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MECHANICAL ACTIVATION OF SUGAR-BEET DEFECATE: EFFECTS ON PARTICLE SIZE, SPECIFIC SURFACE AREA AND SORPTION CAPACITY

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Abstract:

This work quantifies how dry ball-milling parameters govern the dispersity, BET specific surface area and single-point sorption uptake of defecate (sugar-beet carbonation lime residue), and identifies the preferred activation regime under an explicit energy-efficiency criterion. Ten samples were examined: an unmilled dried control (D0) and nine activation regimes covering milling time 5–60 min, ball-to-material ratio 5:1–20:1, mill speed 200–500 rpm and initial moisture 0.9 and 5.0 %. Median particle size d_{50} and BET surface area were recorded for every sample, and sorption activity was assessed in a single-point static test (C_0 = 100 mg/L, dose 2 g/L, 25 °C, 60 min, pH_0 = 7.0) towards phosphate, methylene blue, Congo red and Pb(II). After 30 min of milling d_{50} fell from 73.7 to 7.9 μm (9.3-fold), BET area rose from 6.4 to 28.4 m²/g (4.4-fold) and phosphate uptake increased from 8.4 to 26.3 mg/g (3.1-fold); at 60 min d_{50} rebounded to 9.8 μm and BET dropped to 24.1 m²/g, indicating the onset of agglomeration. Across all ten samples, phosphate uptake correlated almost perfectly with specific surface area (r = 0.993; $q = 0.814 \cdot BET + 3.42$; R^2 = 0.987), and surface-normalised phosphate uptake stayed within a narrow band (0.91–1.31 mg/m² over all ten samples; 0.91–1.08 mg/m² over the nine activated samples). For phosphate, therefore, the gain in sorption activity within the present dataset is explained almost entirely by the gain in specific surface area; an independent contribution of a "mechanically activated defect state" was not resolved by these experiments and can only be proved against an unmilled control brought to the same dispersity by classification. For methylene blue and Pb(II) the surface-normalised uptake was not constant, so the same conclusion does not extend to them without further evidence. The best regime by absolute uptake is D30-500 (27.6 mg/g phosphate), whereas by energy efficiency it is D5 (14.1 (mg/g)/(kW·s/kg)); the two criteria point to different regimes.

Keywords: Defecate, Carbonation Lime Residue, Mechanical Activation, Ball Milling, Specific Surface Area, Phosphate Sorption, Heavy Metals, Energy Consumption, Agglomeration

Introduction

Defecate, the residue formed at the carbonatation (juice-clarification) stage of beet-sugar manufacture, is a large-tonnage by-product. Its carbonate phase and alkaline reaction make it a candidate low-cost reagent-sorbent for separating phosphate ions, dyes and heavy metals from wastewater. In the as-received state, however, the specific surface area of defecate is small and its particles are coarse, which limits sorption uptake. Dry mechanical activation — ball or planetary milling — is one reagent-free

route to a larger surface and higher reactivity.

Defecate is the precipitate produced in the juice-purification cycle of a sugar plant by treatment with lime and carbon dioxide; its principal phase is calcium carbonate, accompanied by organic matter carried over from the juice. The large tonnage of the residue and its useful components make utilisation, rather than landfilling, the appropriate route. Several utilisation directions have been reported. Ławińska et al. converted carbonation lime mud into a controllable granular product by disc granulation [1]. The main practical direction to date has been the neutralisation of acidic soils: González et al. followed the long-term effect of a sugar-mill lime by-product on forest soil and recorded stable changes in soil reaction and in the exchangeable-base composition [2]. A second direction is construction and geotechnics, in which precipitated calcium carbonate obtained from sugar-beet waste has been applied as a soil-stabilising additive [3]. A third, comparatively little-studied direction is the use of defecate as a sorbent for wastewater treatment: Marti and Zeidan tested beet-sugar carbonation sludge for the removal of synthetic dyes and showed that there are grounds for assessing it as a low-cost sorbent [4]. In that work, however, the material was used in its natural state and no attempt was made to raise its activity deliberately.

