Crushed Waste Concrete as Active Filter Material for Phosphate Elimination from Domestic Wastewaters

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ABSTRACT: Crushed waste concrete was used in this study to evaluate its performance as an effective filter for phosphate reduction. Initial batch tests with synthetic phosphate solutions show more than 98% removal efficiency of the substrate (crushed concrete) with a quick equilibrium time of 60 minutes. Equilibrium data were analysed using Langmuir and Freundlich isotherms. The two isotherm models closely correlate with low-to-moderate phosphate concentrations than lower phosphate concentrations, indicating that adsorption mechanism is more prevalent at moderate concentrations. Further batch experiments with wastewater collected from a Decentralised Treatment System (DTS) showed a reduction of BOD, conductivity, hardness and calcium content at 36, 16, 35 and 37% respectively. While no leaching of heavy metals was observed during the batch experiments, a significant reduction of Al, Cr, Pb and Cu was noted while performing the batch experiments with wastewater collected from the DTS. However, the wastewater has to be neutralized with acid before being discharged because of the increase in pH to above 9, caused by the release of calcium from the substrate while in contact with water.

KEYWORDS: Crushed concrete waste, Decentralized Treatment System, Domestic wastewater, phosphate elimination.

I. INTRODUCTION

The rapid urbanisation of cities in India has led to the poor management of its waste being generated everyday. India's largest cities generate more than 38,254 million liters of sewage each day. Of this, it is estimated that less than 30 per cent of what is collected undergoes treatment before it is disposed into freshwater bodies or the sea [1]. These figures exclude sewage generated in informal settlements (slums) and in smaller cities and towns where an acute lack of municipal infrastructure for water supply and sewage collection makes data hard to find. Systems that were designed to manage a city's waste are now not adequate enough to handle the growing amount of solid and liquid waste being generated.

A large amount of the waste, then, is directly discharged into the receiving water bodies, which bear the brunt of ecological damage caused by its pollutants. Phosphate is considered to play a significant role in this as it acts as a limiting nutrient. Phosphates from wastewaters have two major sources: human wastes and detergents. The most common form of phosphates in domestic wastewater is calcium phosphate and those from detergents are mainly in the form of sodium tri-poly-phosphates (STTP). These help soften the hard water and also maintain alkaline conditions in order to increase the activity of surfactants in the detergent. Freshwater and estuarine ecosystems are often nutrient limited and are

particularly sensitive to increases in phosphate levels. Unlike soils, aquatic systems have a low buffering capacity or ability to store phosphorus when it increases above natural levels. If phosphorus is applied to a source of water where it is limiting, the growth of algae and other aquatic micro-organisms will be quickly stimulated.

1.1 The urban approach to the problem:
Although all major cities have centralised treatment plants, their haphazard expansion has made it difficult for these systems to keep pace with the uncontrolled increase in the urban wastewater generated. Some initiatives like the decentralised approach to wastewater treatment at small-scales have reduced to some extent the quantity of raw wastewater being discharged into receiving bodies. As with centralised treatment plants, most of the decentralised treatment plants are only effective at reducing organic content in the form of BOD and COD through secondary biological treatment methods and lack the ability to effectively remove phosphates. Even if the tertiary treatment allows phosphate removal and the residual phosphate concentration in the final effluent is reduced below the standard prescribed by the Central Pollution Control Board (CPCB) (5 mg P/L), their subsequent discharge into surface inland waters will lead to an increase in the mass loading of phosphates. If the water body has a very poor phosphate buffering capacity, it will eventually increase the phosphate concentration above eutrophic levels.

1.2 Options for phosphate elimination:
Conventional tertiary treatment options applied to eliminate phosphates from wastewater include addition of Fe and Al salts to induce precipitation of phosphates, resulting in the formation of sludge. The problem with using these is the preconditioning of wastewater through pH adjustment and the treatment & disposal of sludge. Another conventional option is "Enhanced Biological Phosphorus Removal" (EBPR) method. This involves the alternation of anaerobic and anoxic conditions to stimulate phosphate intake by micro-organisms present. Despite its potential in effective removal of phosphates with less environmental impact, the system tends to become unpredictable after a certain period of time. Also, both these options focus only on phosphate removal and not recovery. Phosphate recovery could reduce the extensive mining of phosphate rocks that is already a finite resource.

