitrate-N (3.88 mg L⁻¹), total-inorganic-nitrogen-N_i (23.12 mg L⁻¹), total-dissolved-solids (555 mg L⁻¹) and conductivity (789 µS cm⁻¹).

Experimental

Nutrient adsorption study: The batch experiments of the adsorption studies were conducted at room temperature (30°C) in 1 L capacity glass jar for 10 days. Collected municipal-wastewater was filtered and dispensed (500 mL) into 24 jars allotted for 8 treatment groups in triplicate. The jars remained open and covered with net. The treatments were: activated-alumina (T-1), ferric-hydroxide (T-2), ferrosorp (T-3) and mixture of ferrosorp, ferric-hydroxide and activated-alumina (1:1:1) (T-4), coarse-sand (T-5), fly-ash (T-6), cattle-dung-cake-ash (T-7) and mixture of coarse-sand, fly-ash and cattle-dung-cake-ash (1:1:1) (T-8).

About 10 g of each prepared adsorbent was added to each jar of wastewater in triplicate. The suspension was stirred daily at a fixed time during the period of experiment using a magnetic-agitator and stirrer at a controllable speed. A control set without adsorbent was also maintained. About 6 mL of water sample was withdrawn carefully with the help of a pipette from each jar every day and analyzed¹⁹ for the concentrations of phosphate-P, ammonia-N, nitrite-N, nitrate-N and total-inorganic-nitrogen (N_i) and pH. The available-phosphorus content of the adsorbents was determined both in the beginning and at termination of experiment by Olsen-method²⁰.

The removal efficiency (Re) of different adsorbents was calculated as:

$$Re (\%) = \left[\frac{C_i - C_f}{C_i} \right] \times 100 \quad (1)$$

Where:

C_i = Initial concentration

C_f = Final concentration

Effects of different pH on removal of phosphate-P and nitrate-N:

Phosphate-P and nitrate-N removal study was carried out for 2 weeks using a batch equilibrium technique to determine the optimum pH required for maximum removal from water. Experiments were conducted in 250 mL conical flask using known weight of the sorbent (Ferrosorp) to equilibrate the known volume (100 mL) of sorbate (phosphate-P and nitrate-N). The effects of different initial pH values (4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0 and 8.5) on the phosphate-P and nitrate-N sorption were determined at different adjusted pH in the beginning using pH buffer.

Phosphate-P desorption study:

Initially ferrosorp samples were sorbed with 3 and 100 mg P/l as KH₂PO₄ at room temperature (25 ± 2°C) for 3 days prior to the desorption study which continued for 17 days. The suspension was filtered and the residue was washed with 10 mL distilled-water for two times to remove excess remaining phosphate-P ions. Then the samples were air-dried (25 ± 2°C) for a week and were used for desorption studies.

Phosphate-P sorbed ferrosorp samples and extractants were taken in 250 mL conical flask and to it 100 mL of three different extractants (0.005M SO₄²⁻ as Na₂SO₄, 0.01 M NaHCO₃ and distilled water) were used in triplicate. The extractants were shaken thoroughly on a horizontal shaker for 4 h. The

Table 2: Characterization of adsorbents tested

Materials	Characteristics					Brunauer-Emmett-Teller analysis	
	Particle-density (g cm ⁻³)	Bulk density (g cm ⁻³)	Porosity (%)	Specific-gravity	Zeta-potential (Mv)	Surface-area (m ² g ⁻¹)	Pore-volume (cc g ⁻¹)
Synthetic							
Activated-alumina	2.38	1.21	49.16	0.97	28.60	138.09	1.8330
Ferric-hydroxide	2.63	0.84	67.94	0.65	-12.70	141.90	1.3430
Ferrosorp	2.79	0.83	69.79	0.70	-8.07	171.00	0.1657
Natural							
Fly-ash	2.26	1.26	44.45	1.02	-23.20	1.847	1.120
Coarse-sand	2.74	1.85	31.88	1.52	-14.60	1.200	---
Cattle-dung-cake -ash	2.30	0.40	82.37	0.35	-8.24	9.750	1.910

samples were then centrifuged at 4500 rpm for 15 min and filtered through Whatman filter No. 42 to determine the concentration²¹. The desorption percentage (Ds) (%) of Ferrosorp was calculated using the following Equation:

$$D_s (\%) = \left[\frac{T-C}{T} \right] \times 100 \quad (2)$$

where, T is the treatment set and C is the control set.

Pot experiment using spent ferrosorp: In order to assess the fertilizer potentials of spent ferrosorp a pot experiment was conducted for 30 days. Ferrosorp was initially suspended (at 250 g L⁻¹) in 400 mL of phosphate-P (100 mg L⁻¹) solution (treated) and shaken at 120 rpm by a mechanical shaker for 48 h for maximum adsorption. The treated ferrosorp was separated by Whatman filter No. 42 filter paper, the obtained spent ferrosorp was washed in distilled water, dried and properly homogenized for employing as fertile soil bed for evaluating the growth of germinated gram (*Cicer arietinum*) in pot trial²².