Milling a carbonate raw material produces at least two effects simultaneously: (a) an increase in specific surface area through particle-size reduction, and (b) the accumulation of crystal-lattice defects, amorphisation and the appearance of newly broken bonds. Guzzo et al. milled limestone in a planetary mill and followed the particle-size distribution and the changes in lattice structure at the same time, showing that both processes depend on milling time [5].

Changes in specific surface area and in surface properties during ball milling of calcite have been recorded by Yoğurtcuoğlu and Uçurum [6], and Acar and Acisli showed that mechanochemical surface modification also occurs in such systems, that is, the changes are not limited to size reduction [7]. Both of these studies concern wet-stirred ball milling, so their findings are indicative rather than directly transferable to the dry regime used here. For dry conditions, Marchini et al. converted carbonate-rich waste (seashells) into nanocrystalline and partly amorphous calcium carbonate by dry ball milling, confirming that mechanical energy alters the phase state directly [8]. The moisture of the milling environment is a separate factor: Shinohara et al. studied the effect of moisture on the grinding of natural calcite and confirmed that it is appreciable [9]. This result justifies strict adherence to a dry activation regime.

Increasing the milling time without limit is not beneficial. Guzzo et al. located the point at which particles in dry ultrafine grinding of limestone begin to re-agglomerate and showed that dispersity and surface indicators deteriorate beyond that point [10]. Knieke et al. described the phenomenon more generally through the distinction between the “apparent” and the “true” grinding limit: the apparent limit arises from re-agglomeration, whereas the true limit depends on the fracture capability of the material [11]. Fadda et al. proposed a population-balance model that separates breakage from re-agglomeration kinetics in dry ball milling [12].

These studies are methodologically important for the present work, because they extend the simplified notion that “longer milling means higher activity” and require the boundary of the useful milling period to be determined experimentally.

Liu et al. compared methylene blue sorption on calcium carbonate samples from different sources and showed that both capacity and mechanism depend on the nature of the raw material [13]. Naseer et al. analysed the mechanism of Pb(II) removal on synthesised $CaCO_3$ microcubes [14]. Huang et al. studied Congo red, methylene blue and Pb(II) simultaneously on a single composite sorbent and showed that the behaviour of these three pollutants on the sorbent surface differs [15]. Such work justifies the comparison of four pollutants under identical conditions in the present study.

Three unresolved issues follow from the studies reviewed above. First, the two effects of mechanical activation — the increase in surface area and the formation of a disturbed lattice state — are often treated together as “mechanical activity”, but their separate contributions to sorption uptake are not measured. Second, defecate, and mechanically activated defecate in particular, has not been studied

systematically against dyes and heavy metals under identical conditions; the existing study reported in the literature concerns unactivated material. Third, the possibility that the energy cost of activation and the absolute-capacity criterion give contradictory answers is not usually discussed openly.

Accordingly, the aim of this work is to quantify the effect of four activation parameters (milling time, ball-to-material ratio, mill speed and initial moisture) on the properties of defecate and on its sorption uptake, to attempt to separate the source of the uptake gain (surface area versus activity per unit surface), and to compare the outcomes given by the absolute-capacity and the energy-efficiency criteria.

Materials and Methods

The object of the study was defecate, a by-product of sugar manufacture. The sample was dried at 105 °C to a residual moisture of 0.9 %. The dried, unmilled sample was designated as the control with the code D0.

Activation was carried out by ball milling under dry conditions. Ten samples were studied in total: the unmilled control D0 and nine activation regimes (the parameter varied is given in parentheses). D5, D15, D30 and D60 — milling time 5, 15, 30 and 60 min (10:1, 350 rpm); D30-B5 and D30-B20 — ball-to-material ratio 5:1 and 20:1 (30 min, 350 rpm); D30-200 and D30-500 — mill speed 200 and 500 rpm (30 min, 10:1); D30-W5 — initial moisture 5.0 % (30 min, 10:1, 350 rpm). In all other regimes the initial moisture was 0.9 %.

The median particle size d_{50} and the BET specific surface area were determined for every sample.