Another technology considered to have a major impact on phosphate removal is active filtration. This method not only allows specific removal of pollutants, but also allows for the application of low-cost materials and waste by-products. Also, very little or no energy is required. This type of cost-effective technology is mostly applied in small-scale decentralized wastewater treatment plants as reed beds, constructed wetlands and filter wells, where sand or soil is used. In the case of reed beds and planted filter wells, plants also contribute to phosphate removal, apart from microorganisms. Removal of nitrogen as ammonia-nitrogen and nitrates is also possible here through plant and microorganism uptake. But the Phosphorus sorption capacity (PSC) in these cases are very poor (<1 mg/g). Hence studies on other cost-effective materials have been the focus of recent investigations.

In order for a substance to be considered a good filter material, it must satisfy all or most of the following requirements:
  - Low cost
  - Ease of availability
  - High PSC
  - Less sensitive to physiological factors like pH and temperature
  - Less sensitive to high organic content
  - Long life time
  - Easy recovery of phosphates from the exhausted material

1.3 Potential of concrete wastes in decentralized systems:
In this study, concrete waste has been selected for the evaluation of phosphate removal as previous studies [2], [3], [4], [5] show that they have the potential to fulfill most of the requirements of a good active filter material. Also, it does not require any preconditioning for pH of the influent wastewater or de-carbonation [3] and classic concrete has a quick equilibrium time of 60 min [6]. Egemose et al., (2012 have shown that release of heavy metals is of no importance for the treated water as their heavy metal content (Cu, Pb, Cr and Cd) is less than 0.01%. The properties of concrete that make it a good filter material is its high calcium content as calcium silicates and calcite and a porous surface structure.

Reference [3] describes the main mechanism of phosphate elimination as the release of calcium from tobermorite, a predominant calcium silicate hydrate in concrete, followed by the formation of hydroxyapatite. Hence, the type of concrete will determine its efficiency. Reference [5] shows field-scale tests using 5 different types of crushed concretes. The highest sorption capacity is shown by gas concrete (19 mg P/g) and the lowest is shown by classic concrete (5.1 mg P/g). Gas concrete showed a longer equilibrium time of 24 hours compared to classic concrete (60 min). The higher PSC value observed in gas concrete is attributed to its higher porous surface compared to other types of concrete. The authors have also reported that concrete in powdered form perform better than gravel form. However, all these studies have shown a marked increase in the pH once the waste concrete comes in contact with the water. Hence, a neutralization or dilution step is advised before final discharge into a receiving body. This has limited the use of crushed concrete to decentralised systems. Another important aspect of considering concrete as a filter material is that it partially addresses the problem of waste generated during construction/demolition activities. Hence, not only is it easily available, its reuse can contribute to reducing the burden at landfills.

1.4 Discrepancies at local scales:
Most of the studies based on concrete waste, have been carried out under certain assumptions and factors that may or may not play a role in its performance. For example, the phosphate load in wastewaters from developed countries is different from those of the developing since the laws governing the use of phosphate in many commercial products like shampoos and detergents are more stringent in developed nations. Many US states, the European Union, Canada, and Japan have limited or banned the use of phosphates in laundry detergents. Some US states are considering banning phosphates in dishwasher detergents as well. Washington State has banned the sale of household detergents with more than 0.5 per cent phosphorous [7]. Indian standards require detergents to have a certain minimum quantity of phosphates as an ingredient (11% for Grade 1 and 7% per cent for Grade 2 detergents). Hence the phosphate load in the Indian scenario will be higher in municipal wastewaters compared to that of developed nations. Around 5 to 30 mg Phosphorus/L in raw municipal wastewater is expected in such situations [8]. This is an important factor to consider since the mechanism of phosphate elimination and maximum removal capacity depends largely on the phosphate load. Most of the studies so far have taken place in developed nations, whose phosphate loads, physiological conditions or even the quality (in terms of chemical and surface characteristics) of concrete may be different from place to place. Hence, their observations may not completely reflect the reality of its performance and applications in urban Indian cities.

II. MATERIALS AND METHODS

2.1 Material preparation:
Waste concrete was collected from an RCC lintel from a demolition site and was pulverised using a pot mill. The particle size ranged from 150-300 micrometers. This was used for the batch studies and characterization.