Twelve small (50 mL) plastic pots were filled with 30 g soil+treated-ferrosorp in different ratios and randomly divided into four groups (3×4): Only soil, spent ferrosorp mixed with soil (1:1), spent ferrosorp mixed with soil (1:4) and only spent ferrosorp. After 1 day of watering the pot with 10 mL of tap water a germinated seed of gram (*Cicer arietinum*) was planted in each pot followed by subsequent watering at 5 mL/pot/day for 14 days. The growth of plants was recorded by measuring the shoot-length and leaf-number at every 5 days interval. Finally, at the end of experiment, biomass, shoot-length, root-length and number of nodes and internodes were recorded.

Statistical analysis: One way analysis of variance was used for analysis of data. If the mean effect was found significant, the ANOVA was followed by a least significant difference (LSD)

test. The strength of the linear relationship between two variables was calculated by computing correlation coefficient (r) between them. All statistical tests were performed at 5% probability level (p<0.05) using statistical package.

RESULTS AND DISCUSSION

Nutrient adsorption study

Characterization of adsorbents: Particle density of different adsorbents was highest (2.79 g cm⁻³) in ferrosorp and lowest in fly-ash (2.26 g cm⁻³), respectively. The cattle-dung-cake-ash had maximum porosity of 82.37% and lowest in coarse-sand 31.88% (Table 2).

Zeta-potential, the indicator of the surface charge on a particle, ranged from -8.24 mV (cattle-dung-cake-ash) to 28.6 mV (activated-alumina) in different adsorbents.

Changes of phosphate-P concentrations of water: Although there was sharp decline in the concentration of phosphate-P of water (Fig. 1) in the treatments with the synthetic group of adsorbents ferrosorp (T-3), ferric-hydroxide (T-2), activated-alumina (T-1) and their mixture combinations (T-4), no such marked decline was registered in the natural adsorbent group comprising coarse-sand (T-5), fly-ash (T-6), cattle-dung-cake-ash (T-7) and their mixture combination (T-8). As a result, two groups of adsorbents were clearly discernable (ANOVA, p<0.05). The concentration of phosphate-P remained consistently high in control (Fig. 1).

Changes of available phosphorus content of adsorbents:

The amount of available phosphorus that remained between 0 and 6.78 mg L⁻¹ in the beginning in different adsorbents increased to a maximum of 23.36 mg L⁻¹ (Fig. 2) which was followed by 21.75 mg L⁻¹ (90%), 14.22, 8.01, 5.15 and 3.74 mg L⁻¹ in ferric-hydroxide, activated alumina,