Sorption activity was assessed in a single-point static experiment: initial concentration C_0 = 100 mg/L, sorbent dose 2 g/L, temperature 25 °C, contact time 60 min, initial pH 7.0. The pollutants studied were the phosphate ion, methylene blue (a cationic dye), Congo red (an anionic dye) and Pb(II). This set of four was chosen to match the comparison scheme used by Huang et al.

Sorption uptake was calculated as $q = (C_0 - C_e)\cdot V/m$. Under the chosen conditions the theoretical maximum uptake is $q_{max} = C_0/\text{dose} = 100/2 = 50.0$ mg/g, and every measured value must lie below this bound; all values reported in this article passed that check. Removal, $\% = q \cdot \text{dose} / C_0 \cdot 100 = 2q$.

Uptake normalised to unit surface area was calculated as q/BET. The strength of the relationship was assessed by the Pearson coefficient r and by ordinary least-squares linear regression; the calculations were performed over all ten samples reported here, and were repeated over the nine activated samples alone as a robustness check.

Results

With increasing milling time, particle size and specific surface area change in opposite directions (Fig. 1). The sharpest change occurs in the first 5 min: d_{50} falls from 73.7 to 31.2 μm, that is, by a factor of 2.4. At 30 min d_{50} reaches 7.9 μm, which is 9.3 times smaller than the initial value. At the same point the BET surface area attains its maximum of 28.4 m²/g, 4.4 times that of the unactivated sample.

At 60 min the trend reverses: d_{50} rises from 7.9 to 9.8 μm and BET falls from 28.4 to 24.1 m²/g. The simultaneous deterioration of particle size and surface area shows that milling has passed into agglomeration: the newly formed high-energy surfaces adhere to one another and form secondary aggregates. This picture agrees with the agglomeration onset recorded for dry ultrafine grinding of limestone and with the concept of the apparent grinding limit. The useful milling period under these conditions is therefore limited to 30 min.

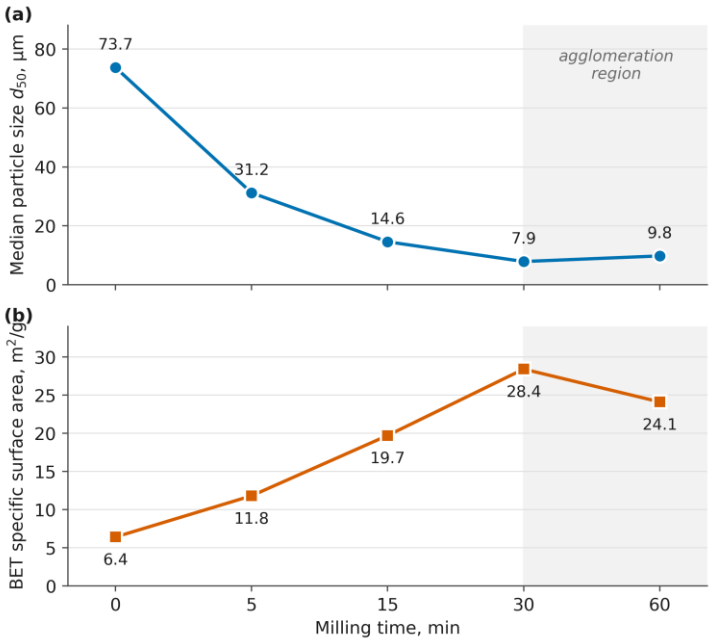

Figure 1. Effect of milling time on (a) median particle size d_{50} and (b) BET specific surface area. Conditions: ball-to-material ratio 10:1, mill speed 350 rpm, initial moisture 0.9 %. The shaded band marks the region beyond the useful milling window, where re-agglomeration sets in.