2.2 Material characterization:
The pH, and electrical conductivity was determined from solution after mixing 2 g of the crushed material with 20 mL of distilled water. Both pH and conductivity was measured using EUTECH PC510 pH and conductivity meter. Elemental analysis was done using Energy Dispersive Atomic X-Ray analyzer (Camscan series 2 with Link AN10000 10/25S Energy Dispersive X-ray Micro Analyzer).

2.3 Adsorption Isotherm studies:
Preliminary batch tests were carried out for adsorption isotherm studies with different initial concentrations of phosphate with a fixed dose of the adsorbent with a hydraulic retention time (HRT) of 60 minutes. The material-to-solution ratio was maintained at 1:25 (2g in 50 mL). In this case, the material is crushed concrete and the solution is an aqueous solution having different phosphate concentrations, through the addition potassium dihydrogen phosphate (KH_2PO_4). The initial phosphate concentrations (C_0) were 5, 10, 15, 20, 25 and 30, 50, 70 and 100 mg/L. An agitation speed of 100 rotations per minute (RPM) was maintained. In order to mimic the ionic strength of wastewater, phosphate solutions were prepared in 0.01M KCl aqueous solution [9]. Langmiur and Freundlich models are used for fitting experimental data in adsorption studies to understand the extent and degree of favorability of adsorption.

2.4 Batch experiment with wastewater collected from DTS:

Batch experiment was carried out with wastewater collected from the DTS with the same material-to-solution and HRT of 60 minutes to check for conductivity, hardness, calcium content and BOD, along with control, which did not contain the substrate in question. The filtrate was also checked for heavy metals using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Thermo Scientific IC74DC142602 with argon as the carrier gas) to ascertain possible leaching or adsorption taking place.

III.   RESULTS AND DISCUSSION

3.1 Material characterization:

The pH of the substrate was observed to be 11 ± 0.006 and conductivity was observed to be 969 ± 3.2 µS. The high pH and conductivity of the solution after coming in contact with the substrate is due to the dissolution of calcium as calcium hydroxide and this is expected to last until its complete dissolution from the substrate. The result of EDAX analysis is shown in Table 3.1.The major elements are silica, calcium and oxygen. Fig. 3.1 shows the EDX spectrum of the crushed concrete specimen. The main elements that interact specifically with phosphates are calcium, aluminium and iron. In terms of precipitation and adsorption, these elements play a vital role.

Table 3.1: Elemental composition of crushed concrete

Element	Percentage Weight
C	7.12 ± 0.18
O	16.79 ± 0.57
Na	0.56 ± 0.06
Mg	0.61 ± 0.08
Al	5.63 ± 0.81
Si	34.54 ± 0.93
K	2.84 ± 0.26
Ca	25.8 ± 0.11
Fe	6.14 ± 0.33
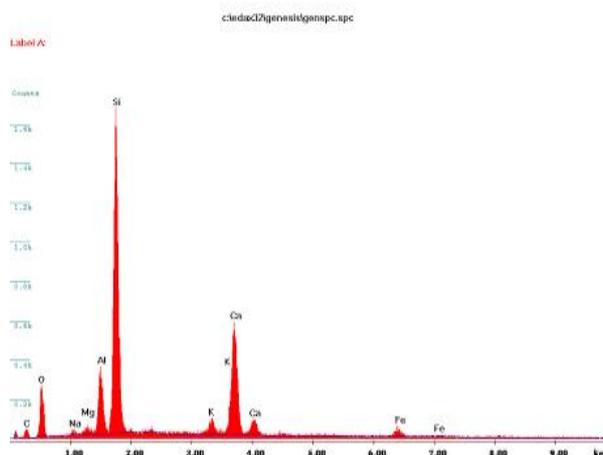
Figure 3.1: EDAX spectrum for crushed concrete