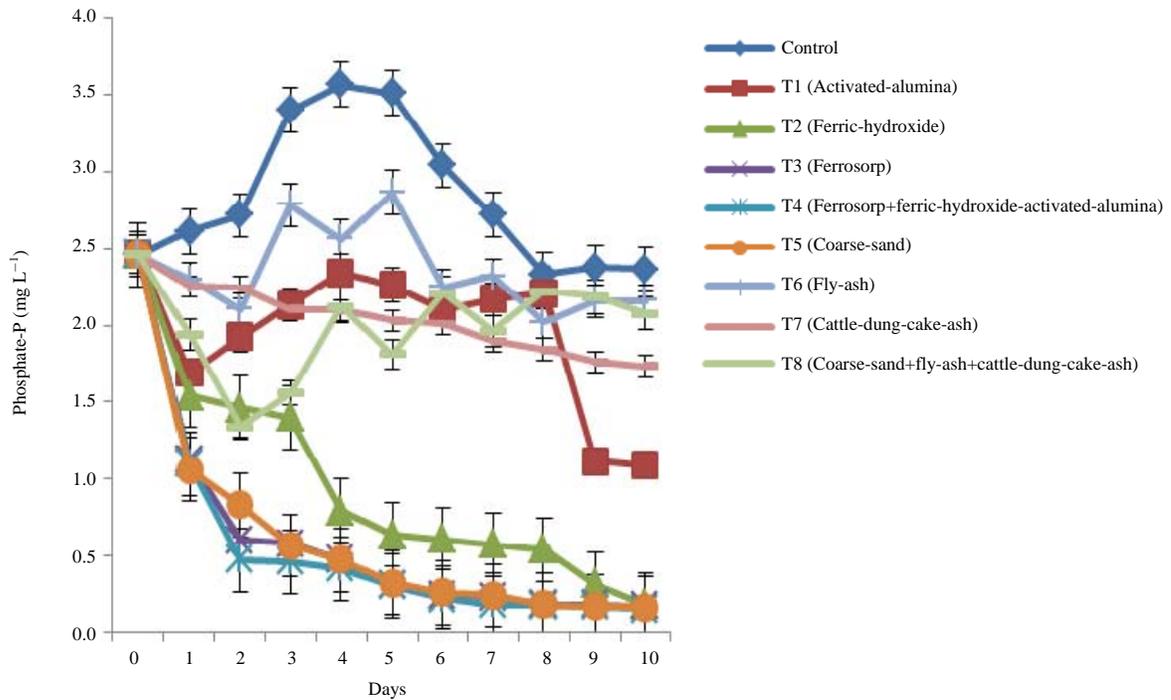


Fig. 1: Time scale variations of phosphate-P concentration of water in different adsorbent treatments employed

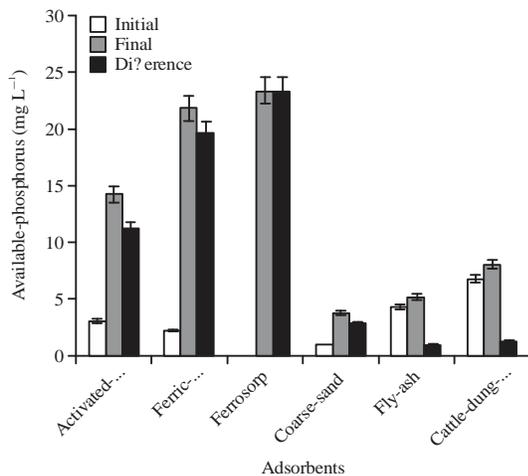


Fig. 2: Responses of available-P content of adsorbents prior to and after termination of experiment

cattle-dung-cake-ash, fly-ash and coarse-sand, respectively. This clearly reflected the variability of phosphate-P adsorption potentials of different adsorbents as: Ferrosorp (T-3)>ferric-hydroxide (T-2)>activated-alumina (T-1)>cattle-dung-cake-ash (T-7)>fly-ash (T-6)>coarse-sand (T-5).

Changes of total inorganic nitrogen (N_i) of water: The initial concentration of nitrate-N (Fig. 3) was completely removed

from the water phase within 3 or 4 days in all but for activated-alumina where complete removal was observed only after 9 days of exposure. Coarse-sand still retained 0.946 mg L⁻¹ of its initial concentration even after 10 days thereby exhibiting its removal efficiency (Fig. 3).

The mean concentrations of residual ammonia-N as well as total-inorganic-nitrogen (N_i) (Fig. 4) remained fairly low in Ferrosorp (T-3) and high in coarse-sand (T-5) indicating the highest and lowest removal capacity in the former and latter, respectively.

The removal percent of ammonia-N was minimum in coarse-sand (T-5) to as maximum as in ferrosorp (T-3) or in ferric-hydroxide (T-2). The mixture combination (Ferrosorp, ferric-hydroxide and activated-alumina (T-4) however, showed the maximum value in between. Likewise, removal per cent of total-nitrogen (Fig. 4) was low (13.41 mg L⁻¹) in coarse-sand (T-5) and high (2.69 mg L⁻¹) in ferrosorp (T-3) or in ferric-hydroxide (T-2) (3.61 mg L⁻¹). Responses of nitrate-N were also similar to that of total-nitrogen.

Changes of pH in water: Water pH which remained 6.7 in the beginning but increased by 0.2-1.0 U during the experimental time period (6.9-7.7). The result revealed that at initial stage the pH of the wastewater was acidic in nature (6.9) which becomes normal or slightly alkaline 48 h of treatment application irrespective of adsorbents (ANOVA, p<0.05) (Table 3).