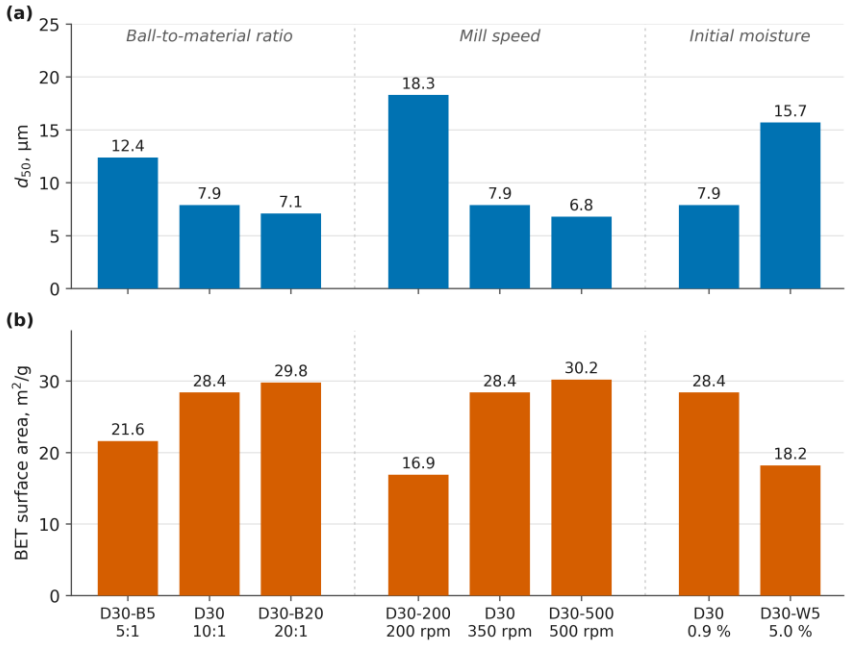

Figure 2. Effect of ball-to-material ratio, mill speed and initial moisture on (a) d_{50} and (b) BET specific surface area. Milling time is 30 min in every regime shown; D30 (10:1, 350 rpm, 0.9 %) is repeated in each block as the common reference.

With the milling time held at 30 min, the remaining three parameters were varied one at a time (Fig. 2). Raising the ball-to-material ratio from 5:1 to 10:1 gives the most appreciable effect: d_{50} falls from 12.4 to 7.9 µm and BET rises from 21.6 to 28.4 m²/g. The change from 10:1 to 20:1 is considerably smaller (d_{50} 7.9 → 7.1 µm; BET 28.4 → 29.8 m²/g), that is, the effect approaches saturation in this direction.

Mill speed proved to be the parameter with the strongest influence. At 200 rpm the outcome is appreciably worse (d_{50} 18.3 µm; BET 16.9 m²/g), whereas at 500 rpm it is the best obtained (d_{50} 6.8

μm; BET 30.2 m²/g). Raising the initial moisture from 0.9 to 5.0 % clearly worsens the outcome: d_{50} rises from 7.9 to 15.7 μm and BET falls from 28.4 to 18.2 m²/g. This may be explained by the greater cohesiveness of the moist material, so that part of the impact energy is spent on plastic deformation and the fine fraction aggregates; the adverse effect of moisture in calcite grinding was also recorded by Shinohara et al. [16].

Activation increased the uptake of all four pollutants (Fig. 3, Table 2). For phosphate, the transition from D0 to D30 raises the uptake from 8.4 to 26.3 mg/g, that is, by a factor of 3.1; for methylene blue it rises from 12.1 to 33.2 mg/g and for Pb(II) from 15.6 to 36.1 mg/g. For Congo red the corresponding rise is from 5.3 to 13.3 mg/g.

The ranking among the pollutants is preserved in all ten samples: Pb(II) > methylene blue > phosphate > Congo red. This ranking does not depend on the activation regime, that is, milling does not change the selectivity of the sorbent but only raises its overall uptake. All values lie below the theoretical bound of 50.0 mg/g, so the mass balance is not violated.

The maximum absolute uptake was obtained in the D30-500 (phosphate 27.6 mg/g) and D30-B20 (27.1 mg/g) regimes; these exceed D30 (26.3 mg/g) by 4.9 and 3.0 %, respectively.