3.2 Adsorption Isotherm Studies:

Batch studies showed removal efficiencies greater than 98% for all initial concentrations. Fig. 3.2 and 3.3 show linear plot for Langmuir and Freundlich isotherms that don't correlate well. However, the plots indicate that low concentrations tend to deviate from linearity while low-to-moderate concentrations tend towards linearity. This shows for that adsorption may be the main mechanism for phosphate removal at low-to-moderate concentrations while co-precipitation may be the main mechanism for phosphate removal at lower concentrations. Considering this, the graph was plotted corresponding to low-to-moderate phosphate concentrations i.e., 20, 25, 30, 50, 70, and 100 mg/L (Fig. 3.4 and 3.5), which strongly correlate to Langmuir and Freundlich isotherms.
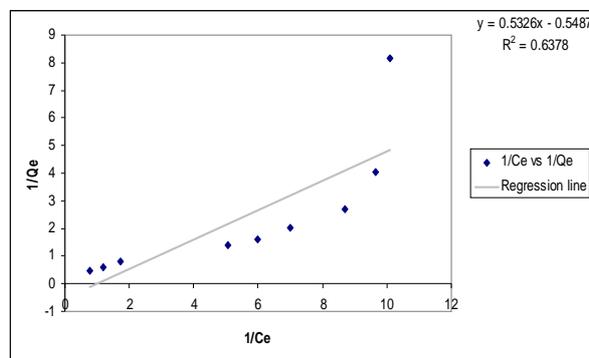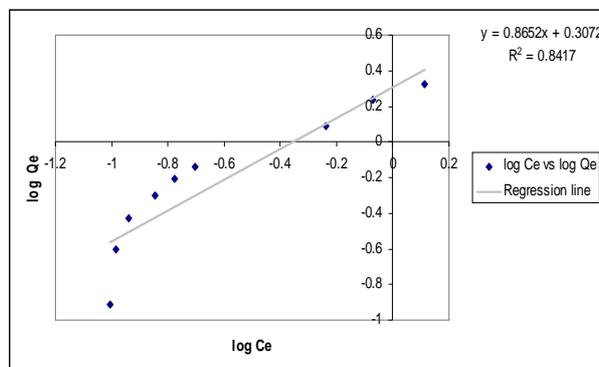

Fig. 3.2: Langmuir Isotherm

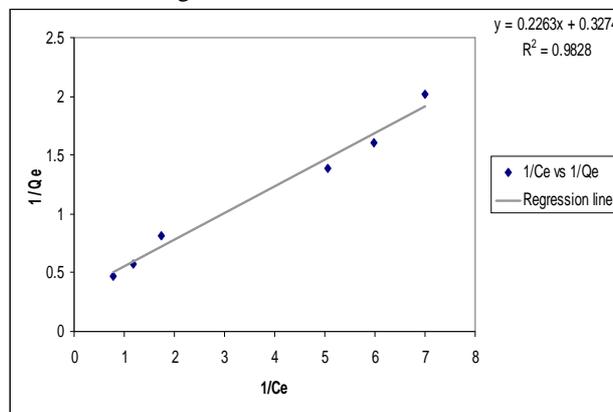

Fig. 3.3: Freundlich Isotherm

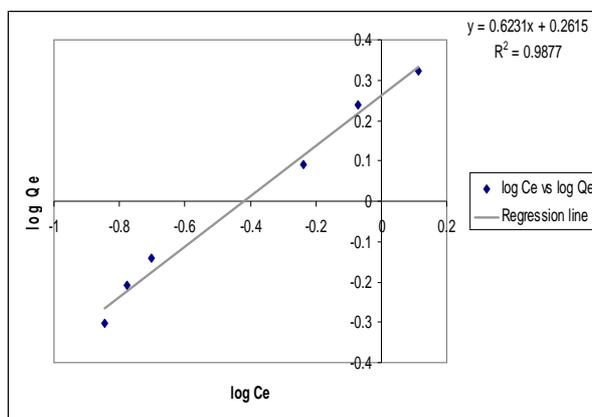Figure 3.4: Langmuir Isotherm fit for low-to-moderate concentrations

Figure 3.5: Freundlich Isotherm fit for low-to-moderate concentrations

The derived values of isotherm constants are given in Table 3.2.

Table 3.2: Isotherm constants for Langmir and Freundlich Isotherm models

Langmuir Isotherm		Freundlich Isotherm	
Qm (mg/g)	K_{ads} (L/mg)	n	K_f (mg/g)
3.054	1.45	1.6	1.826

The maximum phosphate adsorption capacity, calculated from Langmuir equation is about 3 mg/g. The value of the Freundlich constant (n) being greater than 1 indicates that affinities decrease with increasing adsorption density. pH for all solutions was observed to be at 11.4 ± 0.3, indicating the release of calcium as calcium hydroxide.