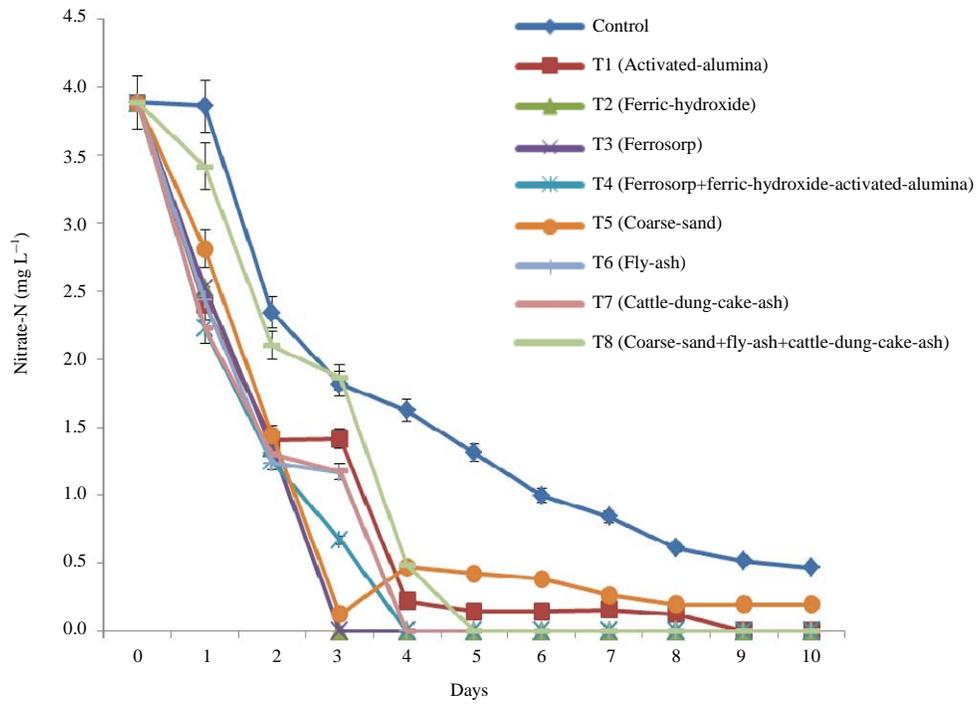


Fig. 3: Time scale variations of nitrate-N concentration in different treatments employed

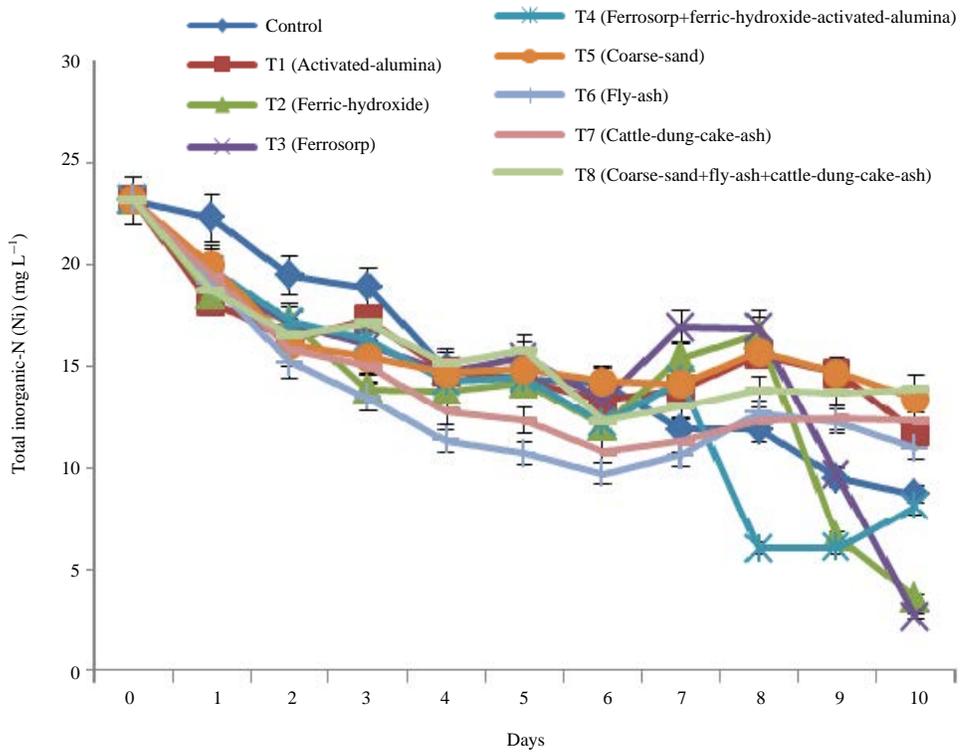


Fig. 4: Time scale variations of total inorganic-N (Ni) concentration in different treatments employed