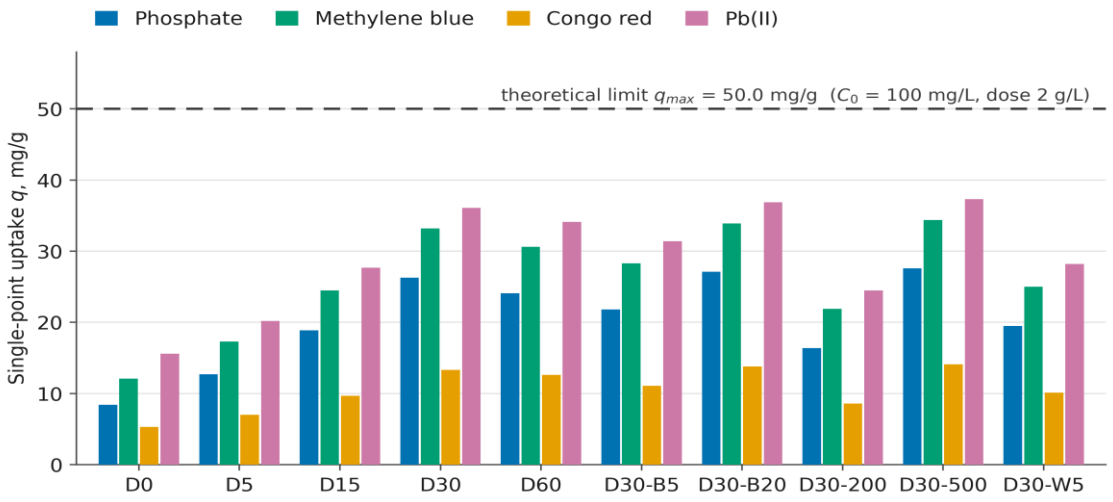

Figure 3. Effect of the activation regimes on single-point sorption uptake. Conditions: C_0 = 100 mg/L, dose 2 g/L, T = 25 °C, t = 60 min, pH_0 = 7.0. The dashed line is the theoretical bound q_{max} = 50.0 mg/g set by the mass balance. Numerical values are listed in Table 2.

Across the ten samples, phosphate uptake is an almost perfectly linear function of BET surface area: r = 0.993, q = 0.814·BET + 3.42, R^2 = 0.987 (Table 3). Excluding the unmilled control D0, whose extreme position could dominate the fit, the relationship is essentially unchanged (r = 0.988; q = 0.802·BET + 3.71), so the correlation is not an artefact of a single high-leverage point.

Surface-normalised phosphate uptake q/BET lies between 0.91 and 1.31 mg/m² across all ten samples, and between 0.91 and 1.08 mg/m² across the nine activated samples. For methylene blue and Pb(II) the corresponding ranges are wider (1.14–1.89 and 1.24–2.44 mg/m² over all ten samples), and the fitted intercepts are correspondingly larger (6.52 and 9.80 mg/g).

Conclusions

Dry ball milling of defecate reduces the median particle size from 73.7 to 7.9 μm (9.3-fold), raises the BET specific surface area from 6.4 to 28.4 m²/g (4.4-fold) and increases phosphate uptake from 8.4 to 26.3 mg/g (3.1-fold) after 30 min of milling.

The useful milling period is bounded at 30 min. At 60 min both d_{50} and BET deteriorate, which indicates the onset of re-agglomeration.

Among the parameters examined, mill speed has the strongest influence, the ball-to-material ratio saturates above 10:1, and raising the initial moisture from 0.9 to 5.0 % is clearly detrimental.

Phosphate uptake is very strongly linearly related to specific surface area ($r = 0.993$; $R^2 = 0.987$), and surface-normalised phosphate uptake is nearly constant (0.91–1.08 mg/m² across the activated samples). The gain in activity therefore arises mainly from the expansion of surface area; an independent contribution from a defect state is not demonstrated within the available data. For methylene blue and Pb(II) the surface-normalised uptake is not constant, so this conclusion is not extended to them.

The best result by absolute uptake was recorded for the D30-500 regime (27.6 mg/g phosphate), whereas the D5 regime leads on energy efficiency (14.1 (mg/g)/(kW·s/kg)). Since D30-500 raises uptake over D30 by only 4.9 % while increasing energy consumption by a factor of 1.8, the choice of regime under production conditions should be settled by techno-economic calculation, taking the cost of energy and the required throughput into account.

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