3.3 Batch experiment with wastewater collected from DTS:
Table 3.3 shows the results of the parameters analyzed during the batch experiment with DTS effluent. The high percentage efficiency is observed with real wastewater as well, indicating that there is not much interference of other pollutants in phosphate elimination. A 36.5% decrease in BOD as compared to control signifies the affinity of organic ligands to the substrate as well. However, the high removal efficiency displayed indicates that the substrate in question is not sensitive to interference by organic ligands. This is consistent with the findings of [10], who observed a reduction of total organic carbon along with phosphate removal in laundry effluent using crushed concrete. Reduction of calcium compared to control is indicative of precipitation of Calcium Phosphates. This explains the corresponding decrease in conductivity and hardness values as well. A 35% increase in silica is reported in this study, due to the high silica content in the substrate.

The effect of the substrate on heavy metal concentrations in the wastewater in shown in Fig. 3.6. Except for Manganese, no leaching of heavy metals was observed. A significant reduction of aluminium, chromium, copper and lead by 44%, 89%, 46% and 58% respectively compared to control was observed. A study by [11] showed adsorption potential of recycled concrete for copper, zinc, and lead. This opens up to another application of waste concrete as reaction walls to protect the ground water, and this can be considered even after the material is exhausted with phosphate accumulation. A reduction in aluminium and chromium has not been reported before this study.

Table 3.3 Parameter values of sample and control subjected to batch test

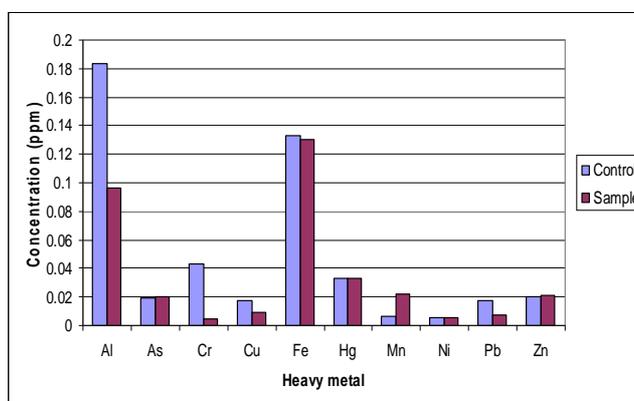| Parameters	unit	Control	Sample	Percentage decrease	Percentage increase
pH		7.54	9.66	-	28.12
Conductivity	µS/cm	1348	1129	16.25	-
BOD	mg/L as O_2	17.33	11	36.53	-
Hardness	mg/L as $CaCO_3$	487	316.66	34.98	-
Calcium	ppm	124.2	78.4	36.88	-
Silica	ppm	2.71	3.65	-	34.69
Total dissolved phosphates	ppm	25.5	0.21	99.18	-

Figure 3.6: Influence of crushed waste concrete on heavy metal concentrations in wastewater

IV. CONCLUSION

The study investigated the mechanism and potential application of crushed waste concrete for treating DTS effluent. Their availability and the fact that various concrete recycling plants producing coarse and fine aggregates has made this material a candidate for serious consideration as a filter material. Promising results were obtained with greater than 98% removal efficiency. The mechanism of phosphate elimination seems to be precipitation as HAP followed by adsorption on the surface, as it has been reported that HAP has high BET surface area [12]. The langmuir and Freundlich isotherm fit at low-to-moderate concentrations show a good correlation with experimental data. The maximum Phosphate sorption capacity calculated from Langmuir isotherm is 3 mg/g. However, since precipitation is also involved, long term column studies is needed for a true estimation of phosphate accumulation capacity. Calcium content is an important factor for the working of the filter material; higher the calcium content, the longer the lifetime of the filter material.

Batch tests with DTS wastewater showed no significant decrease in removal efficiency. Although an affinity of organic ligands to the substrate was observed, the substrate showed no sensitivity to it. The study also showed that the use of the substrate came with an added benefit of reducing both conductivity and hardness, along with BOD reduction. The high pH requires a neutralization step before final discharge into receiving water bodies. However, high pH will counter the

bio-film formation, which will normally retard the functioning of a filter material through short-circuiting. The pH will also serve as an indicator to when the material will become exhausted.

A significant reduction of aluminium, chromium, lead and copper makes this material a good candidate as a reaction wall to protect the groundwater, even after the material is exhausted from phosphate accumulation.

V. ACKNOWLEDGEMENTS

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