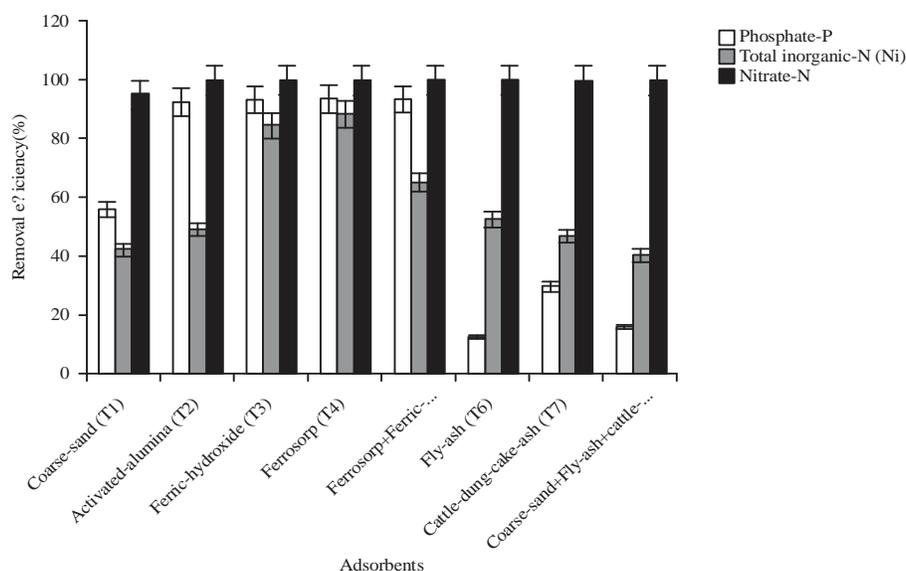


Fig. 5: Removal efficiency of phosphate-P, nitrate-N, total-inorganic-nitrogen Ni from water in different treatments

Table 3: Changes of pH in wastewater

Days	Control	T1	T2	T3	T4	T5	T6	T7	T8
0	6.7	6.7	6.7	6.7	6.7	6.7	6.7	6.7	6.7
1	6.9	7.0	7.0	6.9	7.0	7.0	6.9	7.2	7.0
2	7.2	7.2	7.2	7.1	7.1	7.1	7.1	7.3	7.3
3	7.3	7.2	7.2	7.2	7.2	7.3	7.1	7.3	7.3
4	7.2	7.3	7.2	7.3	7.2	7.3	7.2	7.3	7.4
5	7.4	7.4	7.4	7.5	7.3	7.5	7.2	7.4	7.4
6	7.7	7.6	7.5	7.3	7.4	7.6	7.3	7.4	7.5
7	7.7	7.4	7.4	7.4	7.2	7.6	7.1	7.3	7.4
8	7.7	7.5	7.4	7.3	7.3	7.6	7.3	7.2	7.4
9	7.5	7.5	7.4	7.1	7.2	7.4	7.3	7.2	7.3
10	7.1	7.1	7.2	7.1	7.2	7.1	7.3	7.1	7.3

Removal efficiency: Time and adsorbent quality dependent removal percent ranged from 92-94% for phosphate-P and from 84-90% for nitrate-N (Fig. 5). In general, micropore, surface-area and surface iso-electric-pH value of the adsorbents determine the removal efficiency of the adsorbents. In the present study, maximal removal efficiency of phosphate-P was observed in the synthetic group (T-3, T-2, T-1 and T-4) and reduced removal efficiency in the natural group (T-5, T-6, T-7 and T-8).

Likewise, removal efficiency for total inorganic nitrogen (Ni) (84-88%) coupled with ammonia-N (92%) was also maximum in ferrosorp (T-3) or ferric-hydroxide (T-2) showing no difference ($p > 0.05$) from each other. The second best adsorbent was identified to be the mixture combination (T-4) showing nearly 65% removal of its initial concentration of inorganic-nitrogen (Fig. 5).

Effects of different pH on removal of phosphate-P and nitrate-N: The pH value of the aqueous solution is an

important controlling parameter in the adsorption process. These pH values affect the surface charge of adsorbent, the degree of ionization and speciation of adsorbate during adsorption. There was gradual decline in the concentration of phosphate-P of water over time in all pH conditions, more conspicuous between 4.5 and 6.0 (Fig. 6).

Rate of decline of phosphate-P/h tended to increase with rise from 4.0 to maximum at pH 5.5 and reduced with further rise in pH suggesting pH 5.5 as optimal for phosphate-P removal. Responses of nitrate-N to different pH were similar to phosphate-P but the estimated optimal pH recorded was 4.5. Maximum removal of both phosphate-P (92.7%) and nitrate-N (85.7%) were registered in pH 5.5 and 4.5, respectively (Fig. 6a, b).

Phosphate-P desorption study: Differences in the amount of phosphate-P desorbed by three extractants were clearly discernible. Among the three extractants, 0.01M HCO_3^- extracted the highest percent of the sorbed phosphate-P from

the ferrosorp. This was followed by water and 0.005M SO_4^{2-} (Table 4). The mechanisms by which these anions were adsorbed to the colloid particles were surface-complexation and diffuse-ion swarm association.

Pot experiment using spent ferrosorp: The shoot-lengths of Bengal gram (*Cicer arietinum*) was little higher when grown in the spent ferrosorp mixed with soil in the ratio of 1:4 (11.0 cm) than soil (10.55 cm) or 1:1 mixed ratio (5.87 cm). The

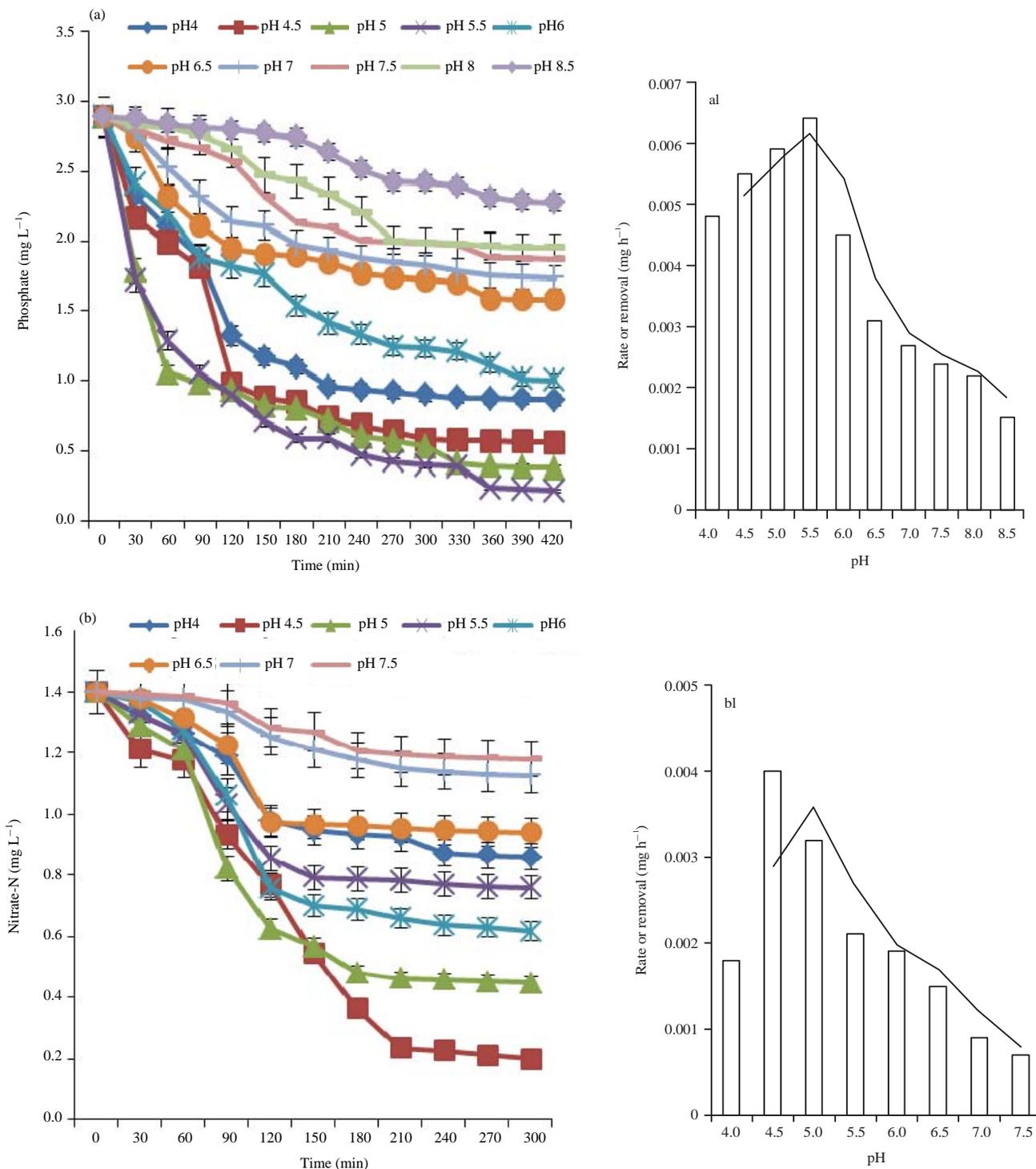


Fig. 6(a-b): Time scale responses of phosphate-P (a) Rate of removal in different pH(a1) and nitrate-N and (b) Rate of removal in different pH (b1) using ferrosorp as adsorbent



Fig. 7: Results of plant growth in 1:1 and 1:4 mixtures of soil and spent ferrosorp along with soil and spent ferrosorp

Table 4: Phosphate-P adsorption and desorption by ferrosorp

Phosphate-P concentration solution	Adsorbed phosphate-P (%)	Desorption(%) by different extracts		
		0.01 M HCO ₃ ⁻	H ₂ O	0.005 M SO ₄ ²⁻
3 mg L ⁻¹	78.9	27.19	17.48	0.871
100 mg L ⁻¹	87.4	75.50	47.58	17.550

Table 5: Responses of different parameters after plant growth

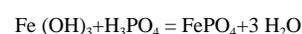
Parameters	Soil	Ferrosorp: Soil ratio- 1:1	Ferrosorp: Soil ratio-1:4	Ferrosorp
Shoot length(cm)	10.55	5.87	11.00	7.40
Root length(cm)	10.00	8.37	10.72	7.50
Number of leaves	37.00	26.00	43.00	28.00
Available-phosphorus of soil (kg ha ⁻¹)	433.66	457.63	207.42	633.92
Total phosphorus of soil (µg g ⁻¹)	48.25	32.50	20.47	24.75
Total-P of plants (µg g ⁻¹)	200.25	357.25	460.75	89.16
Counts of phosphate solubilizing bacteria (CFU × 10 ³ mL ⁻¹)	2.80	1.96	3.60	1.32

shoot-length was 7.40 cm in raw ferrosorp (Fig. 7). Likewise, the leaf number was higher in the ratio of 1:4 (43) followed by soil (37), raw ferrosorp (28), 1:1 (26) (Table 5).

Nutrient adsorption study: In this study a strong direct relationship ($R = 0.952$, $p < 0.05$) of available-phosphorus content of the adsorbents with the phosphate-P removal from water and an inverse relationship with the residual phosphate-P level of water (Fig. 1) indicated that more the removal of phosphate-P from water phase, more will be the deposition of available-phosphorus in the adsorbents (Fig. 2).

Increased surface area^{23,24} pore volume^{25,26} and also zeta potentials²⁷ as well as of the synthetic adsorbents compared

to natural adsorbents explained their high adsorption performance (Table 2). Synthetic adsorbents due to their anions'-complexing capacity, binds the surface groups of pollutants by ligand-exchange reactions and electrostatic-interactions with the charged hydroxide surfaces²⁸ removing phosphate-P at a faster rate. Thus the excellent performance of ferrosorp and ferric-hydroxide with higher values of iron containing particle-density developed a strong affinity towards phosphate-P adsorption^{29,30}. The equation³¹ for the interaction in 2 steps of binding adsorptively to the ferrosorp surface followed by chemical conversion to stable ferric-phosphate-P (FePO₄), as follows:



In control, microbial decay of organic matter might have increased the phosphate-P concentration indicating a possible interference of microbial activities with the adsorption.

Some earlier studies³²⁻³⁴ also confirmed the surface area as an important attribute to regulate adsorption as well as adsorption equilibrium. Removal efficiencies of various adsorbents have been compared (Table 6) under different experimental conditions.

In case of natural adsorbent it appeared that cattle-dung-cake-ash was relatively less effective for phosphate-P removal (29.56%).

The faster rate of removal of nitrate-N than phosphate-P in the water phase was the result of triangular-planar structure of nitrate-N ions whereas phosphate-P ions are tetrahedral-structure. As a result, the smaller size of nitrate-N ions facilitated their capturing by the adsorbents and deposited in the cavities of adsorbents leaving less space available for capturing phosphate-P ions. Hence excepting the coarse-sand which showed 84% removal, all other adsorbents removed (Fig. 3) phosphate-P. Electrostatic attraction between NO₃⁻ and positively-charged surface of ferric ions, activated alumina and fly-ash^{37,44,45} explained their adsorption capacity, whereas, modified sand has the affinity to adsorb ammonia but not the nitrate-N⁴². Evidences suggested that removal of nitrate-N was achieved within 90 min by granular ferric-hydroxide³⁷ which was similar to the present study result (Fig. 4).

Cattle-dung-cake-ash was highly effective for removing nitrate-N (100%) only within 3 days of exposure (Fig. 5). This shows that the adsorbent potential of cattle-dung-cake-ash is of particular interest because of ease of its availability from the dumping ground as discarded cooking waste materials that may cause environmental hazards. Although fly-ash⁴¹ and raw/modified sand³⁹ were reported to be a good adsorbent for phosphate-P removal but in the present study, the fly-ash (82%) along with coarse-sand (94%) could be a promising solution for nitrate pollution in water bodies.

Effects of different pH on removal of phosphate-P and nitrate-N:

The pH of 4.5-5.5 in the acidic range appeared to be optimal for maximum adsorption of nitrate-N and phosphate-P (Fig. 6) by ferrosorp. The -OH groups in the hydrated oxides like hydrous-iron-oxide attract positive charges on the ferric-hydroxide surface⁴⁶ at acidic pH range showing high pH dependence of the surface charges^{47,48}. This pH range was also responsible for 92% phosphate-P removal by the lanthanum-modified-active alumina (nano aperture)¹⁵. However, about 90% removal of phosphate-P using granular-ferric-hydroxide as adsorbent¹⁴ from water was recorded at

Table 6: Comparison of removal (%) of phosphorus and nitrogen from water under different experimental conditions

Adsorbents	Parameters	Literature		References
		Present study (%)	Experimental condition	
Ferric-hydroxide	Phosphate-P	93.22	Column study at pH 7.0±0.2	Zhao <i>et al.</i> ¹⁴
	Total-nitrogen	84.38	Continuous regime on granular- ferric-hydroxide (GFH)	Kartashevsky <i>et al.</i> ²⁵
Activated alumina	Phosphate-P	92.90	Batch adsorption onto granular chitosan Fe ³⁺ complex	Hu <i>et al.</i> ³⁶
	Total-nitrogen	49.00	Nano-aperture-lanthum modified-active-alumina (pH = 4) adsorption time (12 h) from agricultural non-point source of pollution	Luo <i>et al.</i> ¹⁵
Coarse-sand	Phosphate-P	55.85	pH 5.5-8.3 suitable for removal of nitrate-N	Mahmood <i>et al.</i> ³⁷
	Total inorganic nitrogen (Ni)	42.00	C33 sand after 5 h batch study and after 10 h contact	Arias <i>et al.</i> ²⁸
	Phosphate-P	12.26	Raw-sand and modified-sand (fixed bed column) Sand filter	Azhar and Shaza ³⁹
Fly-ash	Phosphate-P	52.63	Class-C fly-ash (pH of 7 and of prepared PO ₄ solution)7.5 g/100 mL At pH 7 for wastewater-treatment	Beaveres and Tully ⁴⁰
	Total inorganic nitrogen (Ni)	52.63	At pH 5-6 and 1 h contact time for nitrate-N removal	Lu <i>et al.</i> ⁴¹
				Ramakrishnaiah and Vismitha ⁴²
				Ragheb ⁴³
				Rajpurkar and Kazi ⁴⁴

optimal pH of 7.0 ± 0.2 . The pH range^{37,44,45} of 4.8-8.3 was recorded for 25-96.9% nitrate-N removal by fly-ash or activated-alumina.

Phosphate-P desorption study: Desorption of phosphate-P by different extractants suggested that bicarbonate increased the negative charge of the soil in the presence of phosphate-P⁴⁹, thus explaining the maximum (75%) extraction capacity of phosphate-P by 0.01M HCO_3^- compared with other extractants (Table 4). After desorption, the equilibrium between the sorbed phosphate-P and the solution phosphate-P could be achieved at higher solution to adsorbent ratio compared to lower one. Phosphate-P ions are principally adsorbed as inner-sphere complex species, the remaining freshly added labile forms of P ions on the surface were readily desorbed by other ions like sulphate, bicarbonate and water molecules due to their bonding through single coordinate linkage⁴⁸.

Pot experiment using spent ferrosorp: The results of pot experiment clearly indicated a positive impact of spent ferrosorp on the growth of Bengal gram showing comparable growth responses in spent ferrosorp mixed with soil (1:4) having $207.42 \text{ kg ha}^{-1}$ available phosphorus and $433.66 \text{ kg ha}^{-1}$ in control soil (Fig. 7).

The present study although yielded a very good result about the potential of natural and synthetic adsorbents in nutrient removal but certain obvious limitations may be mentioned for its application potential in a commercial scale. The availability of adsorbents excepting cattle-dung-cake-ash may be a problem because of their source and quantity of production. Moreover, the study needs to be conducted at a field scale in order to assess its application potential. Prospects are there to evaluate the adsorption potential of the tested adsorbents in some other various combinations for e.g., natural+synthetic adsorbents in different ratios.

CONCLUSION

It may be concluded that synthetic adsorbents exhibited immense potentials for eutrophication control through removal of both phosphate-P and nitrate-N from wastewater. However, due to small size of their ionic structure, nitrate-N was removed more easily and faster than phosphate-P by any of the adsorbents tested. Moreover, the spent ferrosorp can be used as fertile soil bed in managing soil phosphorus including other nutrients in agriculture after sorbing the phosphate-P from aqueous solution, which will also significantly reduce the application of chemical fertilizer responsible for degrading soil

quality. Therefore, it can be inferred from this study that the spent ferrosorp could be an eco-friendly adsorbent and reused as a phosphate-P enriched fertile soil bed in various agricultural practices to enhance the crop production and to avoid the further phosphate-P related eutrophication problem in environmental pollution.

SIGNIFICANCE STATEMENT

The novelty of the study was that some synthetic and natural adsorbents revealed immense potentials for removal of phosphate-P and nitrate-N from wastewater and therefore, found effective to reclaim the wastewater for reuse. Cattle-dung-cake-ash and fly-ash were of particular interests for its application in nutrient removal from wastewater because of ease of its availability from the dumping ground that can otherwise cause environmental hazards and ground water pollution as leachate. More importantly, the spent adsorbent can serve as alternative source of fertilizer for the production of agricultural crops. Hence, it would serve as win-win strategy towards combating environmental pollution and source of alternative fertilizer.

ACKNOWLEDGMENT

Author is grateful to Department of Science and Technology, New Delhi for the award of INSPIRE fellowship for this work. We thank Mousumi Patra, Senior Research Fellow, Department of Biochemistry and Biophysics, University of Kalyani for technical help for the analysis of sample.

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